Metal deposition on silicon from fluoride solutions

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Preface

Motivation

When this study was initiated, there was an increasing interest in the microelectronics world upon the electrochemical methods for the processing of semiconductors. One of the most promising applications was to replace the traditional techniques to obtain metallic layers on silicon (physical vapor deposition, sputtering) by chemical processes of various kinds. The needs of the industry included the coating of complex three-dimensional structures (submicron multilevel interconnects), higher deposition rates (to achieve thicker layers for the fabrication of microstructures), and also the anisotropic etching of the semiconductor materials. Today, these processes are a reality in the microelectronic fabs, and relevant topics in the major electrochemical and solid-state technology meetings.

With the aim of approaching the multidisciplinary field of semiconductor electrochemistry, the Departments of Electronics and Physical Chemistry embarked in a joint project whose latest result is this PhD thesis. The collaboration has made possible to introduce in the University of Barcelona the techniques of electrochemical characterization and processing of semiconductors, but its benefits go far beyond this study. At present, two projects involving semiconductors and electrochemical techniques are under course in the Department of Electronics (electrochemical growth of metals and shape-memory alloys for microactuators), and one in the Department of Physical Chemistry (semiconducting properties of thin metal oxide films). In addition, some lateral results obtained in this thesis will be further investigated in the immediate future.

The systems chosen for the first studies were the deposition of noble metals on the silicon surface, by simple immersion of the samples in aqueous fluoride solutions containing the metal ions. As reported previously [1], deposition proceeds spontaneously in these cases, and is similar to the “displacement deposition” of a metal onto a less-noble substrate. The metal nuclei deposited in this way can be used as a “seed” for subsequent processes,
in order to grow thicker metal layers on the silicon surface [2]. Thus the first experiments were carried out, using platinum, gold, and palladium salts, and a simple experimental setup that only allowed to control the electrolyte composition and the deposition time: The samples were immersed in a beaker containing the solution of interest. The characterization was then made ex-situ using mostly microscopy and chemical analysis techniques.

It was soon clear that the phenomenology and technological applications of metal deposition on silicon from fluoride solutions were wider than their use as a “predeposition” technique (see Applications below). A deeper study under a more fundamental approach seemed appropriate, and set slightly aside the development of deposition recipes for practical applications. Although the experimental setup described above has many advantages from a technological point of view (simplicity, compatibility with batch processing), several drawbacks were evidenced when a systematic study was initiated: the reproducibility was low due to the poor control of the geometric parameters and, most importantly, it did not allow in-situ access to the electrochemical variables of the system. These facts prompted a complete and quantitative electrochemical study of the deposition processes under idealized conditions, namely in a three-electrode cell and exposing only the active (polished) side of silicon to the solution. Of course the “simple immersion” situation had to be revisited afterwards, once the studies on the active side were complete.

Simultaneously, there was an ongoing discussion on whether the silicon surface chemistry in fluoride media was based on fluorine or hydrogen. As evidence on the $Si - H$ termination was piling up, several electrochemical studies published between 1993 and 1996 by Gerischer and Allongue [3, 4, 5, 6] lead to the elucidation of the silicon dissolution mechanism. A stay at Philippe Allongue’s lab in the University Pierre et Marie Curie in 1996, was an excellent opportunity to learn the details of the mechanism and the experimental techniques involved in their studies. In the framework of the thesis, the understanding of silicon oxidative processes allowed to look deeply in their coupling with the reductive reactions (e.g. metal deposition), as well as on other fundamental aspects of semiconductor electrochemistry. The collaboration with Allongue’s group took shape in a cooperative project with the Department of Physical Chemistry, whose preliminary results will also be presented.

**Objectives**

The purpose of this thesis is to develop a global mechanism for the processes involved in the deposition of metals on silicon from aqueous fluoride solutions.
While sticking to the classical concepts of semiconductor electrochemistry, the model must take into account the recent advances in the comprehension of the chemistry of silicon. In-situ electrochemical techniques will be the major tool employed in this study. Occasionally, microscopic and spectroscopic techniques will be used for an ex-situ characterization of certain samples.

**Structure**

This thesis is organized in three parts:

The first two chapters will settle the **Background** necessary for the interpretation of the electrochemical experiments.

- **Chapter 1** is an introduction to the basic concepts of semiconductor electrochemistry. A thermodynamic description of the semiconductor solution interface is first given, and then the kinetics of electron transfer is discussed with special emphasis on simultaneous reactions (mixed potential theory). This chapter has a didactic purpose, and in principle no specific knowledge of electrochemistry or solid-state physics is required.

- **Chapter 2** attempts to gather all the elements that are relevant for the understanding of the chemistry of silicon in aqueous fluoride solutions. Although the data that is presented corresponds mainly to electrochemical experiments, key references on spectroscopic and microscopic studies are also provided. All these works are relatively scattered in the literature, but are essential for the understanding of the dissolution mechanism. The chapter is thus organized as a review, and constitutes one of the original contributions of this thesis.

The **Electrochemical studies of platinum and nickel deposition** correspond to the main experimental body. They are presented in the following four chapters:

- **Chapter 3** outlines the experimental setup, characterization techniques and sample preparation procedures.

- **Chapter 4** is devoted to platinum deposition. The energy levels of the $Pt^{2+}/Pt$ redox system overlap with the silicon valence band, and $Pt^{2+}$ ions act as an oxidizing agent of silicon. Hence the complex phenomenologies of the reactions of platinum deposition and silicon oxidation are presented separately.
Chapter 5 describes the electrochemical study of nickel deposition at two extreme $pH$ values. Nickel was chosen because the energy levels of the $Ni^{2+}/Ni$ system lie within the silicon bandgap, and thus a different deposition mechanism than platinum was expected.

Chapter 6 is an overview of the different reaction pathways for metal deposition on silicon from fluoride media. The analysis of the two previous chapters is extended to other systems and conditions, and the conclusions are correlated with data from the literature.

Finally, the Technological aspects are discussed in chapter 7. Two sets of experiments have been grouped here, obtained at very different stages of the study: First, the ex-situ characterization of samples (prepared using the early experimental setup) is presented as an “image gallery”. Although these studies are mostly qualitative, they have been selected to discuss certain issues that were only indicated in the previous chapters. And second, a comparison between the deposition process by simple immersion (i.e. exposing both sides of the sample to the solution) and protecting the rear side in the cell. This brief electrochemical study is intended to raise the value of the early experiments, as well as to disclose some of their unexpected advantages.

A preliminary study of silicon etching in NaOH solutions using in-situ microscopy has been included in appendix A, to demonstrate the capabilities of these emerging techniques. A selection of the publications related to this thesis can be found in appendix B, and appendix C lists the abbreviations and notation employed in the text.

Applications

There is a great number of processes in the surface-finish industry that are carried out in solution. For example, metal coatings for protective, functional or decorative purpose, or removal of material layers by etching. Although most of these processes are electrochemical in nature (i.e. they involve transfer of electrons between the reacting species), they are often engineered to proceed by simple immersion in the solution, without the external application of electric potentials. It is common usage in the industry to designate them as “chemical” processes. In the context of this study, the term “chemical” would be quite misleading, hence “open-circuit process” has been preferred because it refers to the steady-state potential of the sample, measured in an electrochemical cell (open-circuit potential, OCP). Some applications of open-circuit metal deposition processes on silicon from fluoride solutions are given below.
Deposition activation  Noble metal ions in a solution have a strong tendency to deposit on many substrates (metal, semiconductor, ceramic and polymer). Fluoride is usually added to improve adhesion, by means of increasing substrate roughness [2, 7]. These solutions are employed to predeposit the samples that will be subsequently coated with the metal of interest using other methods at the OCP or under applied potential. The predeposition process, often referred to as “seeding” or “activation”, produces a high density of catalytic (Pt, Pd) nuclei on the sample surface that act as charge exchange centers with the solution [8]. The predeposited nuclei can also be used to produce selective deposits, because metal growth proceeds only on the seeded areas [9]. The small size of the metal nuclei makes these deposition processes compatible with very large-scale integration (VLSI) technology [10, 11, 12].

Characterization of microelectronics materials and devices  Fluoride solutions containing metal ions can be designed to produce enhanced effects at particular sites of the samples. Surface flaws or areas with differentiated electric properties can then be preferential places for deposition and etching. This has been advantageous for certain applications: In the crystal growth industry, the quality of the wafers is controlled with chromium-based solutions, which produce “etch pictures” that reveal crystallographic defects [13, 14, 15, 16, 17, 18, 19]. Microelectronic devices like diodes and transistors are made up of junctions between $p$- and $n$-type regions in a semiconductor. Their dimensions are key parameters for the performance of the device, but these regions cannot be discriminated morphologically. A combination of etching and metal deposition from fluoride solutions (“decoration”) has been used to delineate these junctions and determine diffusion or implantation profiles of dopants [20, 21].

Effect of metallic contaminants in hydrofluoric acid solutions  Hydrofluoric acid is a very common reagent in silicon cleaning processes. When the goal is to keep the surface as smooth and clean as possible, trace amounts of metallic contaminants become a serious problem, because they may give rise to deposits and enhanced corrosion of the surface. The mechanism of these unwanted processes is studied in order to prevent them. Of course, HF purification is a must, but good protection can also be achieved by playing with the conditions and composition of the cleaning solutions [22, 23, 24]. Using a different approach, contamination sensors have been fabricated taking advantage of the modification of the surface electric properties due to the metallic deposition [25].
Chapter 1

The semiconductor | solution interface

1.1 Introduction

Since its birth as an independent field of science after the works of W.H. Brattain and C.G.B. Garrett in the mid-50’s, the study of semiconductor electrodes has greatly influenced the concepts of electrochemistry [26]. Today, the electrochemistry of semiconductors has become the meeting-point of chemistry, electro- and photochemistry, solid-state physics and catalysis. Like in many other fields, the scientific activity has been quite modulated by the interest on the industrial applications, being the most popular the photo-electrochemical energy conversion devices (solar cells) [27]. Although a fully-operative commercial photoelectrochemical cell has not yet been produced, cycles of interest on the field have followed one another, giving rise in this way to a great amount of technological developments as well as fundamental knowledge.

The electrochemistry of semiconductors is a vast and rich multidisciplinary field that studies phenomena of great interest for both solid-state physicists and metal electrochemists: In a semiconductor, electrochemical reactions depend not only on the applied potential but also on the availability of the corresponding free carriers. For instance, it is observed that even at very negative potentials, no hydrogen evolution occurs in the dark on a $p$–type semiconducting electrode, and light is also required to anodically oxidize an $n$–type electrode: light can thus be employed to generate the necessary charge carriers (reactants) in each case of the previous example (electrons in $p$–type semiconductors, holes in $n$–type). Equally interesting is the fact that the electrolyte in which the semiconducting electrode is im-
mersed constitutes an electric contact that allows the characterization of the semiconductor behavior and the properties of the interface, without the need of building solid-state contacts or using sophisticated equipment in vacuum. In this way, the current-potential and capacity-potential characteristics of the semiconductor | electrolyte junction can be evaluated, and basic parameters like the contact and flatband potentials can be accurately measured in solution. A large number of methods for microelectronics processing have been developed in this framework, ranging from surface preparation and characterization, to oxide growth, (photo)etching or deposition, which demonstrate the unique opportunities offered by semiconductor electrochemistry.

Processes occurring at the semiconductor | electrolyte interface at the OCP may also be studied by controlling the sample potential in an electrochemical cell: When the system is under potentiostatic control, reactions can be induced or inhibited selectively to gain insight into the detailed mechanism of the different processes occurring when no potential is applied. For this reason, the present chapter outlines the major concepts of semiconductor electrochemistry that will be employed in the discussion of the silicon | fluoride system, as well as in the following experimental chapters. Being simultaneously addressed to “classical” (metals) electrochemists, solid-state physicists and materials engineers, a few basic concepts of electronics and electrochemistry are first introduced.

**1.2 Energy diagram of the semiconductor | solution interface**

In the description of charge transfer reactions between a semiconductor and an electrolytic solution, electron energy diagrams provide a very useful tool. The energetic distribution of electron states in each phase and their occupancy gives an indication of the possible reaction pathways, because electron exchange always occurs between states of equal energy. This section is dedicated to sketch the energy diagram of electrons at the semiconductor | solution interface, and its changes with the experimental conditions.

**1.2.1 Electrons in the semiconductor**

The density of energy states of electrons in a solid can be obtained by solving Schrödinger’s equation in a three-dimensional periodic lattice of ions. Electronic states are discrete in one isolated atom, but when the orbitals of many atoms overlap to form a solid, their discrete energy states broaden into energy bands. These bands can be considered a continuum of states.
1.2. ENERGY DIAGRAM OF THE INTERFACE

Figure 1.1: Electronic energy states in a semiconductor. A forbidden band gap of energy $E_g$ exists between the top of the valence band (VB) at $E_V$, and the bottom of the conduction band (CB) at $E_C$. The electron affinity and ionization energies are $E_A$ and $E_I$ respectively. All energies are given in relation to the vacuum level $E_{vac} = 0$ (energy of electrons at rest in vacuum). The arrow indicates the thermal excitation of a VB electron to the CB.

The electronic states of an **intrinsic** (chemically pure) semiconductor are those of the conduction band (CB) at energies $E > E_C$ and of the valence band (VB) at energies $E < E_V$ (see figure 1.1). The two bands are separated by the forbidden band gap $E_g = E_C - E_V$. The energy of electrons in solids is expressed in eV with respect to the vacuum level $E_{vac} = 0$ (energy of electrons at rest in vacuum). This is called the absolute energy scale. The energies of the CB bottom (electronic affinity $E_A$) and the VB top (ionization energy $E_I$) are usually given in this scale. They are also shown in figure 1.1.

At $T = 0 \, K$ the VB is exactly filled, and the CB is empty. It can be shown that a filled band does not carry a net electric current, so the material is insulating. At $T > 0 \, K$, some electrons will be thermally excited to the CB, giving the material a certain electrical conductivity. When an electron is excited to the CB, the vacancy left in the VB is an empty valence state of one atom that can easily be occupied by a valence electron of a neighboring atom. Of course this will result in the neighboring atom having an empty valence state, and the process can be repeated several times. For convenience, this phenomenon is described as a **hole** that travels in the opposite direction, rather than as valence electrons successively occupying the vacancies that the others have left behind. Holes are then regarded as positive free charges having an energy in the VB, and also contribute to the conductivity. (Note
that generation of electron-hole pairs can also be promoted by photons of energy $h\nu \geq E_{g}$.

The occupation of the available electronic energy states $N(E)$ (i.e. the energy bands) is now considered. The probability of a state of energy $E$ to be filled by an electron is given by the Fermi-Dirac statistics:

$$f(E) = \frac{1}{1 + e^{\frac{E - E_{F}}{k_{B}T}}} \tag{1.1}$$

where $k_{B} = 8.6 \cdot 10^{-5} \text{ eV/K}$ is the Boltzmann constant and $E_{F}$ is called the Fermi energy: As was explained above, at $0 \text{ K}$ all states of energy lower than $E_{F}$ are filled with electrons ($f(E) = 1$) and the states of higher energy are empty ($f(E) = 0$). As the temperature increases, a distribution is formed around $E_{F}$, for which the occupancy is always $f(E_{F}) = \frac{1}{2}$ (figure 1.2A). The probability distribution for holes is correspondingly $1 - f(E)$.

In many cases, the electron and hole concentrations ($n$ and $p$ respectively) are small. The Fermi energy is then located within the gap, and at a distance from the bands of at least a few times $k_{B}T$. In such conditions, expression 1.1 can be approximated by a Maxwell-Boltzmann distribution:

$$f(E) = e^{-\frac{E - E_{F}}{k_{B}T}} \tag{1.2}$$
1.2. ENERGY DIAGRAM OF THE INTERFACE

The concentration of charge carriers (electrons in the CB, holes in the VB) is the product of the density of states and their probability of occupancy, \( f(E) \) for \( E > E_C \) (electrons) and \( 1 - f(E) \) for \( E < E_V \) (holes). Using expression 1.2 for \( f(E) \):

\[
\begin{align*}
n &= N(E_C) \cdot f(E_C) = N_C \cdot e^{-\frac{E_C - E_F}{kT}} \\
p &= N(E_V) \cdot (1 - f(E_V)) = N_V \cdot e^{-\frac{E_E - E_V}{kT}}
\end{align*}
\]

where \( N_C, N_V \) are the effective state densities at the bottom of the CB and at the top of the VB respectively (their values for \( Si \) are given in table 1.14 below). The product of electron and hole densities is independent of \( E_F \):

\[ n \cdot p = N_C \cdot N_V \cdot e^{-\frac{E_g}{kT}} = n_i^2 \quad (1.5) \]

and for an intrinsic semiconductor \( n = p = n_i \) (intrinsic carrier density).

In semiconductor solids, conduction occurs by movement of electrons in the CB or of holes in the VB. The electric conductivity thus depends on the electron and hole concentrations. Using \( E_F \approx E_V + \frac{E_g}{2} \) in expressions 1.3 and 1.4, the number of carriers is proportional to \( e^{-\frac{E_g}{2kT}} \), i.e. it decreases with increasing bandgap energy at a given temperature. Thus, semiconductors with large bandgap have low conductivities; actually when \( E_g \) is larger than \( 3 \) eV they are called insulators (e.g. diamond \( 5.4 \) eV). Common semiconductors are silicon (\( E_g = 1.1 \) eV) or gallium arsenide (\( E_g = 1.4 \) eV).

The conductivity can be increased by adding atomic impurities in the semiconductor. The semiconductor is then called extrinsic or doped. These external atoms generally introduce additional electronic energy states in the gap, being of most interest the so-called “shallow” impurities. Shallow-donor impurities, such as column-V elements in \( Si \) or \( Ge \), introduce states at energy levels \( E_D \) located close to the CB. These states are filled at low temperature. However, since \( E_C - E_D \) is small (typically a few tens of meV), these states soon become ionized as the temperature is raised, and the “donated” electrons move into the CB. In this regime, the concentration of conduction electrons is approximately equal to the concentration of donor impurities \( N_D \), and the concentration of holes is obtained from relation 1.5:

\[
\begin{align*}
n &\approx N_D \\
p &\approx \frac{n_i^2}{N_D}
\end{align*}
\]

The semiconductor is referred to as “\( n \)-type”. Since \( n \gg p \), electrons in \( n \)-type semiconductors are called majority charge carriers, and holes minor-
ity carriers. The Fermi energy is given by:

\[ E_F = E_C - k_B T \cdot \ln \frac{N_C}{N_D} \]  \hspace{1cm} (1.8)

and it is located close to the CB. This is shown in figure 1.2B.

In a similar way, shallow-acceptor impurities, such as column-III elements in Si and Ge, introduce empty levels close to the VB. At \( T > 0 \) K, the associated holes are located in the VB:

\[ p \approx N_A \]  \hspace{1cm} (1.9)

\[ n \approx \frac{n^2}{N_A} \]  \hspace{1cm} (1.10)

The semiconductor is referred to as “p–type”. In this case \( (p \gg n) \), holes are the majority carriers, electrons the minority carriers and \( E_F \) is located near the VB (figure 1.2C):

\[ E_F = E_V - k_B T \cdot \ln \frac{N_V}{N_A} \]  \hspace{1cm} (1.11)

The energy difference between the Fermi level and the majority carrier band is indicated by the symbols:

\[ \mu_C \equiv E_C - E_F^p = k_B T \cdot \ln \frac{N_C}{N_D} \]  \hspace{1cm} (1.12)

\[ \mu_V \equiv E_F^p - E_V = k_B T \cdot \ln \frac{N_V}{N_A} \]  \hspace{1cm} (1.13)

in \( n \)–type and \( p \)–type semiconductors respectively. They have been indicated in figures 1.2B and 1.2C. Being silicon the material of interest in this work, the position of its Fermi energy within the bandgap is shown in figure 1.3 [28] as a function of the temperature, doping type and density. The dependency of conductivity with doping is given in figure 1.4 [28]. Usual doping densities range between \( 10^{15} \) and \( 10^{18} \) \( cm^{-3} \) in Si. Other relevant parameters of Si at 300 K are given in table 1.14.
1.2. ENERGY DIAGRAM OF THE INTERFACE

Figure 1.3: Fermi level for Si as a function of temperature and doping concentration. From reference [28].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant $\epsilon_r$</td>
<td>11.9</td>
</tr>
<tr>
<td>$N_C \ (cm^{-3})$</td>
<td>$2.8 \cdot 10^{19}$</td>
</tr>
<tr>
<td>$N_V \ (cm^{-3})$</td>
<td>$1.9 \cdot 10^{19}$</td>
</tr>
<tr>
<td>$n_i \ (cm^{-3})$</td>
<td>$1.4 \cdot 10^{10}$</td>
</tr>
<tr>
<td>Bandgap energy $E_g \ (eV)$</td>
<td>1.12</td>
</tr>
<tr>
<td>Electron affinity $E_{A,Si} \ (eV)$</td>
<td>4.05</td>
</tr>
<tr>
<td>Mobility $\mu \ (cm^2/Vs)$</td>
<td>$\mu_n = 1500$ \ (N_D = 10^{15} \ cm^{-3})$</td>
</tr>
<tr>
<td></td>
<td>$\mu_p = 450$ \ (N_A = 10^{15} \ cm^{-3})$</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>28.1</td>
</tr>
<tr>
<td>Density \ ($g/cm^3$)</td>
<td>2.33</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>diamond</td>
</tr>
<tr>
<td>Lattice constant \ ($nm$)</td>
<td>0.543</td>
</tr>
<tr>
<td>Atoms/cm$^3$</td>
<td>$5.0 \cdot 10^{22}$</td>
</tr>
<tr>
<td>Atoms/cm$^2$</td>
<td>$6.8 \cdot 10^{14}$ \ {100} planes</td>
</tr>
<tr>
<td></td>
<td>$9.6 \cdot 10^{14}$ \ {110} planes</td>
</tr>
<tr>
<td></td>
<td>$7.8 \cdot 10^{14}$ \ {111} planes</td>
</tr>
</tbody>
</table>
1.2.2 Electrons in the solution: the redox system

In the previous section, the semiconductor has been described in terms of electronic energy states. Electrolytic solutions are usually described by their redox potential, but regarding the charge transfer between a solution and a semiconductor, it will be advantageous to give a model of the solution in terms of electronic energy states.

1.2.2.1 Fermi energy of the redox system

An electrolyte is a solution containing ionic species, i.e. an ionic conductor. The exchange of electrons between the electrode and the electroactive species of interest in the electrolyte solution, links the reduced and oxidized forms of the electroactive species: they are called the “redox system”. The redox potential is the equilibrium potential of a metallic electrode immersed in the electrolyte solution having a redox system. Only the difference in redox potential between two redox systems can be measured, and therefore all redox potentials must be given in relation to a reference. By convention, the potential of the standard hydrogen electrode (SHE) gives the reference in aqueous solutions. It is essentially a Pt wire immersed in a solution of activity unity in $H^+$ (acid solution having 1.18 M $H^+$), that is bubbled with
1.2. ENERGY DIAGRAM OF THE INTERFACE

Figure 1.5: Correspondence between the energy scales in the solid (reference: vacuum level) and in the electrolyte (reference: standard hydrogen electrode, SHE). In practice, the electrodes employed are the saturated calomel electrode (SCE), now replaced by the Ag/AgCl electrode (their scales differ by only 50 mV).

\[
E_{\text{vac}} = 0 \\
E_{\text{SHE}} = -4.5 \\
E_{\text{redox}} (eV) \\
U_{\text{SHE}} (V) \\
U_{\text{SCE}} (V)
\]

\[
\text{strong reducing agents} \\
\text{strong oxidizing agents}
\]

\[U_{H^+/H_2}^0 = 0 \text{ V/SHE} \quad (1.15)\]

In practice, other reference electrodes are employed (like the saturated calomel (SCE) or the Ag/AgCl electrodes, see figure 1.5), but the measurements are usually converted to the SHE scale.

Redox systems having a tendency to release their electrons (i.e. to be in the oxidized form) are called reducing agents. The negative charge that they inject in the electrode results in a negative redox potential:

\[U_{N^{2+}/Ni}^0 = -0.25 \text{ V/SHE} \]

Oxidizing agents tend to be in the reduced form, i.e. they withdraw electrons from the electrode and have a positive redox potential:

\[U_{Ag^+/Ag}^0 = +0.80 \text{ V/SHE} \]

Note that the superscript in \(U^0\) indicates that the measurement of electrode potential has been carried out under standard conditions. The relation
between \( U^o \) and the electrode potential \( U \) under arbitrary conditions is given below and is further discussed in 1.3.2.1.

The electronic states in the electrolyte are discrete states, localized or “attached” to the ions or molecules of the redox system. The oxidized species correspond to empty states and the reduced species are occupied states. Since electrons are easily released from the (occupied) electronic states of a reducing agent, their energy must be high in the absolute energy scale. In a similar way, the empty electronic energy level in an oxidizing agent must be low. From this qualitative reasoning, it can be seen that the electron energy scale and the redox potential scale must have opposite sign.

The Fermi energy of a redox system is related to the redox potential \( U_{Ox/Red} \) of the redox system as:

\[
E_{F,\text{redox}} = -e \cdot U_{Ox/Red} = -e \cdot \left( U^o_{Ox/Red} - \frac{k_BT}{z} \cdot \ln \frac{[\text{Red}]}{[Ox]} \right) \tag{1.16}
\]

where \([\text{Red}]\) and \([Ox]\) are the concentrations of the redox system in its reduced and oxidized form, respectively (see also 1.3.2.1), and \( z \) the number of electrons exchanged. The activity coefficients in equation 1.16 have been assumed to be unity for simplicity. By convention, \( E_{F,\text{redox}} \) is given in eV in relation to the Fermi energy of electrons in the SHE, \( E_{F,H^+/H_2} \). The energy of electrons in the SHE has been determined to be about \(-4.5 \text{ eV}\) in the absolute energy scale [29, 30]. This allows to correlate the energy scales in the solid and in the electrolytic solution, as is shown in figure 1.5.

### 1.2.2.2 Effect of the solvent

The redox potential of the electrolyte has been used to define the electronic energy of a redox system regardless of its form (oxidized or reduced). This is an approximation because it neglects solvation effects, i.e. the interaction of the ions or molecules of the redox system with the solution. The relative permittivity (dielectric constant) of a solvent is about 100 times higher than that of vacuum \((\epsilon_r(H_2O) = 80, \epsilon_r(vac) \equiv 1)\), so the energy associated with solvation is the order of magnitude of bonding energies. This allows ions to be stable in a solution, whereas in vacuum they are very short-lived.

The net charge of the ion causes the polarization of the solvent in its surroundings, i.e. solvent molecules are oriented around the ion forming an “outer solvation shell”. This solvation shell separates the ion from the counterions (ions of opposite sign) in the solution. In certain cases an “inner solvation shell” can also be present (e.g. in \( PtCl_6^{2-} \), where chlorine is strongly bound to \( Pt^{4+} \) forming a “complex”).
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Considering the simple case of an ion without inner solvation shell (e.g. \textit{Cu}^{2+}) and a polar solvent like water, the polarization of the solvent around the ion determines the electric potential in the center of the “shell”, and thus the energy of its corresponding electronic states. When an electron is transferred to or from the ion, the change in net charge of the ion causes a change in the solvation shell. The rearrangement or relaxation of the solvation shell that follows the electron transfer, is associated to a “reorganization energy” such that the electronic state does not have the same energy in the reduced and oxidized forms of the system as was considered in 1.2.1.1. A correction accounting for these relaxation effects must be added:

It results that the Fermi energy of the redox system given in expression 1.16 is only the average between the energy of the actual electronic states in the oxidized and reduced species (\(E_{ox}\) and \(E_{red}\) respectively):

\[
E_{F,\text{redox}} = \frac{E_{ox} + E_{red}}{2}
\]

They have been indicated in figure 1.6. When an electron is captured by the ion in the vacant state of energy \(E_{ox}\), the water molecules react to the extra negative charge by reorienting their dipoles so that the negative poles move away from the ion. This makes the potential at the ion higher (more attractive to electrons) and slowly shifts the energy of the electronic state towards a lower value. A similar reasoning can be done when an electron is released by the occupied state of energy \(E_{red}\), and leads to an increase in the energy of the electronic state. The relaxation of the solvation shell is called a Franck-Condon electron energy shift, and is accompanied by the dissipation of thermal energy in an amount given by the reorganization energy \(\lambda\):

\[
\lambda = \frac{E_{ox} - E_{red}}{2}
\]

where \(\lambda\) depends on the radius of the ion and the dielectric constant of the solvent. True measurements of \(\lambda\) are difficult, and usually \(\lambda \sim 1\ \text{eV}\) is taken as an approximate value.

Thermal fluctuations in the solvent result in fluctuations in the polarization of the ion. Thus the electronic states of energies \(E_{ox}\) and \(E_{red}\) are better described by probability distributions with maxima located at \(E_{ox}\) and \(E_{red}\). By comparison with an harmonic oscillator, the probability that the electronic state in the reduced species has an energy \(E\) is given by:

\[
W_{\text{red}}(E) = \frac{1}{\sqrt{4\pi \lambda k_B T}} \cdot e^{-\frac{(E - E_{\text{red}})^2}{4\lambda k_B T}}
\]
i.e. a gaussian distribution centered at $E_{\text{red}}$ with a full-width half-maximum $\Delta E_{\frac{1}{2}} = 2\sqrt{4\lambda k_B T \ln 2}$. For the oxidized species the distribution of states is:

$$W_{\alpha\alpha}(E) = \frac{1}{\sqrt{4\pi \lambda k_B T}} e^{-\frac{(E - E_{\alpha\alpha})^2}{4\lambda k_B T}}$$ (1.20)

Taking $\lambda \simeq 1$ eV, fluctuations the order of $\Delta E_{\frac{1}{2}} = 0.3$ eV are obtained around $E_{\alpha\alpha}$, $E_{\text{red}}$. With these corrections that account for the effect of the solvent, the electronic energy diagram of the redox electrolyte is depicted in figure 1.6. The corresponding diagrams in a metallic and semiconducting electrodes have been included for comparison. The redox electrolyte can then be defined either by its Fermi energy $E_{\text{F,redox}}$ and the reorganization energy $\lambda$, or by its electronic affinity $E_A$ and its ionization energy $E_I$ in analogy with a semiconductor (they are respectively $E_{\alpha\alpha}$ and $E_{\text{red}}$ in the absolute energy scale).

The main concept is then that the electronic energy state in the redox system fluctuates due to solvent polarization effects, until electron exchange with the solid occurs by tunneling between states of equal energy. Charge transfer is followed by the relaxation of the solvation shell, which results in the shift of the electronic energy states in the redox system.

Given the concentration of reduced [Red] and oxidized species [Ox] in
1.2. ENERGY DIAGRAM OF THE INTERFACE

solution, the density of filled ($D_{\text{red}}$) and empty electronic states ($D_{\text{ox}}$) in the redox system can be expressed using the distributions 1.19, 1.20:

$$D_{\text{red}}(E) = [\text{Red}] \cdot W_{\text{red}}(E)$$ (1.21)
$$D_{\text{ox}}(E) = [\text{Ox}] \cdot W_{\text{ox}}(E)$$ (1.22)

The density of electronic energy states in the redox electrolyte can be defined as $D_{\text{redox}}(E) = D_{\text{red}}(E) + D_{\text{ox}}(E)$, and expressions 1.21, 1.22 can be rewritten in analogy with expressions 1.3, 1.4 for the semiconductor:

$$D_{\text{red}}(E) = D_{\text{redox}}(E) \cdot f(E)$$ (1.23)
$$D_{\text{ox}}(E) = D_{\text{redox}}(E) \cdot (1 - f(E))$$ (1.24)

where $f(E)$ is again the Fermi-Dirac distribution:

$$f(E) = \frac{1}{1 + e^{\frac{E - E_p,\text{redox}}{k_B T}}}$$ (1.25)

This analogy is a convenient generalization, but it must be stressed that the “electronic energy bands” in the ion are due to the relaxation of its solvation shell following the transfer of an electron. Thus the comparison with the semiconductor bands is limited, for example it is not possible to generate “electron-hole pairs” by illumination. In addition, the energy diagrams for redox systems and solids in figure 1.6 are not equivalent: while the ordinate always corresponds to the energy of electrons, the abscissa represents the probability distribution in the case of the redox system, and the distance to the interface in the case of a solid (metal or semiconductor). This is a more convenient choice specially for semiconductors, as it is explained in the following section.

The fluctuating energy level model outlined here is due to Marcus [31], and it was applied to charge transfer processes in semiconductors by Gerischer [32]. These ideas are the basis for the theory of electron exchange explained in section 1.3.

1.2.3 The semiconductor | solution interface

The distribution and occupancy of the electronic energy states in the bulk of the semiconductor and in the solution have been described separately. In this section, the properties of interphases will be first summarized in a general way, and then discussed in some detail for the case of a semiconductor in contact with an aqueous solution.
1.2.3.1 Charge layers in the interface region

In the bulk of the electrolyte phase, all the solvent molecules are randomly oriented (i.e. no net dipole results) and all the charged species are uniformly distributed (electroneutrality). However, the isotropy and homogeneity of the electrolyte are perturbed near the phase boundaries, for example in the region where the electrolyte contacts the gas phase, the vessel walls or a solid electrode. Near the electrode surface, the electrolyte particles “feel” the interaction with both the electrolyte bulk and the solid, and arrange themselves in a new way. The structure of the interphase region is thus a compromise between the structure of the two phases: On the one hand, the solvent molecules next to the electrode are oriented, and the charged species are redistributed, giving rise to a net charge in the vicinity of the electrode. On the other hand, the electric field resulting from this arrangement induces a charge in the electrode that is equal and opposite in sign to that of the electrolyte. Note that the anomalous distribution of particles in the inter-phase region is a very general result that stems directly from the existence of a boundary between two impenetrable phases. If the particles are dipoles or have a charge, their redistribution further results in the appearance of charged layers. The interphase is then said to be “electrified” [33].

In the absence of current flow, the potential drop that appears over the electrified interphase and the charge stored in every phase are linked by the differential capacitance, \( C = \frac{dQ}{dU} \) (the capacity of storing charge per unit area, usually expressed in \( \mu F/cm^2 \)). The two phases are “capacitively coupled”. In the simplest case, a linear relationship can be assumed and the capacitance associated with the charge layers is given by the formula of the “parallel plate” capacitor:

\[
C = \frac{dQ}{dU} = \frac{\epsilon \epsilon_0}{d}
\]

where \( \epsilon \) and \( d \) are the dielectric constant and thickness of the solvent layer, respectively.

Under a thermodynamic point of view, the equilibrium between two phases is described through the concept of electrochemical potential. The electrochemical potential \( \bar{\mu}_i \) of a species \( i \) is the total work required to carry one mole of particles from the infinite (in vacuo) to the bulk of a phase. It comprises all interactions, both chemical (ion-solvent, ion-ion and solvent-solvent) and electric (due to charged particles crossing an electric field). The driving force for the transport of species is given by the electrochemical potential gradient, so if \( \bar{\mu}_i \) of a species is different in two adjacent phases, the particles will flow through the interphase until \( \bar{\mu}_i \) is equal at both sides (equilibrium). It is illustrative to compare the thermodynamic equilibrium
1.2. ENERGY DIAGRAM OF THE INTERFACE

between two phases that may exchange energy (characterized by equal temperatures) with the equilibrium between systems that may exchange particles (characterized by equal electrochemical potentials) [34].

In the case of interest here, the particles that may be exchanged are electrons, and their electrochemical potential is simply called Fermi energy. (Note that $E_{F,\text{redox}}$ as defined in 1.16 accounts only for the “chemical” component of the electrochemical potential in the absence of electric fields. For an accurate discussion of the chemical and electrochemical potentials, see e.g. reference [33]).

The Fermi energy in the semiconductor and in the electrolyte (i.e. the electrochemical potential of electrons in both phases) are different in general. When the semiconductor and the electrolyte contact, electrons flow from the phase of higher $E_F$ towards the lower, until the Fermi energy in both phases is equal (equilibrium):

$$E_F = E_{F,\text{redox}}$$

(1.27)

This results in the separation of charges of opposite sign, and gives rise to an arrangement of charged layers at both sides of the interface.

The distribution of charges in the interface region is rather complex in general: in the semiconductor, the charge is present in the form of fixed dopant ions, free charge carriers and surface states. In the solution, ions near the interface can be mobile or weakly bound to the surface (adsorbed), and solvent molecules form a strongly polarized medium among these charges.

Once the equilibrium has been achieved, the total charge at the interface must be zero (neutrality):

$$Q_{sc} - Q_{el} = 0$$

(1.28)

The electric potential in these layers can be obtained by solving Poisson’s equation given $\epsilon$ the dielectric constant of the medium, a distribution of charge $\rho(x)$ and the boundary conditions in every case:

$$\frac{d^2 \phi}{dx^2} = -\frac{\rho(x)}{\epsilon \epsilon_0}$$

(1.29)

or, if potentials are expressed as $U(x) = \text{const} - \phi(x)$:

$$\frac{d^2 U}{dx^2} = \frac{\rho(x)}{\epsilon \epsilon_0}$$

(1.30)

This is a convenient coordinate change when dealing with electrons (unity negative charge) because the comparison with energy diagrams is straightforward. The constant is determined by the choice of reference electrode in the electrolyte, and $U$ is called the electrode potential.
The potential drop over the semiconductor and the electrolyte are defined:

\[ \Delta \phi_{sc} \equiv \phi_S - \phi_{sc} \]  
\[ \Delta \phi_{ed} \equiv \phi_{ed} - \phi_S \]  

being \( \phi_S \) the electrostatic potential at the semiconductor | solution interface, and \( \phi_{sc} \) and \( \phi_{ed} \) the potential in the bulk of the semiconductor and the electrolyte respectively. The potential drop over the interphase (Galvani potential) is the sum:

\[ \Delta \phi = \Delta \phi_{sc} + \Delta \phi_{ed} \]  

which is related to the electrode potential as:

\[ U = \Delta \phi + \text{const} = \Delta \phi_{sc} + \Delta \phi_{ed} + \text{const} \]  

If \( C_{sc}, C_{ed} \) are the capacitances of the semiconductor and the electrolyte, the potential drops in these layers are:

\[ \Delta \phi_{sc} = \frac{Q_{sc}}{C_{sc}} \]  
\[ \Delta \phi_{ed} = \frac{Q_{ed}}{C_{ed}} \]  

Rewriting \( \Delta \phi \) and using expression 1.28:

\[ \Delta \phi = \Delta \phi_{sc} + \Delta \phi_{ed} = Q_{sc} \cdot \left( \frac{1}{C_{sc}} + \frac{1}{C_{ed}} \right) = \frac{Q_{sc}}{C_{total}} \]  

where \( C_{total} \) is the total capacitance of the interface (corresponding to the composition of \( C_{sc} \) and \( C_{ed} \) in series).

The capacitance and the potential distribution in the electrolyte and in the semiconductor are described in the two next sections (1.2.3.2 and 1.2.3.3). The partitioning of the potential drop between them is discussed afterwards in terms of their respective capacitances. Although the charge stored in surface states belongs to the semiconductor, it will be left for section 1.2.3.5 for simplicity.

1.2.3.2 The electrolyte double layer

In the interfacial region in solution, the electrostatic potential \( \phi \) is different from that in bulk solution. In the first models developed to describe this region, the main concept was that charges of one sign arranged at the electrode surface (\( Q_\infty \)) are balanced by opposite charges in the same amount in the solution. Although in general the charge distribution in the interfacial
region in solution is much more complex (several charged regions must be considered in the electrolyte), the name “double layer” has been maintained to describe it.

The capacitance of the electrolyte \( (C_d) \) is experimentally found to depend on the ion concentration, and on the potential drop in the electrolyte \( \Delta \phi_d \). A typical dependence of \( C_d \) on \( \Delta \phi_d \) is shown in the dotted line of figure 1.10 for a relatively low electrolyte concentration. As can be seen, the total capacitance can be well modelled by the composition of two independent capacitors arranged in series:

\[
\frac{1}{C_{cd}} = \frac{1}{C_c} + \frac{1}{C_d}
\]

(1.38)

where \( C_c \) is approximately independent of potential, and \( C_d \) is comparable to \( C_c \) at low \( \Delta \phi_d \) but steeply increases for larger potentials of either sign. Thus \( C_{cd} \) is given by the smallest capacitance in every case: \( C_d \approx C_d \) for \( \Delta \phi_d \approx 0 \), and \( C_d \approx C_c \) for large \( \Delta \phi_d \).

The dependence of \( C_d \) with \( \Delta \phi_d \) can be interpreted as follows: At large potentials, the electrode exerts a strong attraction towards the ions and rigidly attaches them to the surface. All the potential drop is restricted to the distance corresponding to the first layer of ions, and the associated capacitance is “saturated” (constant). At low potentials there is a diffuse distribution of ions that is strongly affected by the applied potential. Although the capacitive properties of the electrolyte double layer are often due to the same ions behaving differently under different conditions, the analogy of expression 1.38 with the series capacitors suggest that the interfacial region in solution can be treated as two charged layers having a different behavior. They have been sketched in figure 1.7A:

The **compact layer** is defined by two parallel planes: One at the electrode surface containing the semiconductor charge. The other, located at the closest distance from the solvated surface, that mobile ions may reach without losing their solvation shell. The latter is usually called outer Helmholtz plane (OHP), and the distance of closest approach is \( x_{OHP} \approx 0.5 \text{ nm} \) from the electrode surface (see figure 1.7C). If there are not specifically adsorbed ions at the surface (see below), the two charged planes are separated by a layer of solvent molecules. Solving Poisson’s equation in this simple case yields a linear dependence of the potential with the distance to the surface (figure 1.7B). The capacitance of the compact layer takes the constant value:

\[
C_{c,H} = \frac{\epsilon \varepsilon_0}{x_{OHP}}
\]

(1.39)

This model of the compact layer was developed by Helmholtz in analogy with a parallel plate capacitor (expression 1.26). Usual values of \( C_{c,H} \) are the
order of 10 μF/cm² in aqueous solutions. This corresponds to an effective dielectric constant $\epsilon \approx 5$ for the layer of water molecules, a much smaller value than that of bulk water ($\epsilon = 80$). This difference is related to the limited mobility of the solvent molecules in the compact layer as a result of their strong polarization (the electric field between the charge layers is the order of $10^7$ V/cm taking $\Delta \phi_{{\text{ed}}} \approx 1$ V and $x_{{\text{OHP}}} \approx 1$ nm).

On the other hand, the **diffuse layer** is formed by ions in the solution that are free to move up to the OHP. Assuming a Boltzmann distribution of ions with the distance to the OHP (Gouy-Chapman model), Poisson’s equation yields an exponential dependence of the potential (figure 1.7B). The potential drop in the diffuse layer is less extended into the electrolyte, the more concentrated this is. For example in a 0.1 M solution most of the potential is dropped within 0.1 nm, and thus all the excess charge in the diffuse layer is actually concentrated at the OHP. At lower dilutions the layer thickness increases. The capacitance of the diffuse layer ($C_{{\text{d}}}$ in expression 1.38) calculated using the Gouy-Chapman model is:

$$C_{{\text{d,GC}}} = \sqrt{\frac{2\epsilon^2\epsilon_0 N_{{\text{ed}}}}{k_B T} \cdot \cosh\left(\frac{e\Delta \phi_{{\text{ed}}}}{2k_B T}\right)}$$

(1.40)

i.e. it increases with solution concentration $N_{{\text{ed}}}$, and with the potential $\Delta \phi_{{\text{ed}}}$.

It must be stressed that this picture arises from the electric analogy and not from the direct knowledge of the microscopic structure of the interface, so microscopic models must always be handled cautiously. Note, in particular,
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that the layer thicknesses involved in some cases are the order of interatomic distances. It is also noteworthy that the “charge diagram” of the interface does not result directly from the energy diagram: the charge stored in each of the layers (including the semiconductor charge) must be obtained from the potential drop at each layer by means of the layer capacitance.

A convenient simplification of the above models of the electrolyte double layer can be made under certain conditions: For electrolytes more concentrated than 0.1 M the diffuse layer is much thinner than the compact layer, and $C_{d,GC}$ can be neglected in expression 1.38. This can be regarded as the extreme case of a diffuse layer “concentrated at the OHP”, due either to the high electrolyte concentration or the applied potential (both increase $C_{d,GC}$).

The double layer capacitance is then well approximated by $C_d \approx C_c$. In the absence of specific adsorption, the compact layer is simply formed by solvent molecules and $C_c$ takes the constant value $C_{c,H}$ given by the Helmholtz model (expression 1.39). In this case, the electrolyte double layer is commonly termed **Helmholtz layer** and $C_d$ is written $C_H$. The potential drop over the double layer is then:

$$
\Delta \phi_d = \frac{Q_{sc}}{C_d} \approx \frac{Q_{sc}}{C_H} \equiv \Delta \phi_H
$$

(1.41)

As a useful picture, the solvent molecules in the Helmholtz layer have been compared with the “solvation shell” of the electrode charge [26]. Actually in aqueous solutions $x_{OHP} \approx 0.5 \text{ nm}$ is the thickness of one water monolayer.

**Specific adsorption** Certain ions can lose their solvation shell in the proximity of the electrode and strongly interact with the surface. This phenomenon is called specific adsorption because it depends on the chemical nature of the ion, rather than on its charge. The specifically adsorbed ions are located among the solvent molecules in the compact layer, and their separation from the surface defines the inner Helmholtz plane (IHP, see figure 1.8A).

When there are specifically adsorbed ions on the electrode, the compact layer capacitance is no longer given by expression 1.39. The correction is very complex in general because the number of specifically adsorbed charges depends not only on the potential applied to the electrode, but also on the chemical affinity between the surface atoms and the adsorbed ions (e.g. negative ions can be specifically adsorbed even when the electrode charge is negative). The potential drop between the surface and the IHP can be assumed to be linear, its sign depending on the adsorbed charges (figure 1.8B).

In this case, charge neutrality across the interface is preserved by the accumulation of additional charges (in equal amount to those specifically
adsorbed, and opposite in sign) in the diffuse layer. As an example, the positively-charged electrode of figure 1.8A has specifically adsorbed negative ions. The diffuse layer is then formed by negative charges that balance the electrode charge, plus the positive countercharge of the adsorbed ions. Thus the diffuse layer contains an excess charge of both signs with respect to the bulk solution. However, the potential drop beyond $x_{OHP}$ (shown in figure 1.8B) can usually be neglected due to the large capacitance $C_d$ (the diffuse layer acts as a “charge buffer”).

The tendency of an ion to adsorb specifically is directly related to its solvation. In aqueous solutions, cations are strongly hydrated because the unpaired electrons of the oxygen atom in water molecules are attracted by positive charges. In addition, the charge density is higher in cations (lacking an electron) than in anions (having one excess electron). Thus adsorption phenomena in water usually involves only relatively large anions (having a small charge density like $I^-$, $Br^-$).

In metals (charge density around $10^{22} \text{ cm}^{-3}$), $\Delta\phi_d$ is usually determined by the free charge that is exchanged with the solution. For semiconductors, being the charge stored near the surface much lower (the order of $10^{17} \text{ cm}^{-3}$ in volume, i.e., about $10^{13} \text{ cm}^{-2}$), $\Delta\phi_d$ is often dominated by adsorption/desorption processes which involve larger amounts of charge. For example, 0.1 ML of adsorbed ions like $H^+$ or $OH^-$ in aqueous solutions, correspond to a charge density of $10^{14} \text{ cm}^{-2}$ and $\Delta\phi_d \approx 1 \text{ V}$. For many semiconductors (e.g. $SnO_2$, $Ge$, $GaAs$) in aqueous solutions, the relative adsorption of $H^+/OH^-$ at the surface produces a potential drop over the
double layer equal to:

$$\Delta \phi_d = \text{const} - \frac{2.3k_B T}{e} \cdot pH$$

(1.42)

i.e. $\Delta \phi_d$ decreases about 60 mV per pH unit. (As a reminder, the pH of a solution gives a measurement of the acidity, i.e. the molar concentration of protons ($H^+$), and is defined as $pH = -\log[H^+]$. The concentration of $OH^-$ can be obtained from the dissociation constant of water, $K_w = [H^+][OH^-] = 10^{-14}$).

1.2.3.3 The space charge region

If the Fermi energy of the semiconductor is located within the bandgap, the equalization of the Fermi levels with the electrolyte (expression 1.27) is achieved by the transfer of majority carriers to the latter. At equilibrium, the semiconductor surface is thus depleted of majority carriers, and the “charge layer” (named space charge region, SCR) is due to the fixed ionized dopants in the lattice. Such depletion layer is shown in figure 1.9C for a $n-$type semiconductor. Emptying the $n-$type semiconductor of electrons corresponds to a decrease in the Fermi energy (the electrode potential shifts towards positive values). This “bends” the bands upward in the region contiguous to the interface.

The band bending results from the internal electric field in the SCR: when the $n-$type semiconductor is emptied of free electrons (by electron transfer to the electrolyte, or by applying an external positive potential to the electrode) they are first depleted from the surface, which breaks the neutrality in this region and leaves a positive net charge due to the ionized donors. This fixed charge gives rise to a local electric field in the region contiguous to the surface, that attracts electrons towards the surface (i.e. opposed to the external field). The electric work delivered to an electron by the field in this region results in an increase of the electron energy near the surface, in relation to the semiconductor bulk. The upward band bending of figure 1.9C corresponds to an energy barrier for electrons.

The potential drop over the semiconductor $\Delta \phi_{sc}$ is given by the bending of the bands. In a depleted $n-$type semiconductor, $\Delta \phi_{sc} > 0$ as defined in 1.31. The positive charge $+Q_{sc}$ due to the dopant ions, is balanced by a negative countercharge $-Q_{sc}$ in the electrolyte side. Note that during the formation of the depletion layer, the entire band structure in the semiconductor bulk “shifts” downward, and the bands bend so that the bandedge energy remains constant (the bandedges are “pinned” at the surface). This will be further discussed in 1.2.3.4.
Figure 1.9: Energy band profiles and charge distribution near the surface of $n$– and $p$–type semiconductors: Accumulation (A, H), flatband (B, G) and depletion (C, F). Situations D and E correspond to deep depletion (nonequilibrium) and will be discussed later.
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A similar reasoning can be used in a $p-$type semiconductor (figure 1.9F): emptying the semiconductor of holes (or applying an external negative potential to the electrode) corresponds to raising the Fermi level, and this results in a SCR of negatively ionized acceptors and a positive countercharge in the electrolyte. The semiconductor bands bend downward ($\Delta \phi_{sc} < 0$) and again an energy barrier for majority carriers is built up.

It must be stressed that the diagrams depicted in figure 1.9 are energy diagrams of electrons (given in $eV$ vs. the vacuum level), although they are often read as electric potential diagrams because this is the directly measurable magnitude (given in $V$ vs. a reference in solution). The equivalence between these scales was shown in figure 1.5: they have opposite sign and are shifted by $4.5 \, V$ in the case of the SHE. In this way, applying a positive potential $U_0$ to the electrode, decreases its Fermi energy by $eU_0$. The “water simile” is often useful when handling energy diagrams: Electrons can be regarded as water flowing from “higher” to “lower” states or sliding down the slope of a bent band. Note, however, that holes are usually depicted in the same diagram as electrons, but their energy axis is reversed: The diagram must be viewed upside down in order to employ the water simile with them.

Some useful relations can be given for the semiconductor under depletion conditions (figures 1.9C and 1.9F): the bands are bent such that majority carriers are extracted from the surface in moderate amounts and (in the absence of injection from the electrolyte, and in the dark) the minority carriers are not present. Thus $\rho(x)$ in Poisson’s equation accounts only for the fixed charges due to ionized dopants, and yields a parabolic potential profile across the SCR:

$$U(x) = \frac{eN_{sc}}{2\epsilon_0}(x - W)^2$$

(1.43)

where $N_{sc}$ is the doping density, $x = 0$ at the interface and the electric field extends a depth $W$ into the semiconductor. The potential barrier as seen from the semiconductor bulk (the “surface barrier”) is given by the Schottky relation,

$$U_S = \frac{eN_{sc}W^2}{2\epsilon_0}$$

(1.44)

which in turn gives an expression to estimate $W$. Using $U_S \simeq 1 \, V$, $\epsilon_{Si} = 8$, $\epsilon_0 = 8.8 \cdot 10^{-14} \, CV^{-1} cm^{-1}$, expression 1.44 yields $W \simeq 1 \, \mu m$ for $N_{sc} \simeq 10^{15} \, cm^{-3}$, and $W \simeq 30 \, nm$ for $N_{sc} \simeq 10^{18} \, cm^{-3}$. The thickness of the SCR under depletion is lower in samples of higher doping, because the fixed charges are correspondingly more dense.
The surface charge density in the semiconductor (given in $C/cm^2$) is:

$$|Q_{sc}| = eN_{sc} \cdot W = \sqrt{2e\epsilon_0eN_{sc}} \sqrt{|U_S| - \frac{k_BT}{e}}$$

(1.45)

for a barrier larger than $|U_S| > \frac{3k_BT}{e}$. Taking $U_S \simeq 1V$ in silicon, and $N_{sc} \simeq 10^{15} cm^{-3}$, the space charge is $Q_{sc} \simeq 10^{11} cm^{-2}$. Increasing $N_{sc}$ by a factor 1000, increases $Q_{sc}$ by a factor 30.

The differential capacitance can be derived from equation 1.45 as $C = \frac{dQ}{dW}$. This is called the Mott-Schottky relation:

$$C_{sc} = \sqrt{\frac{\epsilon e_0eN_{sc}}{2}} \cdot \frac{1}{\sqrt{|U_S| - \frac{k_BT}{e}}}$$

(1.46)

Thus the capacity of storing charge in the semiconductor depends on the material ($\epsilon$) and the doping density ($N_{sc}$) as well as on the band bending $U_S$. The capacitance decreases on increasing the band bending, due to the “limited” density of dopant ions that provide the charge in the semiconductor under depletion conditions.

Expressions 1.3, 1.4 with $E_{CS}$ and $E_{VS}$ the conduction and valence band-edges respectively, allow to calculate the equilibrium density of electrons and holes at the semiconductor surface, as a function of the barrier height $U_S$ and the carrier concentration in the bulk ($n_b$, $p_b$):

$$n_s = N_C \cdot e^{-\frac{E_{CS} - E_F}{k_BT}} = n_b \cdot e^{-\frac{eU_S}{k_BT}}$$

(1.47)

$$p_s = N_V \cdot e^{-\frac{E_F - E_{VS}}{k_BT}} = p_b \cdot e^{-\frac{eU_S}{k_BT}}$$

(1.48)

The Fermi energy of the semiconductor can be varied by applying an external potential, and different shapes of the energy bands near the surface are obtained. The flatband (FB) potential, $U_{FB}$, corresponds to the situation in which the bands are flat (figure 1.9B, 1.9G). The surface barrier is then $U_S = 0 V$ and the charge due to fixed ions is balanced by the free charge at the surface. When the charge stored in surface states (see 1.2.3.5) and due to ion adsorption (1.2.3.3) can be neglected, at the FB potential the total charge at the interface is zero:

$$Q_{sc} = Q_{sd} = 0 \quad \text{at} \quad U = U_{FB}$$

(1.49)

Sometimes $U_{FB}$ is used as a reference potential in the semiconductor. As is indicated in the axis of figure 1.9, the determination of the FB potential allows to locate the band edges at the surface in the potential scale, using expressions 1.8 and 1.11 or figure 1.3 in the case of silicon.
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The **accumulation** layer (figures 1.9A and 1.9H) is produced when the bands are bent so that majority carriers are accumulated at the surface (by application of potentials negative of FB in a n-type semiconductor or positive of FB in a p-type). The countercharge in the electrolyte side is then opposite to depletion: positive in n-type, negative in p-type. In this case \( \rho(x) \) must account for the fixed dopant ions plus the excess free charge, and Poisson’s equation yields a potential profile (non-parabolic in general) that is typically extended over \( \sim 10 \text{ nm} \). The SCR under accumulation is thus much thinner than in depletion.

An expression for the SCR capacitance in the accumulation regime can also be obtained [35], and its variation with the potential drop in the SCR is shown qualitatively in figure 1.10. The electrolyte capacitance has also been plotted for comparison.

When the band bending is further increased under depletion conditions, the Fermi energy approaches the minority carrier bandedge at the surface. The concentration of majority carriers is decreased, and in principle an equilibrium population of minority carriers can build up. However, such equilibrium situation (leading to an **inversion** layer) only shows up under very particular conditions in a semiconductor | electrolyte interface [36], and will not be treated here. More commonly, the majority carriers are further extracted and a **deep depletion** layer is formed (figures 1.9D, 1.9E): As in
the depletion layer, only the ionized dopants contribute to $\rho(x)$ in Poisson’s equation, and yield again a parabolic band profile. Note that the deep depletion layer strictly corresponds to a non-equilibrium situation, and therefore a Fermi energy cannot be defined for it. An additional effect may appear in this case, because states of equal energy can be found in both energy bands, spatially separated by only $W$ (see points P and Q in figures 1.9D, 1.9E). Then if the SCR is thin, as it is in highly-doped semiconductors ($N_x \approx 10^{19} \text{ cm}^{-3}$ yields $W \approx 1 \text{ nm}$), the probability for carrier tunneling between the bands is dramatically increased: The high potentials necessary to achieve a deep depletion layer, result in large tunneling currents that bring to (Zener) electrical breakdown.

**1.2.3.4 Partitioning of the potential drop in the interface region**

At the equilibrium, the total charge inside the semiconductor $Q_{sc}$ and in the electrolyte double layer $Q_{el}$ are equal and opposite in sign (expression 1.28). The different charges and their arrangement in these regions has been described in the previous two sections. The potential drop over the interface, $\Delta \phi$, is partitioned between the semiconductor ($\Delta \phi_{sc}$) and the electrolyte ($\Delta \phi_{el}$) depending on their respective capacitances (expressions 1.35-1.37). If the total interface capacitance,

$$\frac{1}{C_{total}} = \frac{1}{C_{sc}} + \frac{1}{C_{el}}$$ (1.50)

is dominated by one of the terms, the potential drop due to the other term can be neglected.

The partitioning of an externally applied potential will be first examined, neglecting for simplicity the capacitances associated to specifically adsorbed ions and surface states (they are discussed later). A qualitative plot of $C_{el}$ and $C_{sc}$ versus potential was shown in figure 1.10. From the relative values of $C_{sc}$ and $C_{el}$, two cases can be distinguished

When the semiconductor is in **depletion**, $C_{el} \gg C_{sc}$ and expression 1.50 simplifies as $C_{total} \approx C_{sc}$. The physical interpretation was that the electrolyte double layer is much thinner than the SCR because its charge density is correspondingly larger than in the depleted semiconductor ($x_{OHP} \approx 0.5 \text{ nm}$ against $W \approx 100 \text{ nm}$, being $N_{el} \approx 10^{21} \text{ cm}^{-3}$ in a 0.1 M solution, and $N_{sc} \approx 10^{16} - 10^{18} \text{ cm}^{-3}$). In this case, most of the potential $\Delta \phi$ applied to the entire interface is borne by the SCR, and is employed in the bending of the bands ($\Delta \phi_{sc}$). While the semiconductor is in depletion (or deep depletion), the energy of the bandedges at the surface remains nearly constant (“bandedge pinning”). This is the usual situation at the semiconductor | electrolyte
interface. In contrast, inside a metal electrode no SCR is developed, and all the applied potential is dropped over the electrolyte double layer.

When larger potentials are applied to the interface, free charge carriers are accumulated at the semiconductor surface. In particular, an accumulation layer of majority carriers can be formed. The carrier density approaches the ion concentration in solution and the SCR thickness is reduced to some nm. In this case, $C_{sc}$ becomes the order of $C_d$ and none of them can be neglected in $C_{total}$. The potential drop over the interface is then partitioned between the semiconductor and the electrolyte double layer. Assuming $C_d$ independent of potential, when the electrode potential approaches $U_{FB}$, the semiconductor capacitance $C_\infty$ is comparable to $C_d$ [37, 38]. The fraction of the applied potential (direct and alternating) dropped over the SCR is:

$$\gamma_{dc} = -\frac{\Delta \phi_\infty}{U - U_{FB}}$$

(1.51)

$$\gamma_{ac} = -\frac{d\Delta \phi_\infty}{dU}$$

(1.52)

where $0 < \gamma < 1$. Figure 1.11 [38] shows the calculated dependence of $\gamma_{dc}$ and $\gamma_{ac}$ with the electrode potential for a $n$-type semiconductor. Both $\gamma_{dc}$ and $\gamma_{ac}$ decrease steeply for potentials negative of $U_{FB}$ (accumulation), showing that in this range most of the applied potential is dropped in the electrolyte. In figure 1.12 [38], the potential drop inside the semiconductor starts to saturate at a band bending near the onset of degeneration ($\Delta \phi_\infty \approx -0.3$ V in $n$ - Si $10^{16}$ cm$^{-3}$). The Fermi energy thus penetrates into the majority carrier band (the semiconductor surface is degenerated), but it does not move much farther. Degeneration is the transition of the semiconductor to the metallic behavior, and indeed the solid behaves as a metal: As was explained above, in metals all the applied potential is dropped over the electrolyte double layer. Since the electrode potential is measured with respect to a reference in the bulk solution (i.e. beyond the double layer), changes in $\Delta \phi_d$ result in the “unpinning” of the semiconductor bandedges: In the example of figure 1.12, changing the electrode potential from $U = U_{FB} - 0.5$ V to $U = U_{FB} - 1.0$ V increases the band bending in $\Delta \phi_\infty \approx -50$ mV, while the bandedges at the surface have shifted an amount $\Delta \phi_d \approx 0.5$ V towards higher energies (negative potentials).

The partition of the applied potential over the semiconductor | electrolyte interface has been outlined in the insets of figure 1.12 for a $n$-type electrode. Bandedge unpinning only occurs at large electrode potentials (the small $\Delta \phi_d < 0$ at equilibrium is due to the positive charge in the depletion layer). However, it must be mentioned that the accumulation of charge carriers at the electrode surface usually involves a flow of current through
the interface. In that case, the potential drop over the interface is no longer purely capacitive, and resistive terms must be taken into account in a quantitative description. Note also that in the case of deep depletion (shown in figure 1.9D) the bandedges are still pinned at the surface, because the Fermi level is not well defined in the surface region (non-equilibrium).

A more general statement on bandedge unpinning can actually be given. The electrode potential $U$ was defined in 1.34:

$$U = \Delta \phi_{sc} + \Delta \phi_{el} + const$$ (1.53)

At the FB potential, $\Delta \phi_{sc} = 0$:

$$U_{FB} = \Delta \phi_{el} + const$$ (1.54)

which means that $U_{FB}$ (or the bandedge energies $E_{CS}$, $E_{VS}$) measured in relation to the reference in solution, are controlled by the potential drop in the double layer, $\Delta \phi_{el} = \frac{Q_d}{C_{dl}}$. In many cases, $Q_d$ is dominated by the charge stored at the surface. Thus all phenomena involving changes in the surface charge can affect the measured value of $U_{FB}$ (bandedge unpinning):

- Accumulation of majority/minority carriers
- Ion adsorption
- Charge trapping in surface states (1.2.3.5)
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Figure 1.12: The band bending, $\Delta \phi_{sc}$, as a function of the applied potential for three values of the electrolyte capacitance $C_H$. Under depletion conditions (positive potentials in the n-type electrode of the figure), there is a linear dependence of the band bending with the electrode potential: all the potential applied to the interphase is dropped within the SCR. Under accumulation (negative potentials in an n-type electrode), $\Delta \phi_{sc}$ tends to saturate and the applied potential is partially dropped in the electrolyte. As a result, the band edges “shift” towards negative potentials. The band bending calculations are taken from reference [38].

For example, if there are specifically adsorbed ions on the surface, their charge may be much larger than the charge that can be stored in the depletion layer. Usually the adsorbed charge $Q_{ad}$, sets a $\Delta \phi_{ad}$ regardless of the electrode potential. The FB potential and the position of bandedges is then fixed by this $\Delta \phi_{ad}$.

1.2.3.5 Surface states

The description of the semiconductor in terms of the energy bands is valid, strictly speaking, in the bulk of the material. A surface is such a strong discontinuity that new electronic states generally appear. These are the surface states.

Covalent crystals (as opposed to ionic) are formed by atoms having small or no difference in electronegativity, which are bonded by sharing unpaired
Figure 1.13: The cleavage of a covalent crystal (A) gives rise to half-occupied orbitals (“dangling bonds”) in vacuum (B). They are named intrinsic surface states. In solution, surface or interface states arise from the polarity of surface bonds (C).

electrons. Crystals of one non-metallic element, like silicon, are always covalent. The formation of a surface can be considered by breakage of the covalent bonds in a plane of a perfect monocrystal in vacuum, which give rise to half-occupied orbitals (“dangling bonds”, see figure 1.13). These surface states are named “intrinsic” (Shockley states for a covalent crystal) and their electronic energy is usually located near the center of the bandgap [39, 40]. The occupancy of these states is given by a Fermi-Dirac distribution (expression 1.1) and produces a net charge on the surface.

Thus in vacuum any surface has almost inevitably a charge localized on it: With only 1% of the surface atoms contributing to surface states, a density of \( N_s = 10^{13} \, \text{cm}^{-2} \, \text{eV}^{-1} \) along 0.1 eV can be achieved, or \( N_s = 10^{12} \, \text{cm}^{-2} \) if a monoenergetic surface state is assumed. That is, surface states are real “charge reservoirs” that can store a charge equal to the SCR, and even larger (1 ML of surface atoms corresponds to \( \sim 10^{15} \, \text{cm}^{-2} \)). Electrons are exchanged between the semiconductor and the surface states, until their Fermi levels are equalized and a SCR is formed. This is shown for a \( n \)-type semiconductor in figure 1.14 (note that in vacuum, \( Q_{sc} = -Q_s \) at equilibrium [41]).

When a semiconductor electrode is immersed in an electrolyte, the interaction with the solvent and the chemical species in solution usually prevail, and the surface state charge may vary. For example, an ideal surface with dangling bonds is extremely reactive, and new bonds will be formed as soon as it contacts with a solution (figure 1.13C). Generally, polar bonds (having a large \( \delta \)) give rise to surface states capable of storing charge. The surface state charge can be added to \( Q_{sc} \), and has a countercharge \( Q_d = -(Q_{sc} + Q_s) \).
in the electrolyte (see figure 1.15). The potential drop over the electrolyte double layer is given by expression 1.41.

The potential drop over the interface in the presence of surface states is shown in the energy diagrams of figure 1.16 for a $n$–type electrode. Note that $\frac{Q_s}{C_{el}} = \frac{eN_s}{C_{el}}$ can reach 100 mV with $C_a = 10 \ \mu F/cm^2$ and only $N_s = 10^{13} \ \text{cm}^{-2}$. Hence, as specific adsorption and carrier accumulation, filling and emptying of surface states produce again a change in the potential drop at the HL that results in bandedge unpinning.

Figure 1.15: Charge distribution near the semiconductor | solution interface: depleted $n$–type semiconductor in the presence of a surface charge $Q_s$. Note the different distance scales in the semiconductor and the electrolyte.
Figure 1.16: Bandedge unpinning by charging of surface states: (AB) As the electrode is brought towards negative potentials ($E_F$ is raised), all the applied potential results in a change of $Q_\infty$ while the bandedges remain pinned at the surface. The surface states are empty and $\Delta \phi_d = \Delta \phi_d^0 = \text{constant}$. Following to decrease the applied potential, the Fermi level is further raised but the charge is now stored in surface states: (C) the surface states are half empty, $\Delta \phi_d = \Delta \phi_d^0 - \frac{Q_{\infty}}{C_{e1}}$ and the bandedges have shifted by $\frac{Q_{\infty}}{C_{e1}}$ towards negative potentials. This potential drop is translated to the double layer. After completely filling the surface states (D), $\Delta \phi_d = \Delta \phi_d^0 - \frac{Q_{\infty}}{C_{e1}}$ and the shift of the bandedges is $\frac{Q_{\infty}}{C_{e1}}$. (EF) the bandedges are pinned again and the applied potential only affects the SCR.

**Fermi level pinning** Experimentally, the filling/emptying of surface states sketched in figure 1.16C, appears as a plateau in the plot of $\Delta \phi_\infty$ vs. the potential applied to the interface (figure 1.16 above). As will be explained in the following section (1.2.3.6), this plot is obtained from the measurement of the interface capacitance. In the absence of surface states (dashed curve) a linear behavior is obtained, because under depletion conditions all the applied potential $\Delta \phi$ is dropped within the SCR ($\Delta \phi = \Delta \phi_\infty + \Delta \phi_H$, with $\Delta \phi_H = \text{constant}$, see 1.2.3.4). However, as $E_F$ approaches $E_{ox}$, the applied potential is employed in charging the surface state (solid curve). A countercharge is built in the electrolyte and the bandedges shift upwards ($\Delta \phi_H \neq \text{constant}$), but the semiconductor band bending $\Delta \phi_\infty$ remains un-
changed. Thus a plateau appears in the plot until the surface states are completely filled. Within this region, $E_F$ is fixed at $E_s$ (the Fermi level is said to be “pinned” at the surface states [42, 43]). The width of the plateau corresponds to $\Delta \phi_H = \frac{2N_s}{U_H}$, which gives an estimate of $N_s$ if $C_H$ is known. Note that when the Fermi level is pinned, the semiconductor behaves as a metal: At equilibrium, $E_F$ is equalized with $E_{F,redox}$ but $\Delta \phi_{ec}$ remains constant. The pinning of the Fermi level has many important consequences in charge transfer reactions (especially under illumination) because charge is transferred from the surface states instead of the bandedges. A complete introduction can be found in reference [44]. The experimental techniques employed to characterize surface states and their effects have been reviewed in references [45, 46].

1.2.3.6 Energy diagram of the interface

The concepts introduced so far concerning the energy states of electrons and their occupancy in the semiconductor and in the electrolyte, will be assembled in this paragraph in order to build the electron energy diagram of the semiconductor | electrolyte interface.

The energy diagram can be directly sketched from experimental measurements in the following way: First, the potential difference between the semiconductor electrode and the reference electrode immersed in the electrolyte is measured with a voltmeter. This is the open-circuit potential (OCP) of the semiconductor electrode, and is noted $U_{OCP}$. If the SHE is employed as a reference electrode, $U_{OCP}$ is given in $V$/SHE (see figure 1.5). Another characteristic potential is the flatband potential ($U_{FB}$) described in 1.2.3.3. $U_{FB}$ can also be measured in relation to the reference electrode (the experimental procedure will be described later). The majority carrier bandedge is then given by:

\[
U_{CS} = U_{FB}^n - \frac{\mu_C}{e} \quad (n - \text{type}) \tag{1.55}
\]

\[
U_{VS} = U_{FB}^n + \frac{\mu_V}{e} \quad (p - \text{type}) \tag{1.56}
\]

where $\mu_{C,V}$ were defined in 1.12 and 1.13 (see figure 1.3 for their values in silicon). The minority carrier bandedge results from the bandgap, $E_g$. Both $U_{OCP}$ and $U_{FB}$ can be placed directly in the potential scale, and the difference between them yields the semiconductor band bending at equilibrium (i.e. at $U = U_{OCP}$):

\[
\Delta \phi_{ec} = U_{OCP} - U_{FB} \tag{1.57}
\]

Note that $\Delta \phi_{ec} > 0$ when the bands are bent upward (see figure 1.17).
Figure 1.17: Construction of the energy diagram for the semiconductor | electrolyte interface: n−-type (left) and p−-type (right). See the text for details on the procedure.

On the electrolyte side, the redox potential $U_{Ox/Red}$ (given in $V/SHE$, see 1.2.2.1) is also placed in the potential scale. In the case of metal ions, and if the reduced form of the $Ox/Red$ system is a solid, $U_{Ox/Red}$ can be estimated as the potential difference between a piece of metal $Red$ (e.g. a wire) and the reference electrode. If the semiconductor electrode and the electrolyte are at equilibrium, their Fermi energies must be equal:

\[ E_{F_{sc}} = E_{F_{redox}} \]
\[ -eU_{OCP} = -eU_{Ox/Red} \]

and thus $U_{OCP}$ is expected near $U_{Ox/Red}$.

If the potential axis is now translated into energies, the potential drop in the electrolyte $\Delta \phi_{ed}$ can be determined. As was shown in figure 1.5, the vacuum level corresponds to a potential $-4.5 \text{ V/SHE}$. In the bulk of the semiconductor, $E_{vac}$ is given by the electronic affinity $E_{A,sc}$ (or $\chi$ using the semiconductors notation; see figure 1.17 and table 1.14 for silicon). The difference between them across the interface, is related to the potential drop at the electrolyte double layer ($\Delta \phi_{ed}$). It can be calculated as:

\[ \Delta \phi_{ed} = \frac{E_{A,sc} + \mu_C}{e} - U_{FB} - 4.5V \quad (n - \text{type}) \]
\[ \Delta \phi_{ed} = \frac{E_{A,sc} + E_g - \mu_V}{e} - U_{FB} - 4.5V \quad (n - \text{type}) \]
As was discussed in 1.2.3.4, $\Delta \phi_{eq} = 0$ in the “ideal case”. If $\Delta \phi_{eq} \neq 0$, it means that a charge is trapped at the surface.

Actually a “theoretical” energy diagram can be predicted from the parameters of the semiconductor and the electrolyte, if $\Delta \phi_{eq}$ is neglected in a first approach: The Fermi energy of the redox species in solution, at a given $[Ox]$ concentration, can be simply calculated from standard redox potential tables using expression 1.16, and then placed in the electrochemical energy scale given by the reference electrode. In figure 1.17, the system $Ox/Red$ has a redox potential $U_{Ox/Red}$ in the SHE scale, and thus a redox energy $E_{F,Ox/Red} = -eU_{Ox/Red}$. In addition, if the reorganization energy $\lambda$ is known for the system $Ox/Red$, the energy fluctuations of its electronic levels can also be estimated.

Assuming $\Delta \phi_{eq} = 0$, the CB edge at the surface is located in the electrochemical scale at an energy $E_{A,sc}$ below $E_{vac}$. Of course, the VB edge is given by $E_g$. At equilibrium, the Fermi energy of the semiconductor must be equal to $E_{F,Ox/Red}$ and then the bending of the bands (i.e. the potential drop inside the semiconductor) is obtained by subtracting:

$$\Delta \phi_{sc} = U_{Ox/Red} - U_{CS} - \frac{\mu_C}{e}$$  \hspace{1cm} (1.62)

As an example, the experimental bandedges of several semiconductors in acidic solution are presented in figure 1.18 [46].

Figure 1.18: Bandedge potentials for several semiconductors in acidic solution. The potential of several redox systems in solution is also shown. From reference [46].
Experimental determination of the flatband potential  The Mott-Schottky relation (expression 1.46) links the semiconductor capacitance \( C_{sc} \) under depletion, and the potential drop in the semiconductor \( \Delta \phi_{sc} \). In the depletion regime, and in the absence of charge trapped at the surface (\( \Delta \phi_{sd} = 0 \)), \( \Delta \phi_{sc} \) can be expressed as a function of the electrode potential using equations 1.53 and 1.54:

\[
\Delta \phi_{sc} = U - U_{FB}
\]  

(1.63)

Thus the Mott-Schottky relation can be rewritten:

\[
\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon_0 \varepsilon N_{sc}} \cdot (\Delta \phi_{sc} - \frac{k_B T}{e}) = \frac{2}{\varepsilon_0 \varepsilon N_{sc}} \cdot (U - U_{FB} - \frac{k_B T}{e})
\]  

(1.64)

The capacitance \( C_{sc} \) can be measured experimentally at different electrode potentials, and the plot of \( \frac{1}{C^2} \) vs. \( U \) that is obtained is linear (“Mott-Schottky (MS) plot”). Its slope yields the semiconductor doping concentration \( N_{sc} \), and the intercept at \( \frac{1}{C^2} = 0 \) allows to determine \( U_{FB} \) (see figure 1.19). It must be stressed that the capacitance that is measured experimentally is the interface capacitance \( C_{tot} \), including contributions of the SCR (expression 1.64 above), the electrolyte double layer (see 1.2.3.3) as well as surface states if they are present. Thus, unless an electric model for each contribution is available, the capacitance measurement must be performed under conditions such that the only significant contribution is due to the SCR: \( C_{tot} \) must be large (as discussed in 1.2.3.4, \( C_{tot} \gg C_{sc} \) under depletion), the frequency high enough so that surface states are “frozen” (usually they do not respond to \( U(\omega) \) beyond some tens of \( KHz \)) and of course, low-impedance electric contacts in the circuit are essential.

Note that another way of presenting the MS plot is:

\[
\Delta \phi_{sc}(U) = \frac{\varepsilon_0 \varepsilon N_{sc}}{2} \cdot \frac{1}{C_{sc}^2(U)} + \frac{k_B T}{e}
\]  

(1.65)

whose slope equals 1 as is expected for the depletion regime (all the applied potential is dropped within the SCR, see 1.2.3.4), and the intercept at \( \Delta \phi_{sc} = 0 \) (i.e. flat bands) yields again \( U_{FB} \). This is shown in the right axis of figure 1.19, and was implicitly used in figure 1.16.

Besides the measurement of the interface capacitance (electrochemical impedance spectroscopy, EIS), several other methods to determine \( U_{FB} \) exist, but they usually require a complex experimental setup: electrolyte electoreflectance using subgap illumination [47, 48, 49], photocurrent under chopped light [43, 45] or photopotential under high-frequency pulsed illumination [50].
1.3 Charge transfer processes at the semiconductor | solution interface

1.3.1 Introduction

When a semiconducting or metallic electrode is immersed in an electrolyte, the electrode achieves the equilibrium when the flow of current in and out of the electrode is the same, and the resulting net current equals zero. The electrode is at the open-circuit potential (OCP), and the current in each direction is called the “exchange current”. If the electrode potential is then forced to shift from the OCP value by applying an external potential (“overpotential”), a net current flows through the interface. In this section, expressions for the current as a function of the overpotential (the “kinetic equation”) will be given both for metallic and semiconducting electrodes.

Such current flow always implies a chemical reaction at the interface, because electrons (that provide conductivity in the solid) have to be transferred to or from ions (that provide conductivity in the solution). In semiconductors, electrons and holes can be treated as individual reactants in interfacial reactions [51], because they are in relatively small concentration. Electrons and holes are envisaged as activated states, sites where reactions can be initiated. If the overpotential applied to an electrode is positive of OCP, oxidative or “anodic” processes are promoted at the electrode surface. For example,
in an electrolyte containing the $Fe^{3+}/Fe^{2+}$ redox system:

\[
\begin{align*}
Fe^{2+} & \rightarrow Fe^{3+} + e^- \quad (1.66) \\
Fe^{2+} + h^+ & \rightarrow Fe^{3+} \quad (1.67)
\end{align*}
\]

i.e. either electrons are injected into the electrode or holes are withdrawn from it, while the reducing agent ($Fe^{2+}$) loses an electron (it is oxidized). The corresponding anodic currents are conventionally taken as positive. If the electrode overpotential is negative, the observed current is “cathodic” (negative) and corresponds to reductive processes, e.g. the reverse of the above reactions: the oxidizing agent $Fe^{3+}$ gains electrons (it is reduced) either by withdrawing them from the electrode or by hole injection. The current signs are shown in figure 1.20. This sign convention is employed when studying metal-semiconductor contacts (the metal is usually grounded) and is the commonly adopted in semiconductor electrochemistry, but not in metal electrochemistry. Note also that since conduction through the bulk of a semiconductor is provided with majority carriers, only currents due to majority carriers can be directly measured. In general the measured current will have several contributions that have to be separated a posteriori.

### 1.3.2 Kinetics of electrode reactions

According to the classical model, the reduction and oxidation currents through an electrode are proportional to the density of charge carriers in the solid and
Figure 1.21: *Energy barrier for the cathodic and anodic processes. The system must reach an “activated state” prior to electron transfer.*

The electrolyte, and to a Boltzmann factor describing an “activated state” that the system must reach for the transfer to occur:

\[
    j_{\text{red}} = k_e \cdot n_S \cdot [Ox] \cdot e^{-\frac{\Delta G_{\text{act}}}{RT}} \quad (1.68)
\]

\[
    j_{\text{ox}} = k_a \cdot p_S \cdot [\text{Red}] \cdot e^{-\frac{\Delta G_{\text{act}}}{RT}} \quad (1.69)
\]

with \(k_e, k_a\) rate constants; \(n_S, p_S\) the surface density of electrons and holes (or unoccupied states for a metal); \([Ox], [\text{Red}]\) the concentration of oxidizing and reducing agent in solution, and \(\Delta G_{\text{act}}, \Delta G_{\text{an}}\) the activation energies for the cathodic and anodic processes. The “activated state” of the transfer process is related to changes in the environment of the ion (solvation shells) prior to electron transfer. It is usually represented as an energy barrier for electrons (see figure 1.21).

Expressions 1.68, 1.69 are general formulas that serve to point out that in metals, the only potential-dependent parameter is the activation energy, while in semiconductors the electrode potential also controls the surface density of carriers. The discussion in semiconductors will be restricted to the limit cases in which the electrode potential acts on either the activation energy or the carrier surface density, but not on both at the same time.

### 1.3.2.1 Metal electrodes

Out of the solution, the Fermi energy in the electrode (given by the metal work function, \(\Phi_m\)) is in general different of \(E_{F,\text{redox}}\). In figure 1.22 it has been assumed \(E_F < E_{\text{redox}}\). When both phases are contacted, they exchange charge in order to balance their Fermi energies: in figure 1.22, the ions in the
Figure 1.22: Equilibrium between the electrolyte and a metal electrode.

Reduced form tend to oxidize, thus injecting electrons into the electrode and building up a negative charge in the solid. This negative charge attracts a positive countercharge from the solution such that a double layer is formed, and a potential $\Delta \phi_H^{eq}$ is built up. This potential drop decreases the rate of electron injection into the electrode and increases electron extraction, until the current in both directions is balanced and equilibrium is achieved ($E_F = E_{F,\text{redox}}$). The equilibrium of a metal electrode immersed in an electrolyte is thus maintained by the potential drop at the double layer, $\Delta \phi_H^{eq}$.

When an overpotential $\eta$ is applied to the metal (constant electron surface density), it acts only on $E_F$, i.e. the energy of the electrons that are exchanged with the electrolyte. If the potential $U$ of a metallic electrode relative to the electrolyte is changed by $\eta = U - U^{eq}$, again the potential drop is borne entirely by the electrolyte double layer. Assuming that the double layer obeys the Helmholtz model ($\Delta \phi_H^{eq} = \Delta \phi_H'$),

$$\Delta \phi_H = \Delta \phi_H^{eq} + \eta \tag{1.70}$$

where $\Delta \phi_H^{eq}$ is the initial double-layer potential (metal at equilibrium with the electrolyte). Any variation in $\Delta \phi_H$ changes the activation energy for electron exchange “seen” by the ions near the electrode surface, because $\Delta G$ is related to the rearrangement of the solvation shells (e.g. the polarization of the solvent around the ion).

The change in $\Delta G$ due to $\eta$ is in general different for the anodic and cathodic processes, and is given by a fraction $\alpha$ of the total energy put into the system, $z \eta$:

$$\Delta G_{an} = \Delta G_{an}^{eq} - \alpha z \eta \tag{1.71}$$
$$\Delta G_{cat} = \Delta G_{cat}^{eq} + (1 - \alpha) z \eta \tag{1.72}$$

where $z$ is the number of electrons transferred in the reaction ($z = 1$ in reactions 1.66, 1.67) and $\alpha$ is called the anodic transfer coefficient. If a
1.3. CHARGE TRANSFER PROCESSES

Positive overpotential \( \eta > 0 \) is applied to the electrode (such as to favor the anodic process), the energy barrier for the anodic reaction is lowered by a fraction \( \alpha \eta \), and the barrier for the cathodic reaction is raised by \( (1 - \alpha) \eta \). If \( \eta < 0 \), the barrier energy is reduced in the cathodic direction and raised in the anodic. The anodic transfer coefficient \( \alpha \) thus accounts for the reversibility of the process: \( \alpha = 1 \) for a certain reaction means that the anodic process can be favored (\( \eta > 0 \)) or hindered (\( \eta < 0 \)), but the overpotential has no effect on the cathodic process (the anodic reaction is therefore irreversible). In a similar way, when \( \alpha = 0 \), the overpotential does not affect the anodic process and acts only on the cathodic. For a reversible reaction, positive overpotentials (\( \eta > 0 \)) lower the barrier in the anodic direction and raise it in the cathodic, exactly in the same amount. And \( \eta < 0 \) lower the cathodic barrier and raise the anodic. The energy put into the system is thus split in two equal parts \( \frac{\alpha \eta}{2} \), and \( \alpha = \frac{1}{2} \). In energetic terms, \( \alpha \) is a measure of the energy barrier symmetry.

Introducing \( \Delta G \) in the expressions 1.68-1.69 for \( j_{ox} \) and \( j_{red} \), and rearranging, the net anodic current through the metal | electrolyte interface is the difference:

\[
\begin{align*}
j &= j_{ox} - j_{red} \\
&= k_a e^{\frac{\Delta G_s}{RT}} \cdot e^{\frac{\eta zF}{RT}} - k_c e^{\eta zF} [\text{Ox}] \cdot e^{-\frac{(1-\alpha)\eta zF}{RT}} \\
&= K_a zF [\text{Red}] \cdot e^{\frac{\eta zF}{RT}} - K_c zF [\text{Ox}] \cdot e^{-\frac{(1-\alpha)\eta zF}{RT}} \\
&= 1.73
\end{align*}
\]

where the surface charge \( e_{nS} \), \( e_{PS} \) has been expressed using the Faraday constant \( F = 9.6 \cdot 10^4 \text{ C/mol of electrons exchanged in the reaction} \). At equilibrium, \( U = \U{eq} \) (the overpotential is \( \eta = 0 \)) and the net current is \( j = 0 \):

\[
K_a [\text{Red}] = K_c [\text{Ox}] \\
1.74
\]

If \( [\text{Red}] = [\text{Ox}] = 1 \), the equilibrium potential of the electrode is named the “standard potential” \( \U{eq} \) \( \equiv U^o \) (see 1.2.2.1) and thus \( K_a = K_c \equiv k_0 \) is the standard rate constant. Rewriting expression 1.73 for [Red], [Ox] different in general, and using the electrode potential \( U = U^o + \eta \):

\[
\begin{align*}
j &= k_0 zF \cdot \left( [\text{Red}] \cdot e^{\frac{\eta zF}{RT}} (U - U^o) - [\text{Ox}] \cdot e^{-\frac{(1-\alpha)\eta zF}{RT}} (U - U^o) \right) \\
&= 1.75
\end{align*}
\]

which is known as the “Butler-Volmer equation” for the electrode kinetics (figure 1.23A). The pre-exponential factor \( k_0 zF \equiv j_0 \) is the “exchange current” (the current that flows in both directions at equilibrium, giving net zero current). Both \( j_0 \) and \( k_0 \) express the rate of an electrode reaction.
At high overpotentials, one term dominates over the other and expression 1.75 reduces to the "Tafel equation":

\[
\begin{align*}
    j &\approx j_{ox} = k_{0} z F \cdot [\text{Red}] \cdot e^{+ \frac{n_F z_F}{k_B T} (U-U^0)} \\
    j &\approx -j_{red} = -k_{0} z F \cdot [Ox] \cdot e^{- \frac{(1-n)_F z_F}{k_B T} (U-U^0)}
\end{align*}
\]  

(1.76)  

(1.77)

for large \( \eta > 0 \) and \( \eta < 0 \) respectively, i.e. the slope of \( \ln j \) vs. the applied potential is \( \pm \frac{n_F}{k_B T} \) ("Tafel plots" of figure 1.23B). It is found experimentally that \( \alpha \approx \frac{1}{2} \) for most reactions on metal electrodes.

Now the equilibrium condition \( (j=0) \) for the metallic electrode can be expressed:

\[
[\text{Red}] \cdot e^{+ \frac{n_F z_F}{k_B T} (U-U^0)} = [Ox] \cdot e^{- \frac{(1-n)_F z_F}{k_B T} (U-U^0)}
\]

\[
U = U^0 + \frac{k_B T}{ze} \cdot \ln \left( \frac{[Ox]}{[\text{Red}]} \right)
\]

(1.78)

which is the "Nernst equation" already given in 1.16. In that case, it was employed to calculate the Fermi energy of a metal electrode immersed in an electrolyte, from the values of the standard reduction potential of the redox system \( U^0 \), and the concentrations of the oxidized and reduced species in solution, \([Ox]\) and \([\text{Red}]\).

### 1.3.2.2 Semiconductor electrodes

The derivation of a kinetic equation for semiconductors is complex because the potential-dependent terms in expressions 1.68, 1.69 are two: The activa-
tion energy (as for metals) and the concentration of charge carriers at the surface \( (n_s, p_s) \). However, in certain simple cases some indications can be given, but the quantitative application of a formalism of the Butler-Volmer type to semiconductors is still under discussion. This section aims to clarify the major concepts, which are sometimes confusing in the literature.

The expressions obtained for metals can be translated rather directly to semiconductors if the surface carrier density can be considered a constant, and the applied potential acts only on the energy of the carriers that can be transferred. Such is the case of a semiconductor in the **accumulation** regime, as was discussed in 1.2.3.4: At large potentials the band bending \( \Delta \phi_{sc} \) saturates, the SCR capacitance \( C_\infty \) increases and most of the applied potential results in a change in \( \Delta \phi_H \) (bandedge unpinning). The surface carrier density is approximately constant (given by the saturation \( \Delta \phi_{sc} \) [38]) and the changes in the electrode potential are almost entirely employed in shifting the bandedge energy (\( E_{CS}, E_{VS} \) are the energies at which carriers are exchanged between the electrolyte and a semiconductor).

Thus, in redox reactions at semiconductor electrodes, the closest analogy with the overpotential defined for metal electrodes is the potential drop over the double layer \( \Delta \phi_H \), because it reflects the lowering of the energy barrier to be tunnelled by transferred charges [52]. In this way, curves of \( \log j \) vs. \( \Delta \phi_H \) (where \( \Delta \phi_H \) is obtained from the shift in \( U_{FB} \) under current flow, see 1.2.3.4) are the parallel of “Tafel plots” in semiconductor electrodes [52]. For example, the kinetics of \( n- \) and \( p- \)type electrodes under accumulation is well described by expressions 1.76 and 1.77 respectively, with \( \eta = \Delta \phi_H(U) - \Delta \phi_{H}^0 \) the overpotential, and \( \alpha \) the anodic transfer coefficient having the usual meaning. The problem is that expression 1.75 cannot be applied to the entire potential range, because the above approximations do not hold when the semiconductor is in depletion. Actually the equilibrium potential \( U^{eq} \) usually corresponds to a depletion layer (see 1.2.3.3), which questions the meaning of the exchange current \( j_0 \) obtained experimentally from 1.76, 1.77 at large overpotentials. As the electrode potential \( U \) approaches \( U_{FB} \), both the activation barrier and the carrier density change, and their contributions to the current are mixed. In other cases, the accumulation regime cannot even be reached, due for example to the pinning of the Fermi level by surface states (1.2.3.5).

To discuss the kinetics of semiconductor electrodes under **depletion**, it is assumed that all the applied potential is dropped within the SCR \( (\Delta \phi_{sc}) \), i.e. the applied potential is employed in bending the semiconductor bands while the bandedges remain pinned at the surface. In this case \( \Delta \phi_H \) is constant, so the activation energy \( \Delta G \) remains constant whatever is the value of \( \alpha \) for the charge transfer reaction.
The applied potential acts only on the concentration of charge carriers at the surface, through the band bending $\Delta \phi_{sc}$ (expressions 1.47, 1.48). In $n-$ and $p-$type semiconductors the majority carrier surface densities are respectively:

$$n_S = N_D \cdot e^{-\frac{\Delta \phi_{sc}}{kT}}$$  \hspace{1cm} (1.79)

$$p_S = N_A \cdot e^{\frac{\Delta \phi_{sc}}{kT}}$$  \hspace{1cm} (1.80)

The net current for electron exchange with the CB is then [36]:

$$j_C = j_{C0} \cdot (1 - e^{-\frac{\eta_{sc}}{kT}})$$  \hspace{1cm} (1.81)

with $j_{C0} = e k_C n_{S0}[Ox]$ and for hole exchange with the VB:

$$j_V = j_{V0} \cdot (e^{\frac{\eta_{sc}}{kT}} - 1)$$  \hspace{1cm} (1.82)

with $j_{V0} = e k_V p_{S0}[Red]$

where $\eta_{sc} = \Delta \phi_{sc} - \Delta \phi_{sc}^{eq}$ is defined by analogy with the overpotential $\eta$ of section 1.3.2.1, and $j_{C0}$, $j_{V0}$ are the exchange currents at equilibrium ($\eta_{sc} = 0$). The values of $j_{C0}$, $j_{V0}$ depend on the overlap between the semiconductor bandedges and the density of states in the electrolyte, as was modeled by Gerischer [53].

Expressions 1.81, 1.82 for $\eta_{sc}$ are sometimes compared with the Butler-Volmer equation for $\eta$ (expression 1.75). An “apparent transfer coefficient” $\alpha' = 0$ arises for electron exchange with the CB, and $\alpha' = 1$ for hole exchange with the VB. However, such $\alpha'$ has nothing to do with the anodic transfer coefficient that accounts for reaction reversibility, and $\eta_{sc}$ is not a real overpotential for the electrode reactions, because the carriers are always transferred to and from the (fixed) bandedges. The “semiconductor overpotential” $\eta_{sc}$ and the values of $\alpha' = 0,1$ in $n-$ and $p-$type semiconductors account only for the availability of (majority) charge carriers at the electrode surface in the depletion regime.

The total current through the semiconductor | electrolyte interface is due to the exchange of carriers with both bands, $j = j_C + j_V$, but in practice it is enough to consider only majority carriers:

$$j \approx j_C = j_{C0} \cdot (1 - e^{-\frac{\eta_{sc}}{kT}})$$  \hspace{1cm} (1.83)

$$j \approx j_V = j_{V0} \cdot (e^{\frac{\eta_{sc}}{kT}} - 1)$$  \hspace{1cm} (1.84)

in $n-$ and $p-$type semiconductors respectively. The appearance of the current vs. potential curves is shown in figure 1.24.
Comparison with solid Schottky diodes  Expressions 1.83, 1.84 can be compared with the current-potential characteristic of a solid Schottky diode (metal | semiconductor junction), which has the form:

\[ j = \pm j_0 \cdot (e^{\pm \frac{\Delta \phi}{m^*T^2}} - 1) \]  

\[ \text{with } j_0 = A \frac{m^*}{m_e} T^2 \cdot e^{-\frac{E_B}{m^*T}} \]  

being \( j_0 \) the saturation current, \( n \) the ideality factor \((n = 1.0 - 1.2)\), \( A \) the Richardson’s constant \((120 \text{ } A/cm^2K^2)\), \( m^* \) the effective mass of carriers, \( m_e \) the electron mass, \( E_B \) the built-in barrier (as seen from the metal), and the positive and negative signs apply for \( p- \) and \( n- \) type semiconductors respectively. At equilibrium, the applied potential is \( \Delta \phi = 0 \).

Schottky junctions are characterized by \( E_B \) and \( n \) as determined from a plot of \( \log \left( \frac{j}{j_0} + 1 \right) \) vs. \( \Delta \phi \). The built-in barrier \( E_B \) can also be obtained from capacitance measurements (intercept at \( \frac{1}{T} = 0 \) of the Mott-Schottky plot, see 1.2.3.6). When the potential applied to the diode is such that a large current flows, the diode is said to be under “forward bias” (semiconductor in accumulation). At “reverse bias” (depletion), only a small saturation current flows. This behavior is called “current rectification”.

When the equilibrium situation corresponds to a depletion layer, the forward current flow in a Schottky diode (expression 1.85) and the transfer of electrons through a semiconductor | electrolyte contact (1.83, 1.84) are analogous. However, in the electrolyte the density of electronic states is much
smaller than in metals ($\sim 10^{30} \text{ cm}^{-3}$ in a 0.1 M solution, against $\sim 10^{22} \text{ cm}^{-3}$ in a metal). The electronic states in the electrolyte are localized, “attached” to ions or molecules, and their energy levels fluctuate over a wide energy range. The exchange current (and therefore the rate) of redox reactions at semiconductor electrodes are always smaller than the exchange current of a semiconductor | metal Schottky barrier with the same barrier height. Therefore, even under forward bias and large electrolyte concentrations, the majority carrier density at the semiconductor | electrolyte interface can be calculated from the potential difference in the Schottky barrier ($\eta_{sc}$), which indicates that the semiconductor surface is always at equilibrium with the bulk [54].

**The Schottky electrode** When studying metal deposition processes on semiconductors, it is interesting to examine the limit case of a semiconductor electrode completely covered with a metal overlayer. Its electrochemical behavior is that of a Schottky barrier in series with a metal electrode, thus it is known as “Schottky electrode” [46, 55, 56]. Outside the solution, it is a Schottky diode whose parameters ($E_B$, $n$) can be predicted and measured using current-potential curves. In a solution, only the metal layer can establish an equilibrium with the redox system ($E_{F, \text{metal}} = E_{F, \text{redox}}$; see 1.3.2.1) and since the semiconductor | metal barrier height $E_B$ is fixed, the other parameters are in principle determined.

**Electrode reactions** The above discussion has been focused mainly on electron transfer kinetics without stating explicitly the reactions occurring at the interface. The case of a redox system whose reduced and oxidized forms are both soluble (e.g. $Fe^{3+}/Fe^{2+}$ in expressions 1.66, 1.67) is a rather particular one. The electron transfer reaction can also result in changes in the electrode, for example if the reduced form of the system is a solid and the cathodic reaction at negative overpotentials produces a deposit on the electrode surface. More importantly, the electrode material itself can be oxidized or reduced: For instance, a semiconductor oxide like $SnO_2$ may reduce to metallic $Sn$ at negative overpotentials. At positive overpotentials, the formation of oxide layers and dissolution of the electrode material can be promoted (e.g. $Si$ in aqueous fluoride solutions).

The anodic reaction of the electrode material will be particularly relevant in the following chapters. The dissolution of surface atoms of covalent solids in contact with an electrolyte, implies both the loss of their binding electrons (i.e. the oxidation of the atoms *stricto sensu*) and the presence of species in solution that can solubilize the oxidation products. In a semiconductor
like $Si$, atoms are bonded in the crystal by means of valence electrons, and the bonding states constitute the VB of the semiconductor [32]. In order to oxidize an atom, those bonding electrons have to be removed from the surface, and this is regarded in electronics terms as the *capture of VB holes in localized surface states*: a bonding or valence electron is permanently lost from a surface bond when a (free) hole is captured or trapped therein. Holes can thus be envisaged as weakening the cohesion of the semiconductor crystal lattice. Provided that the oxidation products can be solubilized, the electrochemical dissolution of a semiconductor requires the existence and availability of holes at the semiconductor surface, which means, in practice, that holes must be photo-generated in an $n-$type electrode, and that anodic bias is required to accumulate holes at the interface with the solution. However, this does not imply that all the detailed steps of a dissolution reaction involve free holes in the VB, as will be seen in section 2.2 for the case of silicon.

### The semiconductor electrode under illumination

As was explained in section 1.3.1, when charge carriers (either majority or minority) reach the surface of a semiconductor they become *reactants* that can participate in the transfer of charge with the electrolyte. In the dark, the conduction in a semiconductor is provided only by majority carriers (electrons in $n-$type, holes in $p-$type). Illumination is a way to bring minority carriers into play, making possible charge transfer reactions that would otherwise not occur, e.g. hydrogen photoevolution on $p-$type electrodes, photocorrosion of $n-$type electrodes. The potential distribution over the semiconductor | electrolyte interface as a result of carrier photogeneration will be first discussed qualitatively, in analogy with a semiconductor | metal junction [41]. An expression for the (photo)current will be given afterwards, and the appearance of the current-potential curves under illumination will be shown for $n-$ and $p-$type electrodes.

The buildup of a potential barrier at the semiconductor surface in equilibrium with a conductor, can be envisaged as a balance between diffusion and drift of charge carriers (due to concentration gradients and electric fields respectively): in the bulk of the semiconductor, both the density of majority carriers and the electric potential are uniform, so $j_{drf} = j_{dirf} = 0$. Near the surface, diffusion and field currents appear due respectively to the decrease in majority carrier concentration, and to the (internal) electric field responsible for the band bending. At equilibrium, these currents are balanced everywhere so that no net current results (see reference [41] for details).

Illumination of a semiconductor with light of energy larger than the bandgap ($1.1$ eV for silicon, i.e. beyond infrared) produces the excitation
of VB electrons into the CB, thus generating extra charge carriers in the bands (electrons and holes in equal amounts) in the region near the illuminated surface. This upsets the balance between diffusion and drift currents at equilibrium, and results in general in the lowering of the energy barrier until both effects are again equalized [41]. If the semiconductor bandedges are pinned (i.e. in the absence of charges trapped at the interface), the lowering of the barrier is translated into a shift of the OCP of the electrode:

\[
\Delta \phi_{ph} = U_{OCP}^{\text{light}} - U_{OCP}^{\text{dark}}
\]

The “photopotential” \( \Delta \phi_{ph} \) shifts OCP towards positive potentials in \( p \)-type semiconductors, and towards negative in \( n \)-type, and its maximum value is given by the band bending at equilibrium, \( |\Delta \phi_{ph}| \leq |U_{FB} - U_{OCP}| \).

Although diffusion and drift have again balanced and no net current flows through the contact at \( U_{OCP}^{\text{light}} \), the situation does not correspond to thermodynamic equilibrium. A convenient parameter to describe the non-equilibrium density of minority carriers in a semiconductor are the “quasi-Fermi energy levels” for electrons and holes, \( nE_F \) and \( pE_F \). They are usually represented as in figure 1.25. Under illumination, the density of majority carriers is not appreciably increased with respect to the equilibrium (dark), and therefore \( nE_F \simeq E_F \) in an illuminated \( n \)-type electrode. But at the same time, the density of holes can be greatly increased and \( pE_F \) may reach values close to the VB. Thus the density of electrons and holes in such non-equilibrium conditions can be calculated with \( nE_F \) and \( pE_F \) instead of \( E_F \) in equations 1.3 and 1.4. However, when the semiconductor is in contact with an electrolyte and the photogenerated carriers become potential reactants, it must be borne in mind that \( nE_F \) and \( pE_F \) are not real energy levels, and the reaction, if it occurs, will mainly proceed through the bands (or surface states). In this case \( nE_F \) and \( pE_F \) only affect the rate of the reaction through the surface carrier density in equations 1.68 and 1.69.

An expression for the electrode current under illumination is given by the Gärnter model [44, 57]. If both the surface state charge and adsorbed charge can be neglected in front of \( Q_{sc} \) and \( Q_H \), and the transfer of carriers to the electrolyte is fast (such that no charge carriers are accumulated at the interface), the bandedges remain pinned at the surface. The (photo)potential difference between the semiconductor and the electrolyte may involve the flow of a current through the interface if the photogenerated minority carriers can reach the semiconductor surface and be transferred to redox species in solution. The current in excess of the situation in the dark is the “photocurrent” \( j_{ph} \). The total current through the interface is thus the sum:

\[
j_T = j + j_{ph}
\]
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Figure 1.25: Quasi-Fermi levels of an n-type electrode under illumination.

where both $j$ and $j_{ph}$ depend on the electrode potential $U$. In a $n$-type semiconductor, $j_{ph} > 0$ corresponding to the transfer of holes to the solution. In a $p$-type, it is $j_{ph} < 0$. The photocurrent $j_{ph}$ also depends on the light flux $\Phi_0$, which is given in photons/cm$^2$s and can be calculated from the measured illuminance (in lx), knowing that 1 lx = $4.1 \cdot 10^{11}$ photons/cm$^2$s for light of $\lambda = 555 \text{ nm}$ (yellow). If the photocurrent is limited by the light flux, the Gäßner model [44, 57] gives the following expression for $j_{ph}$:

$$j_{ph} = e \Phi_0 \cdot \left(1 - \frac{e^{-\delta W}}{1 + \delta L}\right)$$  \hspace{1cm} (1.88)

where $\frac{1}{2}$ (in cm) is the penetration depth of light, $W$ the SCR depth and $L$ the minority carrier diffusion length. The dependence of $j_{ph}$ on the electrode potential is implicit in $W$ through expression 1.44 (using $U_S = U - U_{FB}$).

The photocurrent is also given by:

$$j_{ph} = ep_{ph}^n v_{th} \quad (n - \text{type})$$ \hspace{1cm} (1.89)

$$j_{ph} = ep_{ph}^p v_{th} \quad (p - \text{type})$$ \hspace{1cm} (1.90)

which allows to calculate the concentration of photogenerated minority carriers ($p_{ph}^n$, $n_{ph}^p$ in cm$^{-3}$) from their thermal velocity $v_{th}$ and the measured photocurrent $j_{ph}$.

Current-potential curves The $j-U$ curves of a semiconductor in contact with an indifferent electrolyte were shown in figure 1.24. Here they are discussed in some detail, taking into account the different current components at every potential value and in the presence of photogenerated carriers.
Figure 1.26: Current-potential curves of a p-type electrode in the dark (dashed) and under illumination (solid).

The current-potential plots of a p-type electrode are represented in figure 1.26. In the absence of illumination (dashed line), only holes are present in the semiconductor. At potentials negative of OCP they are depleted from the surface giving rise to a potential barrier that prevents the flow of current. In this range, only a small cathodic current is measured (typically of a few $\mu$A/cm$^2$ in monocrystalline electrodes). Cathodic reactions involving CB electrons (like the HER) cannot be promoted in a dark p-type electrode. At potentials positive of OCP, holes are accumulated at the electrode surface, and they can in principle be transferred to the solution. However, in many cases they result in oxidation of the electrode material (see the subsection “Electrode reactions” above). If the oxidation products are not soluble, an oxide layer is condensed at the electrode surface and may hinder the flow of current (this will be discussed in 2.2.2 for silicon in fluoride media). Note that considerably large currents are already found in slight depletion (before $U_{FB}$), because the charge carriers can overcome the relatively low energy barrier.

Illumination of the p-type electrode (figure 1.26, solid line) results in the generation of electron-hole pairs. Whenever there is a relatively high hole concentration at the surface (accumulation or slight depletion) electrons
are rapidly recombined and yield no visible effect on the measured current. However, under strong depletion (very negative potentials) the electric field in the SCR is so high that separates the photogenerated electron-hole pairs before recombination, thus attracting electrons towards the surface and collecting holes in the bulk. In this way, electrons can participate in cathodic reactions (e.g. HER), and the flow of photoholes into the semiconductor is measured as a negative current. The measured current can be taken as an indication of the cathodic process (due to minority carriers and hence not directly measurable in a $p$–type electrode). When all the photogenerated holes are collected in the semiconductor bulk (beyond a certain negative potential), the photocurrent saturates. This plateau is proportional to the light intensity.

Figure 1.27 shows the $j - U$ plots for a $n$–type electrode, which are essentially symmetric of the $p$–type. The currents measured in this case correspond to the opposite processes: In the dark and at potentials negative of OCP, electrons flow towards the surface (negative current) producing the HER as in metals. For potentials positive of OCP, the depletion layer prevents the flow of current in the anodic branch (figure 1.27, dashed line), which means that a $n$–type electrode cannot be oxidized in the dark. The effect of light is noticed at positive potentials, due to the separation of the photogenerated electrons and holes by the band bending (figure 1.27, solid line): Electrons are collected in the semiconductor bulk and yield a positive current; holes are accumulated at the surface and usually result in oxidation.

### 1.3.3 The electrode mixed potential

#### 1.3.3.1 Simultaneous reactions at an electrode

In some cases, two or more reactions can occur simultaneously at an electrode (parallel reactions). For example, the anodic dissolution of the electrode material with oxygen reduction, corresponding to the corrosion equilibria widely studied in metals [58]. Considering the following two reactions, that proceed simultaneously at an electrode:

\[
R_1 \quad \Rightarrow \quad O_1 + e^- \\
O_2 + e^- \quad \Rightarrow \quad R_2
\]

(1.91)

(1.92)

the Butler-Volmer formalism (1.3.2.1) can be employed to express the corresponding anodic and cathodic current components:

\[
\hat{j}_{a,1} = j_{0,1} \cdot e^{\frac{nF}{RT} \left(U - U_1\right)}
\]

(1.93)
Figure 1.27: Current-potential curves of an n-type electrode in the dark (dashed) and under illumination (solid).

\[
\begin{align*}
\dot{j}_{\text{red,1}} &= j_{0,1} \cdot e^{-(\frac{1-n_1}{2n_1})(U-U_1)} \\
\dot{j}_{\text{ox,2}} &= j_{0,2} \cdot e^{(\frac{\alpha_2}{2n_2})(U-U_2)} \\
\dot{j}_{\text{red,2}} &= j_{0,2} \cdot e^{-(\frac{1-\alpha_2}{2n_2})(U-U_2)}
\end{align*}
\]

(1.94)  
(1.95)  
(1.96)

The total current flowing through the electrode | electrolyte interface is, for the overall process:

\[
\dot{j} = \dot{j}_{\text{ox,1}} + \dot{j}_{\text{ox,2}} - \dot{j}_{\text{red,1}} - \dot{j}_{\text{red,2}}
\]

(1.97)

The steady-state condition in the absence of an applied potential (\(j = 0\)) is achieved at a certain electrode potential \(U_{\text{mix}} \equiv U_{\text{OCP}}\). Assuming that the reverse reactions in 1.91, 1.92 can be neglected:

\[
\begin{align*}
\dot{j} &= \dot{j}_{\text{ox,1}} - \dot{j}_{\text{red,2}} = 0 \\
\dot{j}_{0,1} \cdot e^{\frac{\alpha_1}{2n_1}(U_{\text{mix}}-U_1)} &= j_{0,2} \cdot e^{-(\frac{1-\alpha_2}{2n_2})(U_{\text{mix}}-U_2)} \\
U_{\text{mix}} &= \alpha_1 U_1 + (1 - \alpha_2) U_2 + \frac{k_B T}{e} \cdot \ln \frac{j_{0,1}}{j_{0,2}}
\end{align*}
\]

(1.98)  
(1.99)  
(1.100)
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Figure 1.28: Simultaneous reactions at an electrode. In the steady-state, \( j = 0 \) and the electrode potential is \( U_{mix} \) (“mixed potential”): At \( U = U_{mix} \), the anodic current of one reaction \( j_{ox,1} \) is balanced with the cathodic current of the other \( j_{red,2} \).

If \( \alpha_1 = \alpha_2 = \frac{1}{2} \), expression 1.100 reduces to:

\[
U_{mix} = \frac{U_1 + U_2}{2} + \frac{k_B T}{e} \cdot \ln \frac{j_{0,1}}{j_{0,2}}
\]  

(1.101)

\( U_{mix} \) is named the “mixed potential” of the electrode (figure 1.28), and it is neither the equilibrium potential of reaction 1.91 nor of reaction 1.92.

Thus when two (or more) reactions are simultaneously occurring at an electrode, the rest situation does not correspond to thermodynamic equilibrium (equalization of the Fermi levels of the electrode and the electrolyte): In the absence of an applied potential \( U = U_{mix} \), the net current of one process is equal and opposite in sign to the net current of the other, each of them involving a reaction at the electrode:

\[
\dot{j}_{ox,1} = \dot{j}_{red,2} = \dot{j}_{corr}
\]  

(1.102)

The current \( j_{corr} \) is sometimes called “corrosion current” or “dissolution current”, and must not be confused with the exchange current \( j_0 \) at the thermodynamic equilibrium. The rest situation in these systems can thus be envisaged as an exchange of charge between the two simultaneous reactions.
1.3.3.2 Application to semiconductor electrodes

The concept of mixed potential defined by two simultaneous reactions can also be applied to semiconductor electrodes, taking into account the expressions for the current given in 1.3.2.2. Even in the absence of redox systems in the electrolyte, still the electrode itself or the solvent can exchange charge to the point of defining an OCP [36]. For example the surface of a $SnO_2$ electrode can be reduced to $Sn$, or a $Si$ electrode can be oxidized if simultaneous counterreactions are available. If these electrodes are in contact with pure water, the reactions that dominate the carrier exchange could be:

\[
2H^+ + 2e^- \rightleftharpoons 2H^0 \rightarrow H_2 \quad (1.103)
\]

\[
2OH^- \rightleftharpoons 2OH + 2e^- \rightarrow H_2O_2 + 2e^- \quad (1.104)
\]

i.e. hydrogen gas formation withdraws electrons from the substrate (cathodic reaction) and $H_2O_2$ formation delivers them (anodic reaction), until a potential is reached at which both reactions are balanced.

Thus, when a semiconductor is immersed in an electrolyte, the steady-state situation in the absence of applied potential (OCP) does not necessarily imply the equalization of its Fermi level with the electrolyte (1.2.3.1), but can also be defined by the mixed potential between two reactions. For example if there are electron-accepting species in solution ($H^+$ in reaction 1.103), they can reduce by withdrawing electrons from the electrode material. The corresponding current is cathodic (negative). The electrode is oxidized in this process, and the current associated is anodic (positive). An “equilibrium” potential (mixed potential) is eventually reached when the current flowing in both directions is equalized to yield net current zero. Of course the actual carriers (electrons or holes) involved in every reaction must be taken into account, as well as the band edge energies. A more detailed description will be given in section 2.1 for silicon electrodes immersed in fluoride solutions. The concept of mixed potential will also be used when other redox systems, e.g. of metal ions, are present in the solution (section 2.3).

In practice, the rest situation (OCP) of semiconductor | liquid junctions seldom corresponds to thermodynamic equilibrium. The reverse current in expressions 1.83, 1.84 is usually a leakage current due to surface flaws (independent of $j_0$) and thus the barrier at rest $\Delta \phi_{sc}^{eq}$ is just the band bending required to balance the reverse current. Hence $\Delta \phi_{sc}^{eq}$ is not an adequate origin for potentials ($\eta_{sc} = \Delta \phi_{sc} - \Delta \phi_{sc}^{eq}$) because it cannot be directly related to the properties of the material, and may vary between samples [36]. The surface barrier $U_S = U - U_{FB}$ defined in 1.44 is employed instead. Equations 1.83, 1.84 can then be expressed in a more useful way:

\[
j = j_a - j'_0 - e^{-2}T \cdot 10^{10} \cdot (U - U_{FB}) \quad (1.105)
\]
\[ j = j_0' \cdot e^{\frac{e}{k_BT}(U-U_{F,B})} - j_c \]  \hspace{1cm} (1.106)

for \( n- \) and \( p- \) type semiconductors respectively (\( j_a \) and \( j_c \) are the anodic and cathodic leakage currents).

### 1.3.4 Diffusion-controlled reactions

When the rate of a reaction was discussed in 1.3.2.1 and 1.3.2.2, it was implicitly assumed that the concentration of reactants at the electrode surface is equal to that in the bulk solution, i.e. the reaction is slow compared with the supply of reactants to the surface. The reaction is said to be \textit{kinetically controlled} and it can be recognized because the reaction rate is not affected by solution agitation.

In semiconductor electrodes, the rate is controlled kinetically when the overlap between the electron states in the electrolyte and the semiconductor bands is poor. If the overlap is good, the reaction rate can be so high that the reactants are exhausted near the electrode and the supply of species to the surface becomes rate limiting. The reaction is then said to be \textit{diffusion-controlled}.

In both cases (kinetic and diffusion control) the current through the electrode is a function of the concentration of reactant in solution, but displays a different dependence. Two terms are found in general, one kinetic and another one due to diffusion. For example, in the case of the irreversible reduction of some species \( O_x \) \cite{59}:

\[ \frac{1}{j_{\text{red}}} = \frac{1}{k_c zF[O_x]_b} + \frac{1}{k_{\text{diff}} zF[O_x]_b} \]  \hspace{1cm} (1.107)

where \([O_x]_b\) is the concentration of \( O_x \) in the solution bulk. If a rotating electrode is employed to control the agitation, \( k_{\text{diff}} = 0.62 \cdot D_{\text{ox}} 2/3 \cdot \nu^{-1/6} \omega^{1/2} \), \( D_{\text{ox}} \) being the diffusion coefficient of \( O_x \) in solution, \( \nu \) the kinematic viscosity of the solution and \( \omega \) the angular velocity of the rotating electrode (\( \omega = 2\pi f \), with \( f \) in revolutions per second). Of course, \( k_c \) is independent of agitation. A plot of \( \frac{1}{j_{\text{red}}} \) vs. \( \frac{1}{\nu^{1/6} \omega^{1/2}} \) gives a straight line where \( D_{\text{ox}} \) can be obtained from the slope and \( k_c \) from the intercept. Note that always \( j_{\text{red}} \propto [O_x] \), but in general the proportionality constant carries mixed information of the kinetics and diffusion. Only if the reaction regime can be precisely determined or selected (e.g. using a rotating electrode), the values of \( k_c, D_{\text{ox}} \) can be obtained.

It is possible, in some cases, to switch between the two regimes by playing with the electrolyte concentration. Increasing \([O_x]_b\), the reaction can be made kinetically controlled: There is always an excess of species near the surface regardless of agitation. In expression 1.107, the slope is reduced and
the intercept becomes little dependent on $k_{diff}$. If $[Ox]_b$ is reduced, the exhaustion of the reactant near the surface is facilitated and the reaction becomes diffusion-controlled (the slope in 1.107 is increased and the rate is more sensitive to agitation).
Chapter 2

Silicon in aqueous fluoride media

Concerning the systems treated in the following chapters, metal deposition on silicon from fluoride solutions, there is a great deal of phenomenological data focusing mainly on practical applications, but that often lack of a proper physical and chemical interpretation. Only few of the recently published studies make use of the concepts of semiconductor electrochemistry [4, 48, 60, 61], which is somewhat surprising because their principles were established several decades ago and are supported by a large amount of experimental work. The apparent exclusion of silicon may be due to the fact that most of the efforts of semiconductor electrochemists during the eighties and early nineties have been devoted to solar energy conversion: at that time, the focus was on semiconductors having a bandgap in the visible range, like III-V compounds (GaAs, InP...). The basic chemical and electrochemical behavior of silicon has been studied mostly during this decade, and review works have not been published yet.

In this chapter, the concepts introduced so far are applied to the case of silicon immersed in aqueous fluoride solutions. The energy diagram of the interface is first presented, and the nature of the equilibrium is briefly discussed: at the OCP, the reaction of silicon dissolution (anodic) is balanced with the hydrogen evolution (cathodic counterreaction). The current understanding of the silicon dissolution process (“etching”) is then explained in some detail, on the basis of recently published results. Although the chapter is organized as a review of the literature, a critical interpretation of the results will be given in certain cases.
2.1 Equilibrium considerations

It will be useful to lean on specific experimental results, in order to ease the explanation and give some representative graphs. Unless otherwise specified, the data refer to aqueous solutions ~1 M fluoride, and polished, monocrystalline silicon having a relatively low resistivity (~1 Ωcm). This corresponds to a SCR thickness of a few hundred nm under depletion conditions, and a separation between the majority carrier band and the Fermi energy in the semiconductor bulk of $\mu_C \approx 250$ meV, $\mu_V \approx 200$ meV. Other significant data for Si can be found in table 1.14 and figures 1.3 and 1.4 of chapter 1. When exposed to fluoride solutions, the Si surface is hydrogen-terminated and oxide-free except when large anodic currents flow through the interface. The discussion will be done on n–type electrodes, since most of the experimental studies in the literature have been performed on n – Si. This is due in part to the unstability of p – Si under forward bias.

2.1.1 Experimental energy diagram

The energy diagram of the interface in the above-mentioned conditions can be sketched from the measured values of the OCP and FB potentials (see 1.2.3.6). The OCP of silicon (either n– or p–type) immersed in a fluoride solution is experimentally found near the reduction potential of the $H^+/H_2$ system at all pH values [4, 48, 62]. An expression can be given using equation 1.9 for the reaction $2H^+ + 2e^- \rightarrow H_2$, and the definition of pH:

$$U_{OCP}^n = U_{H^+/H_2}^n = U_{H^+/H_2}^o + \frac{2.3kT}{e} \log[H^+] \quad (2.1)$$

$$U_{FB}^n = -240 - 59 \cdot pH \text{ mV/SCE} \quad (2.2)$$

It has been plotted as a dashed line in figure 2.1. The FB potential of oxide-free n–type silicon lies very close to this value [48]:

$$U_{FB}^n = -180 - 59 \cdot pH \text{ mV/SCE} \quad (2.3)$$

which indicates that the bands of n – Si in fluoride media are flat or in slight accumulation at all pH values ($\Delta \phi_{ne}^n = U_{OCP}^n - U_{FB}^n \simeq -60$ mV). The CB edge is then located $\frac{E_c}{e} = 250$ mV more negative than $U_{FB}^n$ at each pH value, and the VB edge can be predicted using the bandgap energy ($\frac{E_v}{e} = 1.1$ V). Finally, the FB potential of p – Si is expected to be $\frac{E_v}{e} = 200$ mV more negative than the VB edge:

$$U_{FB}^p = +470 - 59 \cdot pH \text{ mV/SCE} \quad (2.4)$$
Figure 2.1: Characteristic potentials of Si electrodes in contact with an aqueous fluoride solution, as a function of pH. The band edge energies and $U_{FB}^p$ are calculated from $U_{FB}^n$. At OCP, $n - Si$ is near FB and $p - Si$ in strong depletion. The experimental determination of $U_{FB}^p (exp)$ lies $\sim 300 \text{ mV}$ more positive than $U_{FB}^p$ predicted from $U_{FB}^n$ (see discussion later). Flatband potential data replotted from G. Schlichthörl and L. M. Peter [48].

yielding $\Delta \phi_{nc}^p = U_{OCP}^p - U_{FB}^p \approx +700 \text{ mV}$, i.e. $p - Si$ is in strong depletion. Both $U_{FB}^n$, $U_{FB}^p$ have been depicted in figure 2.1 [48] as a function of the pH of the fluoride solution. It must be noted that the experimental band bending is not exactly constant with pH, but a slight tendency towards accumulation is found at the higher pH values [4] (not shown in the figure).

Following the procedure explained in 1.2.3.6, the electron energy diagram of the interface is sketched in figure 2.2 for pH1 and pH14. The vacuum level ($E_{\text{vac}} = -4.74 \text{ V/SCE}$ in the electrochemical scale) is located $E_{A,Si} = 4.05 \text{ eV}$ above the silicon CB, and the potential drop at the double layer is calculated with expression 1.60: $\Delta \phi_{dl} \approx -200 \text{ mV}$ at pH1 and $\Delta \phi_{dl} \approx +570 \text{ mV}$ at pH14. Thus, the Si electrodes appear to be in equilibrium with the $H^+/H_2$ system, with larger potential drops in the electrochemical double layer for increasing pH.
Figure 2.2: Electron energy diagrams for n- and p-Si in fluoride media, as deduced from figure 2.1. At all pH values, n-Si is near flatband while p-Si is in strong depletion, both appearing to be in equilibrium with the $H^+/H_2$ system. A considerably large potential drop in the electrolyte $\Delta \phi_{el}$ is found at high pH values.

### 2.1.2 Interpretation of the equilibrium

As was explained in (1.2.3.5), the surface of a covalent solid ideally terminated with dangling bonds is extremely reactive. In particular, when a clean Si surface in vacuum is exposed to water vapor, Si – H and Si – OH bonds are readily formed by dissociation of $H_2O$ molecules, and eventually give rise to an oxide layer that prevents further oxidation [3]. The same result is obtained when the Si is exposed to ambient humidity or immersed in an aqueous solution. This “native oxide” layer can be easily dissolved by adding hydrofluoric acid to the solution: the fluoride species are able to complex the Si oxidation products and remove them from the surface, thus allowing the oxidation reaction to proceed. The oxidation process implies the loss of the bonding electrons of Si atoms, and is therefore associated with a (positive) current of holes from the semiconductor into the solution as the Si atoms are dissolved (see the subsection “Electrode reactions” in 1.3.2.2).

At the rest potential (OCP) the total current through the interface must
be zero, and this oxidation current must be balanced with another one of the same amount and opposite sign. This is what figure 2.2 actually shows: The Si bands are set as to accumulate free electrons at the surface in order to transfer them to the solution. The electron-accepting species can be (in the absence of other redox systems) protons or water molecules, and the cathodic reaction gives rise to hydrogen evolution (corresponding to a negative current). Since the kinetics of both the hydrogen evolution reaction (HER) and the dissolution of Si are slow, slight accumulation or nearly flat bands are enough in $n-Si$, but still strong depletion is required in $p-Si$ in order to produce a surface concentration of electrons (minority carriers) and to decrease the emission of holes over the energy barrier.

The Si surface immersed in an aqueous fluoride solution is thus slowly but continuously dissolved, and the corresponding oxidation current is balanced by a cathodic current due to hydrogen evolution. This picture is essentially maintained at all pH, as is suggested by the approximately constant band bending in both $n-$ and $p-Si$. Note that although the Fermi energy of the Si electrode lies close to the redox potential of the $H^+/H_2$ system, the equilibrium of Si and the fluoride solution is kinetic rather than thermodynamic, in the sense that it does not necessarily imply the equalization of the Fermi levels in both phases: The OCP is defined by the mixed potential of the HER (cathodic half-cell reaction) and Si dissolution (anodic half-cell reaction). In other words, the rest situation is achieved when both reactions exchange charge at the same rate (this is the dissolution current explained in 1.3.3.1).

As was determined by infra-red spectroscopy studies [63], the Si surface atoms are bonded to hydrogen in fluoride solutions of a wide range of pH, and even under the flow of relatively small anodic currents (see 2.2.2). These results gave new insights into the chemical composition and morphology of the interface [64, 65, 66, 67, 68] and finally ruled out the fluorine termination, a belief based in thermodynamic calculations ($Si - F$ bonds are stronger than $Si - H$) as well as in the picture that the hydrophobic silicon surface was teflon-like [69]. Thus, during the simultaneous HER and Si dissolution reactions at the OCP, the $H-$termination is continuously renewed and no specific adsorption occurs. The surface state density of Si in fluoride solutions is very low [70, 71]. It has been estimated as $N_{st} < 10^{12} \text{ cm}^{-2}$ in methanol [72]. As was discussed in 1.2.3.5, this is in agreement with the weak polarity of the $Si - H$ bond (δ small in figure 1.13) and corresponds to a rather "ideal" interface (no Fermi level pinning). Thus the double layer behavior is well approximated by the Helmholtz model as a monolayer of highly polarized water molecules between the electrode charge and the countercharge in the electrolyte. If the fluoride solution is relatively concentrated ($\sim 1 \text{ M or}$
above), the charge in the electrolyte is mostly located at the OHP (less than
1 nm from the electrode surface). The Helmholtz potential is small at low
\( \Delta \phi_H \simeq 0 \), and \( \Delta \phi_H > 0 \) attracts positive ions towards the electrode
at high \( \Delta \phi_H \) (e.g. \( NH_4^+ \), or \( H_3O^+ \) at medium \( \Delta \phi_H \)). In alkaline solutions, the
slightly larger band bending \( \Delta \phi_{sc} \) and the \( \Delta \phi_H > 0 \) account for two facts:
First, that the \( Si \) dissolution rate in fluoride solution is larger at high \( \Delta \phi_H \)
and thus a larger HER rate is necessary to balance it [4]. And second, that
the proton concentration in solution is much lower (10\(^{-14}\) M at \( pH14 \), i.e.
\( \sim 10^7 \) cm\(^{-3}\)).
The equilibrium of \( Si \) in aqueous fluoride solutions can then be envisaged
as a charge exchange that preserves the \( H^- \)termination at the expense of the
dissolution of silicon. These reactions are probably not occurring at the
same places on the surface: Anodic and cathodic sites are defined but during
both processes the \( Si \) surface is covered with hydrogen bonds. Note that
since the \( Si \) surface is \( H^- \)-terminated, the \( \Delta \phi_H \)-dependence of \( U_{OCP} \) and \( U_{FB} \)
is not related with specific adsorption (expression 1.42). Therefore \( \Delta \phi_H \) is
mainly determined by charge transfer as in metals.
It must be stressed that the energy diagram for \( p-Si \) in figure 2.2 has been
deduced from the experimental data on \( n-Si \), and that measurements on
\( p-Si \) only fit qualitatively these predictions. The experimental FB potential of
\( p-Si \) electrodes lies 200–300 mV more positive than \( U_{FB} \) shown in figures
2.1 and 2.2, which does not alter the fact that \( p-Si \) electrodes in fluoride
solutions are in strong depletion (500–800 mV). However, this systematic
discrepancy has not been explained yet. In addition, in \( p-Si \) the amount of
electrons available at the surface for the cathodic counterreaction (HER) is
limited by the recombination with holes (majority carriers), so the HER rate
does not only depend on the band bending \( \Delta \phi_{sc} \) as in \( n-Si \). The doping
density [73] and even the quality of the material [74] limit the diffusion length
of minority carriers thus increasing the dissolution rate.

### 2.2 Anodic oxidation of silicon

As described by the mixed potential theory, one of the two simultaneous
reactions can be favored at the silicon electrode if an external bias is applied.
At potentials negative of OCP (\( n-Si \) or illuminated \( p-Si \)) the HER prevails
over the silicon dissolution and a net cathodic current flows, as in a metal. At
positive potentials the electrode material is dissolved (\( p-Si \) or illuminated
\( n-Si \)), which is a more complex process.

Prior to describe the major experimental features of the anodic oxidation
of silicon, the electronic energy associated with the intermediate reaction
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Figure 2.3: Model for the Si – H bond breaking step by a hole (AB) and the electron injecting step by the formation of a new Si – F bond (C). Structural scheme above, energetic relations below. After H. Gerischer et al. [3].

steps will be briefly discussed. These general schemes will be employed to distinguish between two regimes in the dissolution process (2.2.2), and to explain the “current doubling” phenomenon (2.2.3). The microscopic reaction mechanism will be given afterwards (2.2.4), also including the situation at the OCP described in the previous section, and the HER at negative potentials.

2.2.1 Energetics of the oxidation process

The departure surface is assumed to be terminated by Si – H bonds. For simplicity, the reaction is usually discussed at a kink site on a (111) crystal face, which is less bonded to the lattice than most surface atoms (see 2.2.4 and figure 2.6 later). The (bonding) electrons in Si – H bonds on the surface have energy levels below the VB edge, but these levels are probably broadened at kink sites due to the interaction with the aqueous solvent [3]. In this way the energy levels of the bonding electrons of kink site atoms can act as traps for holes (figure 2.3).

The first step in the dissolution of the kink site atom must be the disso-
cation of the $Si - H$ bond by capture of a hole:

$$Si - H + h^+ \rightarrow Si^\bullet + H^+$$  \hspace{1cm} (2.5)

The dissociation must be promoted by a negatively-charged “nucleophilic” agent such as $F^-$, $OH^-$ or the polar $H_2O$ molecule (for example, the $F^-$ ion would react with the proton to give $HF$). The notation $Si^\bullet$ represents a $Si$ surface atom having an unpaired electron (basically a dangling bond) which is a short-lived state. As was discussed in 1.2.3.5, the energy level of the unpaired electron is no longer in the VB but lies within the bandgap [3, 32] (figure 2.3B). Indeed, such a high energy corresponds to a weakened bond.

The removal of the second electron can be carried out either by excitation of the electron into the CB from the activated surface state (as shown in figure 2.3C) or by the capture of another VB hole. Both processes can occur in silicon and give rise to two different oxidation regimes depending on the hole concentration at the surface, solution $pH$ and the fluoride concentration.

### 2.2.2 Porous silicon and electropolishing regimes

Holes can be accumulated at the surface of a $p - Si$ electrode at positive potentials. Figure 2.4 shows the anodic $j - U$ curve of a $p - Si$ electrode in a fluoride solution 1 $M$, $pH4.5$. Essentially the same curve shows up for $n - Si$ electrodes under (excess) illumination, besides a potential shift due to the difference in FB. Decreasing the light flux, the anodic current saturates as in figure 1.27 (not enough holes are generated). However, the photocurrent plateau in fluoride media is twice as large as in other solutions. This “current doubling” phenomenon is related to the oxidation mechanism outlined below, but for simplicity it will be explained in the next section (2.2.3). The discussion here will be concerned on $p - Si$ electrodes (or $n - Si$ under excess illumination).

As shown by Ozanam and Chazalviel [60, 61], two regimes can be distinguished in the $j - U$ plots of figure 2.4. In the region to the left of the first current peak the dissolution of the electrode proceeds as a strong corrosion that renders a sponge-like surface (it is named porous silicon regime, PS). The range of electrode potentials corresponds to depletion, i.e. the hole density at the silicon surface is low compared with the fluoride concentration in solution. The oxidation rate in these conditions is relatively low and the oxidation products can be readily dissolved. The $H^-$ termination of the surface is thus preserved [60]. In the PS regime, $Si$ atoms are not completely oxidized, but to its divalent state $Si(II)$ [75]. Actually the oxidation process requires the capture of only one hole per dissolved atom, because the remaining bonding electron is injected (excited) into the CB [76, 77]. The silicon
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Figure 2.4: Anodic branch of the $j - U$ curve of $p - Si$ in a 1 M fluoride solution at pH4.5. The sharp current peak found on increasing the hole density at the surface, is due to a change in the oxidation mechanism: from the Porous Si regime (PS) to the Electropolishing regime (EP). The same curve shape is obtained in $n - Si$ under excess illumination. If the light flux is too weak, not enough holes are generated and the reaction remains in the PS regime regardless of potential (dashed curves).

The oxidation reaction in the PS regime can be outlined as follows:

$$Si + h^+ \rightarrow Si(II) + e_{CB}^-$$  \hspace{1cm} (2.6)

and silicon passes to the solution as a neutral species of the form $SiH_xF_y$ [4]. For a reaction valency of 2, an anodic current of 2.66 $\mu A/cm^2$ corresponds to a silicon dissolution rate of 0.1 mm/min [4]. Note that $Si(II)$ is further oxidized to $Si(IV)$ by reacting with water molecules in solution, and $H_2$ is released in this process (gas bubbles are often visible when etching $Si$ in the PS regime).

The region to the right of the first current peak in figure 2.4 is known as the **electropolishing regime** (EP). The hole concentration at the silicon surface and the oxidation rate are higher in this region. In particular, the second peak in the $j - U$ curve corresponds to the onset of hole accumulation [60] or inversion in $n - Si$. In these conditions, the solution can no longer keep the surface free of oxidation products ($H$-terminated) and a thin oxide layer is condensed. This layer is continuously present as the reaction proceeds,
although its stoichiometry and thickness depend on the potential and solution composition: At low potentials the layer is “wet” (hydroxide-like), while at larger potentials a “dry” $SiO_2$ layer appears at the $Si$ | oxide interface. In the EP regime, every silicon atom is oxidized to $Si(IV)$ by the capture of four holes [75]:

$$Si + 4h^+ \rightarrow Si(IV)$$

(2.7)

For a reaction valency of 4, an anodic current of 5.32 $\mu A/cm^2$ corresponds to a dissolution rate of 0.1 $nm/min$. No gas evolution is observed in this case.

Silicon anodization in the PS and EP regimes have found very different applications: Although known for decades, the interest on PS was triggered by the discovery of its visible photoluminescence in 1990 [78], which envisaged many applications in optoelectronics. In spite of its wide use in integrated circuits, silicon is a narrow bandgap semiconductor (1.1 eV, infrared) and its use for visible light detectors or emitters had been ruled out before the discovery. Today, research in this direction has relatively waned due to several technological difficulties. PS is mainly employed as a sacrificial layer in the fabrication of microstructures, but a great deal of data has been gathered on its mechanical, chemical and optical properties [79]. On the other hand, the anodic dissolution of silicon in the EP regime can be employed to electrochemically polish the silicon surface. From a fundamental point of view, the EP regime is also interesting because the stationary nature of the oxide layer facilitates the study of its electrochemical properties [80].

2.2.3 Current doubling

The anodic oxidation mechanism outlined in reaction 2.6 is specific of silicon in the given conditions, and it is not found in other semiconductors like $GaAs$ or $InP$. The injection of electrons into the CB during anodic oxidation was first observed in germanium [81, 82] and was studied in detail in silicon [76, 77, 83, 84]. It can be observed when a parameter other than the electrode potential is employed to control the hole concentration at the surface (and thus the oxidation rate): In $n$—type electrodes under illumination, or using oxidizing agents (hole injectors) in the fluoride solution.

In the first case (photoanodic dissolution of $n-Si$), illumination must be low so that it effectively limits the supply of holes, and then the photocurrent is proportional to the light intensity and independent of the potential beyond a certain point (plateau of figure 1.27). In these conditions the $j-U$ curves of $n-Si$ display a photocurrent two times larger in a fluoride solution ($NH_4F$) than in $NH_4Cl$ (figure 2.5A). This is due to the different oxidation mechanisms in these media: A silicon oxide layer is formed in the absence of
Figure 2.5: Photocurrent multiplication in Si: (A) The oxidation current in $n-Si$ under weak illumination is two times greater in the presence of fluoride than in other electrolytes. After H. Gerischer and M. Ligbke [76] (B) At weak hole concentration and in fluoride media, electrons are injected into the CB during the oxidation reaction (PS regime). (C) Under excess holes or in the absence of fluoride, the oxidation reaction proceeds in the EP regime.

fluoride, which consumes four holes per silicon atom according to equation 2.7 and figure 2.5C. In $NH_4F$, the oxidation of each atom consumes only two holes, because the remaining two electrons are subsequently injected into the CB (equation 2.6 and figure 2.5B). Both reactions can be compared after multiplying reaction 2.6 by 4 to account for the same concentration of photogenerated holes. The measured anodic current in $NH_4F$ is due to the electrons from the photogenerated electron-hole pairs, and the electrons injected during the reaction of silicon with holes. At sufficiently high potentials to prevent recombination, the total current in $NH_4F$ is two times larger than in $NH_4Cl$. This phenomenon is therefore known as “current doubling” or “photocurrent multiplication”.

The same conclusion is obtained if holes are injected from an oxidizing agent in the fluoride solution instead of being photogenerated. This will be discussed in section 2.3.2.

### 2.2.4 Dissolution mechanism

A mechanism for the dissolution of silicon in aqueous fluoride solutions is presented here in a simplified form, extracted from several works by Gerischer and Allongue [3, 4, 5, 6, 77]. The mechanism was induced from electrochemical measurements on $n$-type $Si(100)$ and (111), as well as scanning
tunneling microscopy measurements under potentiostatic control (EC-STM) on \( n - Si(111) \). In those experiments, the use of an \( n \)-type semiconductor allowed the control of the oxidation reaction using light (electrochemical studies), and on the other hand it facilitated STM in-situ imaging. The model is based on:

- The special role played by kink sites on the crystal surface.
- The persistent \( H \)-termination of the surface immersed in aqueous fluoride media.
- The existence of two components in the etching mechanism: One chemical, another electrochemical.

Many experimental facts have been removed to ease the explanation, but the more relevant ones can be found in the latest reference [4].

2.2.4.1 Introduction

In the (111) face of silicon, biatomic steps are found running along the [110] direction. When a step edge zigzags to clear one (double) atomic row, the corner of the zigzag is termed “kink” site. Atoms at such sites (tagged \( K \) in figure 2.6) have two bonds with the lattice while the other two have reacted with the solution (in fluoride solutions they are saturated with hydrogen, giving rise to a nearly unpolar and very little reactive bond). All other atomic sites on a \( Si(111) \) surface (on a terrace, even along steps) have three bonds to the lattice and only one bond to \( H \), so it is not surprising that the (111) boasts the slowest etch rate of all crystal faces: For a comparison, an ideally flat \( Si(100) \) surface is completely terminated by kinks (figure 2.7). The reaction model that follows is discussed at a kink site, which is considered the reactive site.

It is found that two possible pathways coexist in the etching of silicon in fluoride solutions: One \textit{chemical} (not related with the charge at the silicon electrode) and another \textit{electrochemical} (involving free charge carriers in the semiconductor). Their relative rates depend on (and can be controlled with) \( pH \) and the potential applied to the silicon electrode. As an example, the absolute etch rate of \( n - Si \) at the OCP is plotted (in a logarithmic scale) as a function of \( pH \) in figure 2.8A. The partition between the electrochemical and chemical reactions (\( \Gamma = \frac{R_p}{R_p + R_c}, \Gamma = 1 \) corresponding to a purely electrochemical reaction) is shown in figure 2.8B. It can be seen that at the OCP the etching reaction is mainly electrochemical at low \( pH \), whereas at high \( pH \) the chemical component prevails. Of course under anodic bias and in the
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Figure 2.6: Crystallographic model of a Si(111) face showing a kink site (labelled K) on a biatomic step running along the [110] direction. The step height is 0.31 nm. In fluoride solutions, kink atoms have two bonds to the crystal and two bonds saturated with hydrogen atoms, whereas all other surface sites have only one bond to hydrogen.

Figure 2.7: Crystallographic model of an atomically flat Si(100) face. The surface is completely terminated by kinks, each having two bonds to the crystal and two bonds saturated by $H$ atoms.
Figure 2.8: (A) pH—dependence of the total etch rate ($R$) and the electrochemical etch rate ($R_{EC}$) of n–Si in fluoride solution. (B) pH—dependence of the fraction $\Gamma = \frac{R_E}{R}$, $\Gamma = 1$ corresponding to a purely electrochemical reaction. After Allongue et al. [4].

presence of holes, the etching mechanism tends to be more electrochemical regardless of $pH$.

The strong difference in the OCP etching rate at low ($\sim 0.03$ nm/min) and high $pH$ ($\sim 1$ nm/min) is in apparent contradiction with the approximately constant band bending that is found for all $pH$ (figures 2.1 and 2.2) and that accounts for the cathodic counter-reaction (HER). But the high etching rate in alkaline fluoride media is mainly due to the chemical path, and the electrochemical reaction varies only between $\sim 0.03$ nm/min at pH1 and $\sim 0.1$ nm/min at pH14, in agreement with the slight tendency towards accumulation discussed in 2.1.1 and 2.1.2. Thus the electrochemical dissolution at the OCP is always balanced with the HER, and the dissolution current is larger at high $pH$. Using the factors given in 2.2.2, the dissolution current can be estimated as $0.8 \, \mu A/cm^2$ at pH1 and $2.7 \, \mu A/cm^2$ at pH14.

Note that the main character (the reactant) in the reaction schemes to follow, is the water molecule: In the hydrolysis reaction, water molecules are broken while the OH groups and the H atoms keep their respective electrons. All other relevant molecules are nucleophilic agents (they have an affinity for protons) that facilitate certain reaction steps. Hence they act as catalysts: mostly $OH^-$ and $F^-$ at high $pH$ and $HF$ or $HF_2^-$ at low $pH$. It is important to keep in mind that the polarity of the chemical bonds involved in each reaction step depends on the relative electronegativities of the atoms.
that constitute the bond, i.e. ordered by polarity: \( Si - Si < Si - H < H - O < Si - O < Si - F \) [85]. As in the original references the discussion is focused on the kink sites, and the electrode is a low-doped \( n - Si \) (when relevant). A generalization in both directions will be given afterwards.

### 2.2.4.2 Chemical reaction

The model is shown in figure 2.9A and is the prevailing mechanism at the OCP in high \( pH \) solutions. A water molecule reacts directly with a \( Si - H \) surface bond at a kink site (hydrolysis reaction), which is the rate-determining step because the polarity of the \( Si - H \) bond is very low. The resulting \( Si - OH \) is quickly replaced by a \( Si - F \) bond, whose high polarity is capable of polarizing the \( Si - Si \) bonds underneath. The \( Si - Si \) (back) bonds are broken by two successive hydrolysis reactions, that bind the \( OH \) groups to the \( Si \) atom being attacked, and the \( H \) atoms to the surface \( Si \) atoms. The result is the species \( HSiF(OH)_2 \) (oxidation state (II) of silicon), which is neutral and unstable in solution. By further hydrolysis another \( H_2 \) molecule is produced, and possibly a certain substitution of the \( OH \) groups by fluoride, which is a more effective complexing agent of silicon.

The \( pH \)-dependence of the chemical path can be explained with the participation of \( F^- \) ions as catalysts (or \( OH^- \) in a second term), since their concentration in solution increases with \( pH \) (see figure 2.10 and references [61, 86]). Note that the resulting situation is equal to the departure, with the surface \( H \)-terminated and the kink site shifted one atomic row. The most important point of this chemical path is that the direct reaction with water can only occur at “weak” surface sites (kinks). This is at the origin of the markedly anisotropic character of the chemical reaction, as it will be discussed later.

### 2.2.4.3 Electrochemical reaction

This is the reaction that prevails under anodic bias, and still at the OCP provided that the \( pH \) is low. Since free charge is involved, the situations of depletion (anodic potentials) and FB-accumulation (OCP) must be treated separately. They have been represented in figures 2.9B and 2.9C respectively, for a dark \( n - Si \) surface.

Under anodic potentials the energy bands are bent upwards and the semiconductor surface is depleted of free electrons. If one of the electrons that constitute the \( Si - H \) bond (and have an energy near the VB edge) is injected into the CB by thermal activation, the bond is irreversibly dissociated giving rise to a proton (\( H^+ \)) and a radical \( Si^\cdot \) (a silicon atom with an unpaired
Figure 2.9: Structural 2-D model of the n – Si dissolution reaction (ABC) and hydrogen evolution reaction (D). Reaction products are preceded by a minus sign (−). State (b) is an empty surface state; state (b') is state (b) filled with one supplementary electron. After Allongue et al. [4].
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![Graph](image)

Figure 2.10: Calculated fraction $\alpha$ of the different chemical species in a fluoride solution, as a function of pH (total fluoride concentration 7.5 M). After Verhaverbeke et al. [86]

The detachment of an electron as discussed in 2.2.1). This process can also be envisaged as the thermal generation of a hole. The probability that the dissociation

$$Si - H \rightarrow Si^* + e^-_{CB} + H^+$$

(2.8)

occurs is low at room temperature, because silicon has a relatively large bandgap. But if a very polar ion in solution approaches the reactive site, its strong electric field might well help the thermal activation of the electron. In this way, fluoride species like $F^-$ at high pH or HF and $HF_2^-$ at low pH, can indeed act as catalysts. The catalytic effect of fluoride species can also be seen in more “chemical” terms as a temporary association between $F^-$ (or HF, HF$_2^-$) and the $H^+$, while the bonding electron is injected into the CB. In any case, the leading role of the catalyst in this electrochemical path, points to a lesser importance of the kinks as reactive sites. The electrochemical reaction proceeds with the formation of a $Si - OH$ bond by hydrolysis, after injection into the CB of the electron in the dangling bond (as it was explained in 1.3.2.1, the electron energy in the dangling bond is near the mid-gap, so this is a much easier process than the abovementioned). The $Si - OH$ bond is an intermediate step that will account for the formation of an oxide (see below) but if the fluoride concentration is high enough, a fast replacement $Si - OH \rightarrow Si - F$ occurs. From here on, the reaction proceeds by hydrolysis
of two water molecules as for the chemical path, and silicon atoms again enter the solution as Si(II) neutral species.

Note that the rate-determining step of the electrochemical path is the substitution \( Si - H \rightarrow Si - OH \), whose rate is proportional to the concentration of the catalysts \( F^- \) or \( HF, HF_2^- \) depending on \( pH \). It is also worth mentioning that the two electrons injected into the CB can be measured as a current at sufficiently positive potentials (electrons are majority carriers in \( n - Si \)): The reverse current in the dark is actually due to these processes (“current doubling”), and its value correspondingly increases at high \( pH \) (not shown in the figure) [4].

At the OCP (figure 2.9C) the electrochemical reaction scheme is very similar to the above described, but the presence of free electrons at the semiconductor surface must be taken into account (the \( n - Si \) electrode is in weak accumulation at the OCP, as it was shown in 1.3.2.1). The negative charge inside the semiconductor produces a repulsive force on the nucleophilic agents and on the dipole of the water molecule, affecting mostly the reaction rate. From a microscopic point of view, the surface state associated with the radical \( Si^* \) is occupied under weak accumulation, and gives rise to a silicon atom with two electrons (i.e. one net negative charge, \( Si^{\ominus} \)). Thus protons adsorbed at the surface may easily restore the \( H^- \)-termination, and the dissociation of the \( Si - H \) bonds becomes reversible:

\[
Si - H \rightleftharpoons Si^{\ominus} + e_{CB}^- + H^+ \tag{2.9}
\]

The rate of \( Si - OH \) bond formation by hydrolysis is therefore reduced, but the reaction is otherwise the same. The following steps proceed also as in the anodic case.

The \( pH \)-dependence of the (electrochemical) etch rate suggests that the weakly polar \( Si - H \) bond (having the negative charge near the \( H \) atom) behaves as a weak acid: It is more dissociated as the \( pH \) increases, and the \( H \) atoms in \( Si - H \) bonds are continuously “exchanged” with atoms from the solution [87]. However, this exchange is not a simple permutation with a proton; instead, the exchange is made with \( H \) atoms from water molecules and imply the oxidation of \( Si \) atoms.

### 2.2.4.4 Interpretation of the model

The mechanism outlined above can be applied to other conditions. For instance, in the anodic dissolution of silicon in the presence of holes (\( p - Si \) or \( n - Si \) under illumination) it is enough to replace the thermal activation step of the “first” electron (process \( a \rightarrow b \) in figure 2.9B) by the capture of a hole in the \( Si - H \) bond. Again, this hole current can be measured directly in
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$p - Si$ (for holes are majority carriers) or through the photogenerated electrons in $n - Si$ (that are collected in the bulk at positive bias). The “second” electron (injected into the CB) directly produces a current in $n - Si$ but it must be measured by recombination with holes in $p - Si$.

The formation of an oxide can be discussed on state $c$ of the electrochemical path (figure 2.9B): If too many $Si - OH$ bonds exist at the surface (either because there is a strong hole accumulation, or because fluoride concentration is too low to replace them), some of the $Si - OH$ bonds may condense into $Si - O - Si$ structures [88]. This is the initial stage of oxide formation and corresponds to the onset of the electropolishing regime. The oxide can be chemically dissolved in low-$pH$ fluoride solutions, where mostly $HF$ (and its dimer $(HF)_2$) are present. Oxide dissolution is aided by the polarity of both $Si - O$ and $H - F$ bonds, and the process stops at the silicon | oxide interface.

Finally, under very negative bias the hydrogen evolution reaction (HER) is favored in $n - Si$ (and in $p - Si$ under illumination) following the scheme shown in figure 2.9D (Volmer-Heyrovsky reaction [58]). In this case all etching reactions are stopped in $n - Si$ [4], but not in $p - Si$ in the dark [89] because the field created by the hole depletion layer in $p - Si$ is much weaker than that created by the electron accumulation layer in $n - Si$. Therefore $p - Si$ continues to be etched at cathodic bias.

Regarding the reaction sites in the crystal, a kink site has been employed for the discussion. A posteriori, this is only strictly necessary for the chemical path (which starts with direct hydrolysis at a preferential site). The electrochemical path is initiated with the dissociation of a $Si - H$ bond and in principle this can occur anywhere on the crystal surface (along a step, on a terrace).

Whether the detailed steps of this model are accurate or not, two general ideas can be kept as the main conclusions:

- The $H$-termination of silicon in aqueous fluoride solutions stems from kinetics, because the restoration of the $Si - H$ bonds is never a rate-limiting step. This was confirmed by ab initio calculations [90].

- The $pH$-dependence of the chemical reactivity of silicon results exclusively from the changes in reactivity of identical surface sites ($\equiv Si - H$, $= Si = H_2$).

As a final remark, note that the rest situation of silicon in fluoride media indeed corresponds to a balance between the electrochemical dissolution (OCP case, figure 2.9C) and the cathodic hydrogen evolution (figure 2.9D).
Figure 2.11: Electrochemical AFM image of a n – Si(111) surface immersed in a 2M NaOH alkaline solution (image: 1µm × 1µm × 2nm). The Si surface undergoes a layer-by-layer dissolution, and pitting on the terraces (see Appendix A).

From a microscopic point of view, both the band bending and the position of the band edges are adjusted to generate Si• radicals or \(\text{Si}^{\equiv}\) surface groups, which are the intermediates in the dissolution and hydrogen evolution reactions.

### 2.2.5 Application to the preparation of atomically-flat silicon surfaces

The fact that Si(111) surfaces can be made atomically flat in fluoride solutions at high pH [67] can be easily understood in the framework of this model. As was discussed above, the chemical reaction occurs preferentially at the kink sites and leads to completely anisotropic etching, whereas the electrochemical path is relatively isotropic. Atomically flat silicon surfaces can then be prepared by etching of Si(111) under conditions where the rate of the chemical reaction is much larger than the electrochemical, i.e. at high pH [4] (see figure 2.8). Since the main reactant is the water molecule, other solutions (not containing fluoride) can be employed to flatten the Si surface provided that the pH is high: NaOH [5, 88], boiling water [91, 92, 93, 94] and
deoxygenated water [95]. An example is shown in figure 2.11 and an atomic force microscopy (AFM) study will be presented in appendix A. Conversely, Si(100) surfaces are strongly pitted in these solutions, leaving pyramidal structures corresponding to (111) facets [96].
Chapter 3

Experimental

3.1 Characterization techniques

Many characterization techniques have been employed in the experiments of the following chapters, but only two will be described here in detail: First, the experimental setup for the electrochemical studies, given its relevance for chapters 4, 5 and 6. And second, the application of atomic force microscopy (AFM) to the direct visualization of reactions on electrode surfaces (electrochemical AFM).

3.1.1 Electrochemical studies

As has been extensively used in the discussion of chapters 1 and 2, the potential of an electrode immersed in an electrolyte (working electrode, WE) is related to the Fermi energy of electrons, and the current informs about the reactions occurring at the interface. For the electrochemical characterization of a system, it is thus essential to measure and control the sample potential and the current passing through it. Two difficulties are immediately encountered: First, there is no direct access to the potential of the liquid, and all potential measurements must be done with respect to a well-characterized system in the solution. This system acts as a reference electrode (RE) and gives the potential of the WE without participating in the reactions. For example, electrons in a Pt wire immersed in a 1.18 M H\(^+\) (acid) solution that is bubbled with H\(_2\) at a pressure of 1 atm, reach the equilibrium situation at a potential of 4.5 V with respect to the vacuum level (which is the physically well-defined reference for potentials: the electrons at rest in vacuum) [29]. This complex setup constitutes the normal or standard hydrogen electrode (SHE) that was mentioned in 1.2.2 and figure 1.5. In practice, more compact electrodes than the SHE are used, like the saturated calomel electrode

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(SCE), recently replaced by the $Ag - AgCl$ electrode. Their potential scales are very similar and differ by 0.24 V from the SHE. They were also presented in figure 1.5. Reference electrodes are commercially available with a proper encapsulation to protect them and to minimize contamination to the solution under study. When working in fluoride solutions, additional precautions must be adopted because the glass encapsulation can be attacked. In the experiments of the following chapters, the RE was a Metrohm SCE electrode [97] with a frit and shrinking tube double-compartment made of Polyethylene (HF-resistant, EG&G model G0194 [98]).

Once the sample potential can be measured against a reliable reference, a second problem arises: the potential of the RE is constant as far as no current flows (i.e. the reference system is in equilibrium), and therefore the RE cannot be employed to apply potentials and measure currents. In addition, there is very little control on the exact resistance of the electrolyte and thus on the potential drop throughout the liquid. To avoid any uncertainty on the measurement of the potential at the RE, all the current is forced to flow through an auxiliary electrode (the counter electrode, CE) by means of a potentiostat. A simplified electric diagram is shown in figure 3.1 with the three electrodes in the electrochemical cell. The potentiostat is an electric control system that applies a bias between the sample (WE) and the CE such that the WE reaches the desired potential ($U_{in}$ in figure 3.1). In this way the measurement of the current flow through the WE (done in the CE branch of the potentiostat) does not compromise the determination of the WE potential (done with the RE). Of course, the potential applied by the potentiostat between WE and CE is in general larger than the potential set between WE and the RE ($-U_{in}$), because as soon as a current $I$ flows through the WE-CE, a potential $R_d \cdot I$ is dropped in the electrolyte ($R_d$ being the electrolyte resistance). In any case, a large-area Pt grid must employed as CE so that the current-limiting electrode is always the sample under study (WE). Note that these difficulties are only due to the liquid; in the study of solid metal-semiconductor junctions, the metal itself can be used as a reference, and grounding it sets $U_{metal} = 0$ regardless of the current flow.

In the experiments, the electrodes were controlled using either a manual potentiostat (HQ Instruments 105) connected to a signal generator (EG&G Universal Programmer 175 [98]) and an analog plotter (Philips PM8033), or with a computer-interfaced potentiostat (Solartron 1287 [99]). The capacitance measurements (described in section 1.2.3) were performed with a frequency response analyzer (Solartron 1255 [99]) using a measurement signal of 10 mV at 25 KHz.

The measured current $I$ must always be normalized to the area of the WE exposed to the solution, to yield the current density $j = I/A_e$, which
is the physically meaningful magnitude. The sample holder of figure 3.2 [100] was built in order to have a controlled area of the sample exposed to the solution (\( A = 0.3 \text{ cm}^2 \)), and to prevent the “stray” processes at highly reactive spots like the Si chip edges or the rear side. It has a Teflon [101] body and lids, secured with nylon screws, and the joints are made of Viton [101]. The chips are placed on a steel cylinder that provides the electric contact. In certain experiments (chapter 7) the samples were simply immersed in the solution, without protection and without electric access to the sample potential. For comparison, an electrochemical study was also carried out in the sealed sample holder exposing only the rear side of Si samples to the fluoride solution.

### 3.1.2 Atomic force microscopy

Atomic force microscopy (AFM) allows to record the three-dimensional topography of a surface with sub-\( nm \) resolution and practically no limitation concerning the environment of the sample (gas or liquid). The heart of an AFM is a force transducer formed by a cantilevered tip and a sensor of the cantilever deflection. A typical example is shown in figure 3.3, although other cantilever shapes and deflection sensors exist. In the simplest case, when the tip is brought to contact with the sample, the cantilever bends upwards and the deflection \( \delta \) is measured by the sensor. This deflection can be translated into a force if the cantilever spring constant \( \kappa \) is known. As representative
values, $\kappa \sim 1 \, N/m$, $\delta \gtrsim 1 \, nm$, and forces as small as $F = \kappa \cdot \delta = 1 \, nN$ can be easily detected. Such forces can also be controlled if an accurate positioner is added to the setup: In figure 3.3, the force transducer is fixed and the sample is attached to piezoelectric XYZ positioners, which can be designed to have sub-$nm$ accuracy within a range of several $\mu m$. In this way the tip-to-sample distance can be varied (by applying a potential $U_z$) and the force between them can be readily measured through the cantilever deflection. Actually the force between tip and sample can be fixed at a desired value $F_0$, if the difference between $F_0$ and the measured force $F(t)$ is fed back to the Z positioner: When $F(t) < F_0$, $F_0 - F(t) > 0$ and $U_z \propto (F_0 - F(t))$ pushes the sample against the tip. When $F(t) > F_0$, the sample is retracted. Only at $F(t) \simeq F_0$, $U_z = 0$ and the feedback loop reaches its “equilibrium”. Besides, the sample can be moved back and forth, row by row, choosing the suitable potential functions $U_x(t)$ and $U_y(t)$. In this way the tip is scanned over the sample surface. At every instant $t$, when the tip apex is at the coordinates $(x, y)$, the $z$ position is adjusted so that the deflection equals the setpoint $F_0$. The result of this automatic procedure is that the trajectory of the Z
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Figure 3.3: Principle of operation of an atomic force microscope (simplified diagram). The cantilevered tip, together with the deflection sensor, are a transducer of the forces acting between the sample and the tip. If the sample XY position is scanned while keeping the force constant, a topographic map of the sample surface can be obtained (see text for details).

The above description corresponds to one of the simplest operation modes of the AFM, the contact or “repulsive mode”, at constant force. Other modes and imaging conditions exist, and other forces (not related to mechanical contact) can also be measured, like electric or magnetic. In particular, the intermittent-contact or “tapping” mode [102] is widespread and can be used in a great variety of samples: To operate the AFM in tapping mode, the cantilevered tip is forced to oscillate at \( \sim 100 \) KHz with an amplitude of several nm. On approaching the tip to the sample, the tip hits the surface and the proximity to the sample can be measured through a reduction in the...
oscillating amplitude. As in the contact mode, the tip senses the repulsion of the sample but only during a short period of time in every cycle. In this case, surface topographies are obtained by setting a fixed oscillating amplitude during the XY scan, with the additional advantage that adhesion and friction forces can be minimized.

Note that the resolution of a topographic AFM image is only limited by the sharpness of the tip and the electric or mechanic noise. Moreover, there are no constraints on the medium in which the tip (and sample) are immersed, and AFM imaging can be performed in air and, more interestingly, in solution. In particular, the AFM tip can be “introduced” in an electrochemical cell (where the sample is the WE) and electrochemical processes can be monitored in-situ and in real time with nanometer resolution (electrochemical AFM, EC-AFM).

In the following chapters, AFM images were acquired ex-situ in an Extended Multimode Nanoscope III [103] operating in tapping mode. The cantilevered tips were NCH Pointprobes, manufactured in monocrystalline Si by Nanosensors [104]. The experimental procedure for AFM imaging in solution under potentiostatic control will be detailed in appendix A, together with a preliminary study of Si etching in NaOH solution.

### 3.1.3 Other techniques

The relatively short dynamic range of AFMs make them unsuitable for general inspection of samples, say up to the mm range. For that purpose, electron microscopies were also employed (scanning and transmission electron microscopy, SEM and TEM respectively). They have the additional advantage of a qualitative chemical analysis (electron dispersive X-ray spectroscopy, EDX). SEM and TEM allowed to study the uniformity of metal deposits on the sample surface in the range 10 nm – 10 mm, as well as to elaborate chemical maps with a resolution around 1 μm. Sample cross-sections can also be imaged by SEM and TEM (using different preparation techniques), with atomic resolution in the case of TEM. Cross sections for SEM were simply cleaved with a diamond tip, and placed perpendicular on the sample holder with Ag epoxy. Cross section preparation for TEM is a much more complex process that may introduce artifacts. Two different techniques were employed for comparison: In the standard procedure, the samples were cut and stacked in a “sandwich”, that was subsequently thinned in a series of steps. Both sides of the sandwich were mirror-polished and then a concave polishing was applied to one of the sides. The sample was finished by ion-milling with an Ar gun under liquid N₂ cooling, to avoid diffusion or crystallization of the deposits due to heating. A cleavage procedure for the
TEM cross-sections was also used [105], because it does not require the ion milling step: $Si(100)$ samples were polished until they are some tens of $\mu m$ thin, and then cleaved in $\sim 1$ $mm^2$ chips with a fine diamond tip. Due to the preferential cleavage in (110) planes, a few of the resulting pieces have atomically-sharp corner edges running in the [110] direction, such that near the edge, the sample is thin enough to be imaged by TEM. Inspection of the chips under the optical microscope allows to make a preliminary selection of the specimens, which are then mounted in special sample holders and finally examined in the TEM.

The SEMs employed in the experiments were a Leica Stereoscan S-360, a Hitachi 2300 and a Cambridge S-120 equipped with a Link AN-10000 EDX. The acceleration potentials ranged between 2 and 20 $KV$. TEM images were obtained in a Philips CM-30 ($300$ $KV$), having a Link LZ-5 EDX.

X-ray photoelectron spectroscopy (XPS) provided a quantitative chemical analysis of the samples. XPS depth profiles were obtained by successive measurement and sputtering cycles with an $Ar$ ion gun. The equipment employed was a Perkin Elmer PHI 5500, and the acquired spectra were processed with the Multipak 5.0A software. Samples to be analyzed by XPS were withdrawn from the solution, rinsed, blown dry with pure $Ar$ and immediately introduced in the ultra-high vacuum chamber to minimize the contamination from the environment.

### 3.2 Sample preparation

When working with silicon and fluoride solutions, often a few minor experimental details turn out to be essential to achieve reproducible and reliable results. Although they are seldom described in the literature, some of them will be given in this section as a set of practical tips.

#### 3.2.1 Silicon surfaces

Monocrystalline $Si$ is usually available in the form of polished wafers that can be cut or cleaved into chips of the required size. The $Si$ substrates employed in this study were (100)–oriented and occasionally (111), both $n$–type ($P$ doped, $1$ $\Omega cm$ resistivity, $N_D \approx 5 \cdot 10^{15}$ $cm^{-3}$) and $p$–type ($B$ doped, $1$ $\Omega cm$ resistivity, $N_A \approx 10^{16}$ $cm^{-3}$), manufactured by Siltronix [106]. They had one polished side, which was exposed to the solution through the sample holder of figure 3.2 (area $0.3$ $cm^2$). At the doping densities given above, the Fermi energy is located at about $\mu_C \approx 0.25$ $eV$ below the CB in $n$–$Si$, and at $\mu_V \approx 0.2$ $eV$ above the VB in $p$–$Si$ [28]. In this kind of
studies, semiconductor samples of relatively low conductivity are employed to have a relatively thick SCR that prevents carrier tunneling through the energy barrier (Zener breakdown, see section 1.2.3). Si having a resistivity 1 – 10 Ωcm develops a SCR of about 1 μm and usually works well. Good ohmic contacts (i.e. about a few Ω and independent of potential) can be realized on the sample rear side by metal evaporation in vacuum after oxide stripping in HF. Prior to metal deposition, the semiconductor surface must be highly doped (n⁺ for n – Si, p⁺ for p – Si) so that the junction has an ohmic behavior. In particular, AuSb evaporation can be employed for n – Si (Sb acts as an electron donor in Si) and AuAl for p – Si (Al acts as an acceptor), followed by a 600°C anneal [107]. Another recipe is doping n – Si with liquid POCl₃ followed by Al evaporation (in this case P acts as a donor), and direct evaporation of Al on p – Si. The anneal is 1 h at 450°C for both Si types [108]. If evaporation equipment is not available, nearly the same results can be obtained using an easier method: The back of the Si chip is painted with an InGa alloy at the eutectic point and then contacted to a metallic plate. The InGa alloy is obtained with a mixture of Ga 80%, In 20% in weight, heated up to 160°C and slowly cooled. It remains liquid at room temperature. The ohmic quality of the contacts can be improved, especially on p-type samples, by generating defects on the sample surface to be contacted (e.g. by scratching with a diamond tip).

Of course, all measurements should be performed in darkness unless the effects of light can be accounted for. Visible illumination (as the produced by a regular bulb) has a frequency spectrum centered at around 2 eV and is far enough to photogenerate electron-hole pairs in Si (E₂ = 1.1 eV). Halogen lamps are often preferred due to its higher power output. The halogen lamp employed in the experiments under illumination was a FiberLite, yielding a light flux of 4 · 10¹¹ photons/cm²s.

### 3.2.2 Cleaning and deposition solutions

As will be shown in the following chapters, metal (and organic) contamination is critical when studying Si in fluoride media. High purity reagents and clean labware and environment are therefore essential, as well as deaeration of the solutions with Ar or N₂ in order to remove the dissolved O₂ (if both Ar and N₂ are available, Ar is preferable when working with open beakers, because it is heavier than air and it remains at the solution surface, thus providing a longer-lasting deaeration). A standard cleaning process widely used in the Si microelectronics industry is the RCA etch [67, 109, 110]. It comprises two
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steps for the removal of organic and inorganic contaminants, respectively:

\[ NH_4OH : H_2O_2 : H_2O \ (1 : 1 : 5), \ 75^\circ C, \ 15 \text{ min} \]  \hspace{1cm} (3.1)

\[ HCl : H_2O_2 : H_2O \ (1 : 1 : 6), \ 80^\circ C, \ 15 \text{ min} \]  \hspace{1cm} (3.2)

This procedure leaves a clean, oxidized surface (oxide thickness about 1 nm), similarly to the sulfuric peroxide mixture (SPM or “Piranha”, \( H_2SO_4 : H_2O_2, \ 4 : 1 \) at 90°C). Another possibility to remove organic contaminants is the sequential cleaning in hot trichloroethylene, acetone and ethanol [4] followed by water rinse and immersion in boiling chromic mixture (\( H_2SO_4 : H_2CrO_4, \ 1 : 1 \)), or a commercial labware washing product [111].

The cleaning procedures employed in this work varied depending on the experiments: In the electrochemical measurements of chapters 4-6, samples were degreased with methanol and introduced in the sample holder of figure 3.2 after making the electric contact with \( InGa \). Further processes were carried out using the holder and taking advantage of the electrochemical setup (e.g. to electrochemically polish the sample, see below). In the experiments of chapter 7, the degreased samples were simply immersed in the solutions of interest without an electric contact, and only the illumination and solution stirring were qualitatively controlled. In the in-situ AFM experiments, a longer cleaning procedure and careful electrochemical control were required (see appendix A).

In all cases, the sample holder and labware were cleaned either in the Piranha solution (glass, Teflon, \( Pt \) electrodes), chromic mixture (glass) or in Labwash [111] (glass, plastic) followed by a thorough rinse in triply-distilled MilliQ water (18 M\( \Omega \)cm resistivity) [112]. Since fluoride solutions etch all kinds of glass (silicates), plastic labware must be employed in the experiments. Teflon PTFE [101] is often used, although a more common and cheaper polymer, high-density polyethylene (HDPE) provides a similar resistance in most of the applications at ambient temperature. As was explained earlier, reference and \( pH \) electrodes are usually made of glass and must also be protected. The \( pH \) of fluoride solutions can also be measured using a paper indicator (Acilit, Merck [113] has a resolution of \( \sim 0.5 \) \( pH \) decades), or a Teflon \( pH \) electrode [97].

The as-purchased \( Si \) wafers are often contaminated with hydrogen in the region near the surface [114], which results in poor reproducibility and distortion of the electric measurements, such as the SCR capacitance (see 4.3.2 and reference [115]). As an example, the MS plots of untreated \( n- \) and \( p - Si \) are shown in figure 3.4ab. Chemical polishing [116] or electropolishing [61, 115] can be employed to remove the contaminated \( Si \) layer with the tools available in a standard electrochemical laboratory, and require no
Figure 3.4: Mott-Schottky plots of Si electrodes immersed in a 5M aqueous fluoride solution (pH1), prior to the electropolishing process (a: p – Si, b: n – Si) and afterwards (c and d respectively). The non-linear behavior in plots ab is due to Si subsurface contamination [115] (see text for details).

extra equipment. The corresponding MS plots after removal of a few μm of material can be seen in figure 3.4cd. A series of thermal oxidation in a furnace and oxide stripping steps can also be used to solve this problem, and have the additional advantage of smoothing the Si surface, especially interesting in surface preparation for in-situ microscopy. During the experiments of chapters 4-6, Si chips were systematically electropolished as a part of the sample pretreatment, in order to have a well-defined departure surface. EP was carried out in a 1 M fluoride solution at pH4.5 during 15 min, being the EP potentials +4.0 V/SCE for p – Si, and +3 V/SCE and the suitable illumination for n – Si. The EP current was ~1 mA/cm². Note that the power of the lamp limits the maximum fluoride concentration (and EP current) in n – Si, but for convenience the same EP solution was used with both electrode types. After EP, the remaining oxide was dissolved in HF 40% (Suprapur, Merck [113]) during a few seconds, until the surface showed an hydrophobic behavior (H−terminated).

As was explained in chapter 2, Si is slowly attacked in fluoride solutions even at the OCP. For this reason, when Si oxidation and its consequences (e.g. increase in surface roughness and hydrogen incorporation [115]) are to be prevented during an experiment, the electrode can be kept “safe” at poten-
tials slightly negative of OCP. At a HER current beyond some 100 $\mu A/cm^2$ in $n-Si$, the electrochemical dissolution reaction is stopped in $n-Si$ and minimized in $p-Si$ [5]. When metallic ions are present in the solution, the safe potential range may become narrower or even not exist at all.

Deposition solutions were prepared from reagent-grade chemicals (Merck [113]) and MilliQ water [112]. Metal salts were supplied by Merck and Johnson-Matthey [117] and were added in the fluoride solution after adjusting the $pH$ to the desired value. Alkaline fluoride solutions were prepared from concentrated 40% $NH_4F$, and acid solutions from 40% $HF$, the $pH$ being adjusted with either $NH_4OH$ or $H_2SO_4$. Metal concentrations were in the range 10 $\mu M$ – 10 $mM$ and will be specified in every case.

3.2.3 Other techniques

Some metal films were deposited on silicon using vacuum evaporation techniques, in order to compare them with the electrochemically grown layers. The equipment employed was an Edwards Auto 306 evaporator (having a filament or crucible made of tungsten), a JEOL JFC-1100 ion sputter and a homemade electron beam evaporator (Departament de Física Aplicada, UB).
Chapter 4

Electrochemical Study of Platinum Deposition

In this chapter, the deposition of platinum on silicon from fluoride solutions is studied under controlled conditions: The experiments are carried out in an electrochemical cell under potentiostatic control, and only the mirror-polished “active” side of silicon is exposed to the solution. The aim is to sketch an energy diagram as complete as possible for the interface between silicon and an aqueous fluoride solution containing Pt(II) ions. In the first section (4.1) a preliminary mechanism is presented, based on the mixed potential between a cathodic reaction leading to metal deposition and the anodic dissolution of the silicon substrate. This mechanism is subsequently refined by studying in more detail the cathodic and anodic “half-cell” reactions (4.2 and 4.3 respectively).

4.1 Deposition mechanism: general aspects

4.1.1 Experimental results

The silicon substrates employed in this study were (100)—oriented and occasionally (111), both n— and p—type. They had one polished side, which was exposed to the solution through the cell of figure 3.2 (area 0.3 cm²). All electrochemical experiments were carried out in darkness in the “three-electrode configuration” using either the manual or the computer-interfaced potentiostats described in chapter 3. Capacitance measurements were performed with a measurement signal of 10 mV at 25 KHz.

Prior to all experiments, Si samples were electropolished in order to have a well-defined departure surface [115]. The remaining oxide was dissolved in
HF 40% for a few seconds, until the surface showed an hydrophobic behavior (H—terminated). The fluoride concentration in the deposition solutions was 2 M (HF 40% was diluted 1:10 in MilliQ water), corresponding to pH2. In certain cases, solutions 0.6 M NH₄F at pH4.5 were also used. Pt(II) was added as K₂PtCl₄ salt (Johnson-Matthey) in the acid solution, to yield concentrations in the range 30 μM – 2.5 mM.

After a few minutes of exposure to the fluoride solution containing Pt(II) ions, some metallic nuclei are deposited on the Si surface. They produce a “haze” that is visible to the naked eye. A SEM picture is shown in figure 4.1. EDX measurements confirmed that the bright nuclei are composed of Pt. In the non-deposited regions, some etch pits and a general increase in substrate roughness is found in relation to the original Si surface. This is best appreciated using AFM (see figure 4.2). Both n— and p—Si samples exhibit the same general behavior, with differences mainly concerning the distribution of nuclei and etch pits over the surface (this and other morphological aspects will be discussed in chapter 7).

The rest potential (OCP) of n— and p—type samples in HF 1:10 (pH2, no Pt(II) added) was found at \( V'_{OCP} \approx V''_{OCP} \approx -0.4 \text{ V/SCE} \). The FB potentials were obtained from the corresponding Mott-Schottky plots: In
the “blank” fluoride solution, $U_{fb}^n = -0.5 \text{ V/SCE}$, $U_{fb}^p = +0.4 \text{ V/SCE}$. The FB values are not greatly affected by the presence of Pt(II) ions in the solution within the first minutes. However, the OCP of the electrodes immediately shifts towards positive potentials. As representative values, $U_{ocp}^n = -0.1 \text{ V/SCE}$, $U_{ocp}^p = 0.0 \text{ V/SCE}$.

The equilibrium potential of the $\text{PtCl}_4^{2-}/\text{Pt}$ system can be obtained from the standard reduction potential $U_{\text{PtCl}_4^{2-}/\text{Pt}}^o = +0.5\text{ V/SCE}$ and expression 1.78:

$$U = +0.5 \text{ V/SCE} + \frac{0.059}{2} \text{ V} \cdot \log[\text{PtCl}_4^{2-}]$$

being $[\text{PtCl}_4^{2-}]$ the concentration of Pt(II) ions added to the fluoride solution. For solutions $30 \mu\text{M} - 2.5 \text{ mM } \text{PtCl}_4^{2-}$, the equilibrium potential given by equation 4.1 ranges between $+0.37$ and $+0.42 \text{ V/SCE}$. An experimental verification was obtained from the OCP of a Pt wire immersed in the solution, $U_{Pt} \simeq +0.3 \text{ V/SCE}$.

The system was further characterized by measuring the $j - U$ curves in the dark. They are shown in figures 4.3 ($p$-type) and 4.4 ($n$-type), where dashed plots (A) correspond to the aqueous fluoride solution and plots B and C were recorded after addition of the metal. An increase in the reverse current in both $n-$ (anodic) and $p-$Si (cathodic) occurs in the presence of $\text{PtCl}_4^{2-}$ ions, and this current is proportional to the $\text{Pt(II)}$ concentration in
solution. Using a Pt wire as the working electrode, the \(j - U\) curve displays a cathodic plateau at a current value close to that found in \(p - Si\) at the same \(PtCl_2^-\) concentration (figure 4.3D).

The measured current plateaux in \(Si\) are plotted in figure 4.5 as a function of the \(Pt(II)\) concentration, and yield slopes in the \(log - log\) scale of 1.0 for \(p - Si\) and 0.4 for \(n - Si\). The dependence of the reverse current on the \(Pt(II)\) concentration suggests a limitation by the mass transport conditions in solution (diffusion). This effect was verified by recording the \(j - U\) curves while the \(Pt(II)\) solution was stirred: the faster the stirring, the larger the reverse currents. Playing with solution stirring at constant \(Pt(II)\) concentration is very convenient because it does not require to change the solution. However, it may affect reproducibility (e.g. when changing the \(Si\) sample) unless the relative positions of the sample and the magnetic stirrer are very well fixed inside the cell. Rotation of the sample instead of the solution is preferable (diffusion can then be controlled and quantified using the rotation speed in \(rpm\)), but the design of the sealed sample holder of figure 3.2 did not allow such experimental setup.

4.1.2 Discussion

The ensemble of these results allow to sketch the major features of the deposition of platinum on silicon from fluoride solutions. The images of figures 4.1 and 4.2 already suggest that two simultaneous processes are occurring at the \(Si\) surface: The reduction of \(Pt(II)\) ions in solution (producing the deposition of metallic \(Pt\)) and the oxidation of the \(Si\) substrate (leading to dissolution in fluoride media). The electrons released in the anodic reaction can in principle be transferred through the semiconductor substrate to the sites where the cathodic reaction occurs. This is sketched in figure 4.6.

The energy of the electrons involved in such transfer can be seen in the electron energy diagram of the interface (figure 4.7), where dashed lines indicate the situation in the blank fluoride solution and the solid lines correspond to the \(Pt(II)\)–containing solution. The diagram was built from the following data: In \(n - Si\), the CB edge is located at an energy \(\mu_C \simeq 0.25 \text{ eV}\) higher than \(-eU_{FB}^n\), and in \(p - Si\) the VB edge is \(\mu_V \simeq 0.20 \text{ eV}\) below \(-eU_{FB}^p\). The band bending is given by

\[-e\Delta\phi_{sc}^n = -e(U_{OCP}^{n,p} - U_{FB}^n)\]  

(4.2)

and yields \(\Delta\phi_{sc}^n = +0.1 \text{ V}\), \(\Delta\phi_{sc}^p = -0.8 \text{ V}\) in the fluoride solution; \(\Delta\phi_{sc}^n = +0.4 \text{ V}\), \(\Delta\phi_{sc}^p = -0.4 \text{ V}\) after addition of \(PtCl_2^-\) (\(\Delta\phi_{sc}^{n,p} > 0\) corresponds to upward band bending). In the electrolyte, the redox level of the system
Figure 4.3: Dark current-potential curves of a $p-$ Si electrode (ABC) and a Pt electrode (D) immersed in a 2M fluoride solution. Curve A corresponds to the blank solution (no metal added), curve B to 300 μM PtCl$_4^{2-}$ and curves C and D to 2.5 mM PtCl$_4^{2-}$.

Figure 4.4: Dark current-potential curves of a $n-$ Si electrode immersed in a 2M fluoride solution (A), and after addition of 300 μM PtCl$_4^{2-}$ (B) and 2.5 mM PtCl$_4^{2-}$ (C).
Figure 4.5: Hole injection currents at different PtCl$_2^-$ concentrations in the common electrolyte (2M fluoride). The current values are obtained from the cathodic and anodic plateaux of figures 4.3 ($p$ – Si) and 4.4 ($n$ – Si) respectively.

Figure 4.6: Simultaneous electrochemical processes on a Si electrode exposed to a fluoride solution containing Pt(II) ions: Surface Si atoms are oxidized and supply the electrons for the metal deposition reaction.
4.1. DEPOSITION MECHANISM: GENERAL ASPECTS

Figure 4.7: Experimental electron energy diagram of the interface between Si and a fluoride blank solution at pH2 (dashed lines), and in the presence of 1 mM Pt$^{2+}$/Pt (solid lines).

$PtCl_4^{2-}$/Pt is $-eU_{PtCl_4^{2-}/Pt}$, with $U_{PtCl_4^{2-}/Pt} = +0.3$ V/SCE. The system $H^+/H_2$ is located at $-eU_{H^+/H_2}$ with $U_{H^+/H_2} = -0.3$ V/SCE. Note that the band edge energies obtained in $n$- and $p$-Si differ by $\sim 200$ mV. As was discussed in 2.1.2, this systematic discrepancy remains unexplained.

As can be seen, in the absence of metal ions $U_{n,p}^{m,p}$ lie close to $U_{H^+/H_2}$ and thus the Si electrodes in aqueous fluoride solution appear to be in thermodynamic equilibrium with the $H^+/H_2$ system. This corresponds to strong depletion in $p$-Si in agreement with the explanations of chapter 2, but the $n$-Si electrode is found at slight depletion instead of the expected FB or accumulation. This may be due to an error in the determination of the FB potential (values of $U_{FB}^n$ in the literature [4] are $\sim 100$ mV more positive), but it can also be indicative of a contamination problem: As in the deposition solutions, trace amounts of $Pt(II)$ in the fluoride solution would result in a shift of the OCP towards positive values.

After addition of $PtCl_4^{2-}$ to the fluoride solution, the Fermi energy of the Si electrode $E_{F}^{n,p} = -eU_{OCP}^{m,p}$ should in principle equalize to $-eU_{PtCl_4^{2-}/Pt}$ to achieve thermodynamic equilibrium. That is, change 0.7 V towards positive potentials, from $-0.4$ V/SCE to $+0.3$ V/SCE. However, the OCP only shifts about $0.3 - 0.4$ V, instead of the expected $+0.7$ V. In order to understand
the nature of the equilibrium in this case, the situation in the absence of Pt(II) ions must be first analyzed in detail.

The steady-state of Si electrodes in the fluoride solution at the OCP, was described in chapter 2 as a dynamic equilibrium between two reactions, one anodic (Si oxidation and dissolution) that is balanced with another cathodic (H\(^+\) reduction and \(H_2\) evolution). Indeed, the covalent nature of Si makes it unstable in aqueous solutions, where a native oxide layer is readily formed that prevents further oxidation. In the presence of hydrofluoric acid, this oxide is dissolved and the oxidation reaction continues, giving rise to an anodic current. If no potential is applied (OCP) the net current through the interface must be zero, and therefore the anodic current must be balanced with a cathodic one. The cathodic reaction can be the reduction of protons or water molecules (hydrogen evolution reaction, HER) if no other electron-accepting species are available in the solution. The two balanced reactions, Si dissolution and the HER, are called respectively the anodic and cathodic “half-cell” reactions. The OCP of the Si electrodes in fluoride media is thus given by the mixed potential between the two reactions: \(U_{OCP}\) in every case is the potential at which the anodic and cathodic reactions occur at the same rate. This is achieved at \(U_{OCP}^{n,p} \approx U_{H^+/H_2}\) (figure 4.7, dotted lines).

Now if the anodic process is favored under certain conditions, the electrode potential (and thus the band bending) will adjust itself so that a cathodic current is produced: The OCP then shifts towards negative potentials (electron accumulation in \(n-Si\), stronger hole depletion in \(p-Si\)). In a similar way, if the cathodic process is favored by some reason, the electrode potential shifts towards positive values in order to deplete electrons and accumulate holes at the surface, thus enhancing the anodic reaction.

Metal ions burst into this scenario by adding metal deposition as an alternative cathodic process: They can reduce to the metallic form on the surface by gaining electrons from the Si electrode. The case of the \(PtCl_4^{2-}/Pt\) system is particularly dramatic because its energy levels lie close to the Si VB, and therefore they interact mostly with VB (bonding) electrons: Unlike free electrons in the CB (whose availability at the surface depends on the semiconductor doping type and band bending), bonding electrons are always present at the interface with the electrolyte. Hence they are always ready to be transferred to the solution (to the \(PtCl_4^{2-}/Pt\) system in this case). Actually such process is described in terms of charge carriers as the injection of a hole (a mobile electron vacant) into the semiconductor VB. Of course both the transfer of an electron (negative charge) from the semiconductor to the solution, and the injection of a hole (positive charge) from the redox system into the semiconductor correspond to a negative current (cathodic process).
4.1. DEPOSITION MECHANISM: GENERAL ASPECTS

It is therefore to be expected that the presence of $Pt(II)$ ions in the solution sets a hole injection current into the $Si$ regardless of its band bending (i.e. independent of the electrode potential). Indeed, the experimental $j – U$ curves of $p – Si$ in $Pt(II)$ solutions (figure 4.3) are well reproduced by adding a constant (potential-independent) cathodic current $j_{inj}$ to the blank $j – U$ curve (figure 4.3A) [118]. In other words, the blank curve “shifts” downward an amount $j_{inj}$ given by the concentration of $PtCl_{4}^{2-}$ and by solution stirring. The $j – U$ curve in the presence of $Pt(II)$ can be further interpreted taking into account the band bending in the $p – Si$ at every potential value, and the fact that holes are majority carriers: At very negative potentials, the bands are strongly bent downwards and all of the injected holes are collected in the semiconductor bulk, giving rise to a negative current. At very positive potentials, the upwards band bending in $p – Si$ results in the accumulation of holes (either injected from the solution or present in the semiconductor bulk) at the electrode surface. Under these conditions, the $Si$ surface atoms can be oxidized by capturing a hole (i.e. by permanently losing a bonding electron), which is a process associated with a positive current. At the OCP, the band bending is such that holes can flow from the semiconductor bulk towards the surface, giving rise to an oxidation current exactly equal to the $Pt$ deposition (hole injection) current. Thus the “corrosion current” as defined in 1.3.3 is:

$$j_{corr} = -j_{inj}$$

(4.3)

and therefore, the higher the $Pt$ deposition rate, the higher the simultaneous oxidation rate of $Si$. Note that the electrons depicted in figure 4.6 belong to the VB and thus the charge exchange process would be best described by holes following the opposite trajectory.

The effect of a hole injection current in the $j – U$ curve of $n – Si$ is somewhat more complex, due to the “current doubling” and recombination phenomena that are not evidenced in $p – Si$. In particular, at very positive potentials electrons are depleted from the surface and cannot recombine with the injected holes, which are accumulated at the interface with the solution. Under these circumstances, $Si$ can be oxidized. As was discussed in 2.2.2, at low hole concentrations (PS regime) every injected hole oxidizes one $Si$ atom to $Si(II)$ following reaction 2.6:

$$h^{+} + Si \rightarrow Si(II) + e_{CB}^{-}$$

(4.4)

The electron produced in this process is injected into the VB and thus it can be collected in the $n – Si$ bulk under upwards band bending (positive potentials). It is measured as a net positive current. Note, however, that this current gives a rather indirect measurement of the hole injection rate $j_{inj}$. At
negative potentials, electrons are accumulated at the surface and recombine with the injected holes before they can result in Si oxidation. This gives rise to a cathodic current plateau that allows a more direct measurement of \( j_{\text{inj}} \). At more negative potentials, electrons are accumulated in larger amounts and the HER wave shows up. In some cases, though, and specially at low \( pH \), the HER current masks the plateau and it hardly appears as an elbow in the cathodic branch of the \( j - U \) curve. These aspects will be discussed in detail in chapter 6.

It is worth mentioning that in \( p - Si \) the electrons injected into the CB as a result of the oxidation reaction do not show up as such, but as a current of holes flowing towards the interface that recombine with the injected electrons. Thus during the anodic dissolution of \( p - Si \) at moderate potentials (PS regime) only half of the holes accumulated at the surface are actually involved in the oxidation reaction (the other half is recombined with the electrons produced in the reaction).

In the conditions used in the experiments, the injection current \( j_{\text{inj}} \) depends on \([\text{PtCl}_4^{2-}]\) and solution stirring, i.e. it is controlled by the rate at which \( \text{PtCl}_4^{2-} \) ions arrive at the electrode surface. Pt reduction is thus not limited by the rate of charge exchange with the semiconductor (kinetically limited), but by the supply of \( \text{Pt}(II) \) species to the interface (diffusion-limited). The comparison with the current plateau found in a Pt electrode (figure 4.3D) further confirms this point, in agreement with other studies [76]. Given the limitations imposed by the experimental setup (solution stirring against electrode rotation), the only reasonable comparison between \( n- \) and \( p- \) type samples can be made by varying the metal concentration in the non-stirred solution. The data shown in figure 4.5 (\( j_{\text{inj}} \) was measured from the reverse (saturation) current in both \( p- \) and \( n - Si \) can be fitted by the general expression

\[
j_{\text{inj}} = k \cdot [\text{PtCl}_4^{2-}]^\alpha
\]

Thus in the \( \log - \log \) scale:

\[
\log j_{\text{inj}} = \log k + \alpha \cdot \log[\text{PtCl}_4^{2-}] \quad (4.5)
\]

where \( \alpha \) is the order of the reaction. In \( p - Si \), \( \alpha = 1 \) together with the fact that \( j_{\text{inj}} \) depends on the agitation, demonstrate again that Pt deposition is diffusion-limited. The constant \( k \) can be determined from the intercept at \([\text{PtCl}_4^{2-}] = 1 \) M but it was not considered because in this case \( k \) carries mixed information of both the kinetic rate and the diffusion coefficient (they cannot be decoupled due to the lack of well-defined diffusion conditions under solution stirring). In \( n - Si \), \( \alpha < 1 \) indicates the existence of a different rate-determining process: As was discussed above, the reverse current that is
4.2 CATHODIC HALF-CELL REACTION

measured in $n-Si$ should be equal to $j_{inj}$, but is strictly due to the “current doubling” phenomenon. Most likely, the measurement of $j_{inj}$ in this case is limited not by the injection of holes into the VB from the Pt ions, but by the injection of electrons into the CB during the subsequent $Si$ oxidation reaction.

In summary, it has been shown that when a $Si$ electrode is exposed to a fluoride solution containing $PtCl_4^{2-}$ ions, two reactions proceed simultaneously on the electrode surface at the OCP: First, $Pt(II)$ ions reduce to metallic Pt by injecting holes into the $Si$ VB (cathodic half-cell reaction). And second, the capture of the injected holes at the electrode surface results in $Si$ oxidation and dissolution in the presence of fluoride species (anodic half-cell reaction). The overall process is limited by diffusion of $PtCl_4^{2-}$ ions to the $Si$ surface. As free charge carriers, the injected holes have a certain mobility in the semiconductor, so in general the cathodic and anodic reactions occur at different regions of the surface (called anodic and cathodic sites). Although the energy diagrams discussed so far help to illustrate the overall process, they must be refined to account for the heterogeneity of the surface: Growing metal nuclei are present at the cathodic sites, and a dissolution reaction is under course at the bare silicon regions (anodic sites). They are treated separately in the two next sections.

4.2 Cathodic half-cell reaction

The energy diagrams shown in figure 4.7 demonstrate that the bonding electrons of the silicon surface atoms can always be transferred to the $Pt(II)$ ions in the electrolyte. Such transfer results in the deposition of Pt atoms on the cathodic sites of the surface, producing nanometer-sized metallic contacts to the semiconductor. The situation at the steady-state regime in the cathodic sites is the growth of Pt nuclei by metal-on-metal deposition, with the electrons being transferred through the $Pt|Si$ interface. The equilibrium at these sites is therefore established all throughout the semiconductor | metal | electrolyte interface, and must be treated in detail.

The energy diagram at such a “double” interface can be studied in the electrochemical cell using a $Si$ sample fully covered by Pt, so that the $Pt(II)$ electrolyte does not contact the $Si$ surface. The Pt film would then be simultaneously in equilibrium with the $Si$ and the electrolyte. This limit case was briefly discussed in 1.3.2.2 and is known as “Schottky electrode”.

The equilibrium between the Pt film and the electrolyte implies that their Fermi energies are equal:

$$E_{F,Pt} = -eU_{Pt} = -eU_{PtCl_4^{2-}/Pt} = E_{F,redox} \quad (4.7)$$
i.e. the potential of the metal layer must be \( U_{Pt} = U_{Pt\text{C}^{2-}/Pt} \).

Regarding the \( Pt|Si \) interface alone, it is a Schottky diode whose energy barrier can in principle be obtained from the electronic affinity of the semiconductor \( E_{A, Si} \) and the metal work function \( \Phi_{Pt} \). However, in the case of a covalent semiconductor like \( Si \) in contact with a metal, the interface state density is so large that the semiconductor Fermi energy is pinned at the energy of the interface states. This sets an energy barrier of the diode that is not related directly to \( E_A, \Phi_n \) and is usually obtained experimentally. The barrier for the \( Pt|Si \) junction (as “seen” from the metal) is \( E_{B,n} = 0.75 \text{ eV} \) for \( n - Si \) and \( E_{B,p} = E_g - E_{B,n} = 0.35 \text{ eV} \) for \( p - Si \) [119].

When the Schottky electrode is immersed into the solution, the Fermi energies are equalized throughout the semiconductor | metal | electrolyte junction. Under these conditions, if the \( Pt|Si \) barrier height is fixed, then the energy of the semiconductor band edges is in principle determined. This is shown in figure 4.8 for a \( n - Si \) electrode with a \( Pt \) overlayer: As can be seen, the FB potential of this Schottky electrode must be expected near \(-0.2 \text{ V/SCE} \). However, the practical realization of the \( Pt|Si \) Schottky electrode encountered several experimental difficulties: In order to obtain a \( Si \) surface covered with a uniform \( Pt \) layer, evaporation techniques in vacuum were attempted in a first stage. \( Pt \) could not be deposited using common tungsten filament or crucible evaporators, because they blow at relatively low temperatures (before a liquid \( Pt \) drop can be formed and the evaporation rate stabilized). Electron-beam evaporators or sputtering systems having a \( Pt \) disk target are therefore necessary, but the layers prepared using either of these techniques on \( HF \)-etched \( Si \) samples were poorly adherent and easily detached on rinsing with water.

As an alternative, electrochemical deposition was attempted using several approaches. It was soon clear that the experimental verification would not be possible in the presence of fluoride in the solution, because even the more continuous and adherent (electrochemically deposited) \( Pt \) films yielded values of \( U_{FB} \) corresponding to a clean \( Si \) surface. These \( Pt \) layers are still too porous to prevent the direct contact between the fluoride solution and the \( Si \) substrate in certain regions. It was thus interpreted that in fluoride solutions the anodic regions (bare \( Si \)) prevail in the energy distribution at the surface of the electrode, and further efforts were focused in fluorine-free solutions. In these conditions, a thin insulating oxide layer is most probably present at the bare \( Si \) areas, which allows the electrode to behave as if it was fully covered with \( Pt \) (only the \( Pt \) nuclei establish an electric contact with the solution). Measurements of \( U_{OCP} \) and \( U_{FB} \) of the Schottky electrodes were carried out in \( H_2SO_4 \) solutions (without \( HF \)).
4.2. CATHODIC HALF-CELL REACTION

The best results were obtained with Pt layers electrochemically deposited from 0.1 M H$_2$SO$_4$, 1 mM PtCl$_6^{2-}$ solutions. The deposition conditions ranged from −1.5 to −2.0 V/SCE (j ~ −10 mA/cm$^2$) for t ~ 10 min, and although the as-produced Pt films can be torn off with regular sticky tape (Scotch), the measurement of $U_{FB}$ and $U_{OCP}$ in the deposition solution confirms the calculated values within an error of 100 mV. As is shown in figure 4.9, prior to Pt deposition $U_{FB} = −0.5$ V/SCE and $U_{OCP} = −0.1$ V/SCE (band bending $\Delta \phi_{sc} = +0.4$V). After Pt deposition, $U_{FB} = −0.1$ V/SCE and $U_{OCP} = +0.4$ V/SCE ($\Delta \phi_{sc} = +0.5$ V, which gives the expected barrier height $\epsilon \Delta \phi_{sc} + \mu_C = 0.75$ eV). The OCP ($U_{OCP}^f$) of this Schottky electrode (and thus the potential of the Pt overlayer) is very close to the OCP of a Pt wire immersed in the same solution ($U_{Pt} = +0.3$ V/SCE), in agreement with the diagram of figure 4.8. The experimental band diagrams have also been sketched in figure 4.9.

These measurements on the Schottky electrodes will provide an estimate of the Si bandages at the Pt nuclei during the deposition of the metal from fluoride solutions (heterogeneous surface). The values $-\frac{E_{F,S}}{e} = −0.35$ V/SCE, $-\frac{E_{F,Pt}}{e} = +0.75$ V/SCE (figure 4.9) will be employed to calculate the band bending at the cathodic sites, using the Fermi energy of the
Figure 4.9: Mott-Schottky plots of bare Si (○) and a Pt | n–Si pseudo-Schottky electrode (●) in a Pt(II) solution. The positive shift provides an experimental verification of the prediction of figure 4.8.

electrode in every case \(E_F = -\epsilon U_{OCP}\). It is interesting to note that in the cathodic areas the energy barrier for holes is 0.35 eV, i.e. an almost ohmic barrier: Pt(II) ions can thus reduce to metallic Pt by injecting holes through the Pt|Si interface, as is shown in figure 4.10.

The Pt|Si contacts were further characterized by recording their \(j - U\) response out of the solution ("dry" Schottky characteristic). The measurements could not be carried out on Pt–evaporated samples neither on Pt–deposited from \(H_2SO_4\) due to the poor adherence of the metal films. Instead, Pt layers were electrodeposited from fluoride solutions at different \(pH\) values and tested in air. Note that the deposition of Pt from fluoride solutions at the OCP is not suitable in this case, because the simultaneous Si dissolution reaction results in the degradation of the electronic properties of the interface (these aspects will be discussed in the next section).

To take advantage of the computer-interfaced potentiostat, the “dry” \(j - U\) characteristics were acquired with the Si as working electrode, and
4.2. CATHODIC HALF-CELL REACTION

Figure 4.10: Due to the relatively low energy barrier for holes in a Pt|Si Schottky junction, electrons can be transferred from the Pt nuclei to the Pt\(^{2+}\) ions in solution by hole injection through the Pt|Si interface.

short-circuiting the counter and reference electrodes to contact the metal layer (potentials are thus referred to the metal, as is the usual convention in electronics). The procedure employed to fit the }-\(U\) curves was the following: after expression 1.85, the plot of \(ln(-j/(1-e^{jU/B}))\) vs. the potential applied to the semiconductor, yields the ideality factor \(n\):

\[
n = \frac{1}{m \cdot 0.059 \text{ mV/dec}}
\]  

(4.8)

where \(m\) is the slope of the plot for \(U > 0\) [120]. The barrier height \(E_B\) can be calculated from the reverse current \(j_0\) (obtained from the plateau in the logarithmic plot at negative potentials, or from the extrapolation of the positive branch at \(U = 0\)) using expression 1.85:

\[
j_0 = A \frac{m^*}{m_e} T^2 \cdot e^{-\frac{E_B}{k_BT}}
\]

(4.9)

with \(A\) the Richardson’s constant (120 \(A/cm^2K^2\)), \(m^*\) the effective mass of minority carriers, \(m_e\) the electron mass and \(T\) the absolute temperature. The fit of the }-\(U\) curve of a commercial Schottky diode is shown in figure 4.11C as an example.

Regarding the Pt—deposited samples, the deposition parameters tested were the following:

- \(HF : H_2O (1 : 10), 1 \text{ mM } PtCl}_4^{2-} (pH 2)\) on \(p-Si\) at \(-1.0 \text{ V/SCE}\) during \(5 - 20 \text{ min}\) (the negative potential was only applied to prevent
Figure 4.11: Transformed $j - U$ plots of Pt|Si junctions obtained by several electrochemical methods (A and B) and measured under dry conditions. Curve C corresponds to a commercial Schottky diode and illustrates the fit of the parameters.

$Si$ oxidation by collecting the injected holes). The dry $j - U$ and Mott-Schottky measurements yield consistent values of the surface barrier $E_B \sim 0.5 \text{ eV}$ (0.25 eV smaller than expected). The ideality factor obtained from the $j - U$ plots is 1.7 at best (figure 4.11A).

- 10 mM $(NH_4)_2PtCl_6$ in 0.4 M $HN_a2PO_4$ ($pH = 4$ with HF), following the recipe given in [120]. $Pt$ was deposited on $n-Si$ by applying a double potential pulse (40 ms at $-3 \text{ V/SCE}$ for rapid nucleation, then 10 min at $-1.2 \text{ V/SCE}$ for slower growth). From the $j - U$ plot (figure 4.11B), $E_B \sim 0.7 \text{ eV}$ and $n \sim 2.0$ at best.

- $NH_4F(40\%) : H_2O$ (1:10), 10 mM $PtCl_4^{2-}$ ($pH8$ with $NaOH$). The potential applied to the $n-Si$ sample was $U = -0.8 \text{ V/SCE}$ for $t \sim 3 \text{ min}$. The dry $j - U$ plot was not exponential, but Mott-Schottky measurements in 0.1 M $H_2SO_4$, 10 mM $PtCl_4^{2-}$ were fairly linear and yielded $E_B \sim 0.85 \text{ eV}$.

It is worth mentioning that although all samples displayed a rectifying behavior, in some cases the $j - U$ plots became ohmic after one current measurement, possibly due to local heating at the microscopic contact points.
4.3 Anodic half-cell reaction

The fact that the $j-U$ curves of $n-Si$ shown in figure 4.4 are consistent with the “current doubling” mechanism at positive potentials (electron injection into the CB) is already a proof that the $Si$ dissolution reaction proceeds in the porous silicon (PS) regime. In the present section, this will be explicitly discussed and a comparison will be made with other oxidizing (hole-injecting) agents. In addition, the time evolution of the energy diagram at the anodic sites will be presented and discussed in terms of the progressive permeation of the $Si$ electrode with hydrogen, a by-product of the dissolution reaction.

4.3.1 Porous silicon formation

As was explained in 2.2.2, the concentration of holes at the surface of a $Si$ electrode relative to the fluoride concentration in solution, determines not only the rate of the dissolution reaction but also its mechanism. This can be evidenced by controlling the hole concentration at the surface with the potential applied to a $p-Si$ electrode (or a $n-Si$ under excess illumination). At potentials slightly positive of OCP there is a relatively low hole concentration at the surface and the oxidation reaction proceeds as $Si \rightarrow Si(II)$ with electron injection into the CB (current doubling, reaction 2.6). After such partial oxidation, $Si(II)$ is readily dissolved by the excess fluoride species in solution, which strongly corrodes the electrode leaving an $H-$terminated surface. Under these conditions, $Si$ is said to be dissolved in the PS regime (see 2.2.2 for further details and references).

The maximum dissolution rate in the PS regime is defined by a sharp current peak $j_{max}$ (figure 2.4): Beyond this current peak, the hole concentration is too large and the oxidation products start to condense at the surface, which allows the $Si$ atoms to be further oxidized to $Si(IV)$. An oxide layer is then formed at the surface, whose dissolution becomes the rate-limiting step of the overall reaction. This is the electropolishing regime (EP).

The value of the current density peak $j_{max}$ that sets the border between the PS and EP regimes, depends on the $pH$ and fluoride concentration of the solution: The more concentrated the solution and the lower its $pH$, the better it can dissolve $Si$ oxide and thus higher values of $j_{max}$ are obtained [61].
Figure 4.12: $j-U$ plot of $p-Si$ in a 2M fluoride solution (anodic branch). Increasing the electrode potential (i.e. the hole concentration at the surface), the Si oxidation reaction changes from the PS to the EP regime. The maximum current in the PS regime is $j_{\text{max}}$.

In the fluoride solutions employed in the experiments (2M, pH2), $j_{\text{max}} \sim 20 \ mA/cm^2$ as is shown in figure 4.12. Approximately the same peak values were obtained in $n-Si$ under excess illumination. Note, however, that the $j-U$ curve of $n-Si$ is shifted towards negative potentials because $U_{FB}^n < U_{FB}^p$ (see figure 2.4).

As was discussed in the previous section, the hole concentration at the $Si$ surface can also be controlled by a redox system whose electron energy levels overlap with the VB. In the conditions employed in the experiments ([PtCl$_4^{2-}$] $\leq$ 2.5 mM, solution stirring), PtCl$_4^{2-}$ ions are capable of setting a hole injection current into the $Si$ VB of several hundred $\mu A/cm^2$, which is well below the maximum current for oxide condensation in the 2M fluoride solution ($\sim 20 \ mA/cm^2$). Thus, the anodic counterreaction should occur in the PS regime.

The morphological, chemical and electrical properties of the anodic sites (bare $Si$ regions) can then be expected to be analogous or very similar to those of anodically-prepared PS: Indeed, the etch pits that can be seen in the substrate of figures 4.1 and 4.2b already indicate a certain porosity of the $Si$ surface. In addition, during anodic $Si$ dissolution in the PS regime, the surface $Si-H$ bonds are continuously renewed [60] and by comparison,
the anodic regions of the surface can also be assumed to be $H$–terminated during the $Si$ dissolution process at the OCP. Visible photoluminescence (PL) is another well-known property of anodized PS [78], and is consistently found in $Si$ samples deposited with $Pt$ from fluoride solutions at the OCP: Under illumination with an ultraviolet light, the deposited samples display an orange-red glow that is visible to the naked eye. The PL results will be further discussed in chapter 7.

It is also worthwhile to compare the double process of $Pt$ deposition and $Si$ dissolution in the PS regime, with a method employed to prepare thin PS-like layers on $Si$ at the OCP: The so-called “stain etch”. These solutions are composed of fluoride and an oxidizing agent whose reduced form is a soluble species: Usually the system $NO_2/NO_2^-$ is employed by adding $HNO_3$ to the solution [121], but others have also been reported [122]. The operating principle is thus the same: $NO_2$ is reduced to $NO_2^-$ by injecting holes into the $Si$ VB ($U^0_{NO_2/NO_2^-} = +0.7 \text{ V}/SCE$). No deposition results from this process (as it does in the case of $PtCl_4^{2-}$), but a hole concentration is also built at the surface that corrodes the $Si$ in the presence of fluoride in the solution. Moreover, the relative ratio of $NO_2$ (oxidizing agent) and $HF$ ($Si$ oxide complexing agent) in the solution allows to select the etch rate, and more importantly, to switch between the PS and EP regimes. For example, $HNO_3 : HF : H_2O$ solutions having low $HNO_3$ and high $HF$ concentration produce stain-etched layers that display PL, whereas solutions having high $HNO_3$ and low $HF$ concentrations result in “chemical” (OCP) polishing of the $Si$ surface [116]. A similar effect can be expected during metal deposition on $Si$ from fluoride solutions, as will be discussed in chapter 6.

For a comparison, some stain-etched samples were prepared at the OCP in a solution 0.3 M $NaNO_2$ in concentrated $HF$ during 1 min, and the PL emission was verified under a ultraviolet lamp. The appearance of the surface is shown in the SEM image of figure 4.13, where the similarity with the Si substrate of figure 4.1 can be appreciated.

### 4.3.2 Hydrogen incorporation into silicon

Despite all the parallelism between the $Si$ dissolution in the anodic regions and the formation of PS by anodisation in fluoride media, one feature of PS formation is remarkably absent during the OCP deposition of $Pt$ on $Si$: Hydrogen evolution. Indeed, during the acquisition of a $j - U$ plot of $p - Si$ in a fluoride solution in the absence of $PtCl_4^{2-}$ (figure 4.12), gas bubbles appear at the electrode surface at potentials negative of the current peak $j_{\text{max}}$. The gas is $H_2$ [123] and the ratio is one $H_2$ molecule per $Si$ atom
dissolved [124]. On reaching the current maximum, the bubbles are suddenly detached from the surface due to the condensation of a mixed oxide and the change in oxidation mechanism. This anodic $H_2$ evolution results from the homogeneous (in-solution) hydrolysis of Si etch products [4]: In the PS regime, $Si$ is oxidized and dissolved as $Si(II)$, and it further reacts with water molecules in the solution. The reaction can be outlined (regardless of the actual form of $Si(II)$ species) as:

$$Si(II) \rightarrow Si(IV) + 2e^-$$  \hspace{1cm} (4.10)

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$  \hspace{1cm} (4.11)

Hydrogen evolution should then be expected at the anodic sites (bare $Si$ regions) during the $Pt$ deposition from fluoride solutions. The fact that it is not observed prompted a more detailed study of the anodic half-cell reaction. As was mentioned in section 4.2, in the presence of fluoride in the solution, the electrode potential $U_{OCP}$ does not appreciably change with $Pt$ coverage (i.e. with the time exposed to the deposition solution). The mixed potential of $Si$ in 2$M$ $HF$ alone is $-0.4 \text{ V/SCE}$, and it shifts to $\sim 0 \text{ V/SCE}$ at most in the presence of $PtCl_4^{2-}$, to balance the hole injection current. In contrast, the equilibrium potential at the cathodic regions ($Pt$
nuclei) should lie around +0.3 V/SCE ($U_{P_{C_{Si}^-}/P_{Si}}$). The electrode potential is thus practically governed by the anodic regions (bare Si).

On the other hand, the MS plots employed to determine the FB potential of Si electrodes, are found to slowly change with the deposition time. The time evolution of the MS plots measured in $n-$ and $p-$Si electrodes immersed in a 2M HF, 2.5 mM PtCl$_2^-$ solution at the OCP is shown in figure 4.14 as an example. A shift in the extrapolated $U_{FB}$ can in principle be interpreted as a shift in the band edge energy ($E_{CS}$, $E_{VS}$). However, at constant $pH$ and in the absence of specific adsorption, no changes in $E_{CS}$, $E_{VS}$ are to be expected: the anodic regions are $H-$terminated as corresponds to PS, which rules out $OH^-$, $F^-$ or $Cl^-$ adsorption. For the same reason, the only states capable of storing large amounts of charge near the surface are the interface states at the Pt/Si junctions. This could indeed produce a shift in the band edge energy, but to a fixed value, i.e. independent of the immersion time (Fermi level pinning). Moreover, the sign of the FB shift in that case should be opposite to the obtained in the experiments (see figure 4.9). The phenomenon must then be attributed to some dynamic process that is occurring simultaneously, most likely at the anodic sites.

Actually, similar shifts in the MS plots have been reported to occur during the anodic formation of PS, and were interpreted in terms of the progressive permeation of the Si electrode by hydrogen produced during the Si dissolution reaction [115]. The presence of hydrogen in the Si crystal (as well as in other semiconductors) is known to cause important modifications in its structure and electric properties [125]. In particular, it has been shown that hydrogen atoms introduce electronic energy states near the Si midgap that act as electron donors in $p-$Si ($H \rightarrow H^+ + e^-$) and acceptors in $n-$Si ($H + e^- \rightarrow H^-$). Thus the presence of H in the Si crystal produces a doping compensation in both $p-$ and $n-$Si [126]. This results in a change in the interface capacitance and therefore leads to a shift in the MS plot ($\frac{1}{C_{SC}}$ vs. $U$) as the $H-$permeated surface layer is formed. The extrapolation of the initial plot at $\frac{1}{C_{SC}} = 0$ yields the expected $U_{FB}$ of the electrode. In the “shifted” plots, the parabolic dependence of $C_{SC}$ with the potential (i.e. linearity of the MS plot) is maintained because the capacitance measurements are always performed at large band bending (deep depletion). However, the extrapolation of those plots no longer corresponds to the FB potential, because the SCR has a non-uniform doping concentration.

Assuming that the shift of the MS plots is entirely due to the compensation in surface doping, the band edge energies (and thus $U_{FB}$) can be considered to remain fixed. This situation has been sketched in the inset of figure 4.14: The semiconductor bands are bent “twice” and the apparent (extrapo-
\[ \Delta U_{FB} = \frac{e N_A}{2 \epsilon \epsilon_0} \left( 1 + \alpha \frac{N_S}{N_A} \right) \cdot \delta^2 \]

where \( N_A \) is the bulk doping in \( p-Si \) and \( \alpha = \pm 1 \) for an \( n / p \) overlayer. For \( n-Si \) the same expression holds with \( N_D \) instead of \( N_A \), except that the shift is negative and \( \alpha = \pm 1 \) for an \( p / n \) overlayer. The model is shown in figure 4.15 (note that the bottom of the PS layer is taken as the origin of distances because the PS layer does not participate in the calculation of the interface capacitance [115, 127]).

Furthermore, the layer thickness \( \delta \) is given by the competition between the diffusion of \( H \) into the substrate (diffusion coefficient \( D_H \)) and the etching
4.3. ANODIC HALF-CELL REACTION

Figure 4.15: Model for the calculation of the interface capacitance and $\Delta U_{FB}$ (equation 4.12). A $H-$permeated layer (HL) of thickness $\delta$ is considered to form underneath the porous Si (PSL). The doping of the HL ($N_S$) is different from the bulk doping ($N_{A,D}$). After Allongue et al. [115].

rate of the silicon substrate, $R$ [115]:

$$\delta(t) = \sqrt{D_H t} - Rt \quad (4.13)$$

Replacing $\delta(t)$ in expression 4.12, the time evolution of the apparent FB shift can thus be fitted as a second-order polynomial:

$$\sqrt{\Delta U_{FB}} = A_0 + A_1 \sqrt{t} + A_2 t \quad (4.14)$$

where $A_0$ should be near zero and $A_1$, $A_2$ yield the unknown diffusion coefficient $D_H$, and the relative doping of the layer $\alpha \frac{N_S}{N_{A,D}}$:

$$D_H = \left( \frac{R A_1}{A_2} \right)^2 \quad (4.15)$$

$$\alpha \frac{N_S}{N_{A,D}} = \frac{2 \varepsilon\varepsilon_0}{e N_{A,D}} \cdot \left( \frac{A_2}{R} \right)^2 - 1 \quad (4.16)$$

The etch rate $R$ is a parameter that results directly from the anodic current passed during PS formation, taking into account that 2.66 $\mu$A/cm$^2$ correspond to an etching rate of 0.1 $nm/min$ for a reaction valency of 2:

$$R = j_{corr} \cdot \frac{0.1 \, nm/min}{2.66 \, \mu A/cm^2} \quad (4.17)$$
In order to quantify the incorporation of $H$ into $Si$ during the OCP deposition of $Pt$, the time evolution of the MS plots was followed in both $n-$ and $p-Si$ in different deposition solutions ($30 \ \mu M$, $300 \ \mu M$, $2.5 \ \text{mM} \ \text{PtCl}_2^-$, no stirring). The first MS measurement was performed in the “blank” fluoride solution to obtain the FB potential. After addition of the $Pt(II)$ salt, the sample was kept at OCP and subsequent capacitance measurements were acquired every $\sim 5 \ \text{min}$ during $\sim 30 \ \text{min}$. A table of the apparent FB shift $\Delta U_{FB}$ vs. deposition time was obtained by subtracting the “initial” $U_{FB}$ from the MS extrapolations at the different measurement times. The results have been outlined in figure 4.16 as $\sqrt{\Delta U_{FB}}$ vs. $\sqrt{t}$ in order to show the parabolic fit. The experimental points for $n-Si$ have been plotted as negative, both for clarity of the graph and to remind that the MS extrapolation shifts towards negative potentials in $n-Si$. Every curve has been tagged with the corresponding $Pt(II)$ concentration in the solution.

As can be seen in figure 4.16, the data series from the OCP deposition experiments are well fit by the model of “anodic” $H$ incorporation into $Si$. This indicates that $H$ may also be incorporated during the OCP dissolution of $Si$, and is yet another confirmation of the parallelism between $Si$ anodisation and deposition-induced PS formation. In particular, the MS shifts are greater for higher $Pt(II)$ concentration because this sets a higher hole injection rate, and thus a higher dissolution rate $R$ ($j_{corr} = -j_{m,j}$ in expression 4.17). In order to obtain $R$ in this case, the injection current was measured as the current plateau at reverse bias in $n-$ and $p-Si$ (large positive and negative potentials, respectively, see 4.1).

The evolution of MS plots was also monitored in $p-Si$ while the electrode potential was kept at $-2 \ \text{V/SCE}$ between MS measurements. Under these conditions, MS plots were unchanged within $\sim 1 \ \text{h}$ and the extrapolation always gave the “initial” $U_{FB}$ value in the $Pt-$free fluoride solution. This is consistent with the fact that the anodic half-cell reaction is stopped at negative potentials (the injected holes are collected in the semiconductor bulk). The same result was obtained for $30 \ \mu M$, $300 \ \mu M$, $2.5 \ \text{mM} \ \text{PtCl}_2^-$ in the fluoride solution.

Table 4.18 lists the injection current $j_{m,j}$ measured in $p-$ and $n-Si$ in the deposition solutions. After fitting the plots of figure 4.16, expressions 4.15, 4.16 yield the values of the hydrogen diffusion coefficient $D_H$ and the relative surface doping $\frac{N_s}{N_A,B}$ (the negative sign indicates that surface doping is opposite to bulk doping). They are also given in the table, together with the calculated thickness of the surface layer $\delta$ (expression 4.13) at the end of every deposition experiment:
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Figure 4.16: Parabolic fit of the FB potential shifts obtained from figure 4.14 at the OCP, and different PtCl$_4^{2-}$ concentrations. Values of $\sqrt{\Delta U_{FB}}$ for $n-Si$ have been plotted as negative to remind that MS plots shift towards negative potentials. The abscissa corresponds to the deposition (and etching) time at the OCP. Each experimental point in the series is the extrapolation of one MS plot, relative to its initial value (freshly electropolished Si in HF alone).

<table>
<thead>
<tr>
<th>$Si$</th>
<th>$[Pt(II)]$</th>
<th>$j_{inj} (A/cm^2)$</th>
<th>$D_H (cm^2/s)$</th>
<th>$\frac{N_p}{N_{A,D}}$</th>
<th>$\delta (nm)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$</td>
<td>30 $\mu M$</td>
<td>$5 \cdot 10^{-5}$</td>
<td>$2.3 \cdot 10^{-13}$</td>
<td>+0.28</td>
<td>192</td>
</tr>
<tr>
<td>$p$</td>
<td>300 $\mu M$</td>
<td>$1.5 \cdot 10^{-4}$</td>
<td>$1.2 \cdot 10^{-12}$</td>
<td>+0.25</td>
<td>320</td>
</tr>
<tr>
<td>$p$</td>
<td>2.5 $mM$</td>
<td>$3 \cdot 10^{-4}$</td>
<td>$4.0 \cdot 10^{-12}$</td>
<td>+0.60</td>
<td>540</td>
</tr>
<tr>
<td>$n$</td>
<td>30 $\mu M$</td>
<td>$3.5 \cdot 10^{-5}$</td>
<td>$2.6 \cdot 10^{-14}$</td>
<td>-16.5</td>
<td>30</td>
</tr>
<tr>
<td>$n$</td>
<td>300 $\mu M$</td>
<td>$5 \cdot 10^{-5}$</td>
<td>$1.0 \cdot 10^{-13}$</td>
<td>-5.5</td>
<td>85</td>
</tr>
<tr>
<td>$n$</td>
<td>2.5 $mM$</td>
<td>$2 \cdot 10^{-4}$</td>
<td>$1.4 \cdot 10^{-12}$</td>
<td>+0.05</td>
<td>290</td>
</tr>
</tbody>
</table>

The modified layer appears to be slightly thinner in $n-Si$ substrates, and has a $p-$type character at low corrosion rates. In $p-Si$, the surface layer has a $p^{-}$ character (the doping compensation is not complete), in contrast with the $n^{-}$ doping ($\frac{N_p}{N_A} \sim -0.3$) reported during anodic PS formation [115]. This
can be explained by the relatively thinner (i.e., more concentrated) layers obtained in that case ($\delta \sim 20$ to $50$ nm).

Note that the dependence of $D_H$ with the corrosion rate is in principle not to be expected in a diffusion coefficient. But $D_H$ in expression 4.13 is an “apparent” diffusion coefficient, because it includes the changes in the hydrogen concentration at the reaction interface: Hydrogen is a by-product of the dissolution reaction, so the larger $j_{corr}$ is, the faster that $Si$ is dissolved and the higher the hydrogen concentration in the proximity of the surface (bottom of the PS layer). The values of $D_H$ have been plotted in figure 4.17 in order to compare them with the apparent diffusion coefficients obtained during anodization experiments [129]. Although the values of $D_H$ during Pt deposition are approximately one order of magnitude larger, the comparison is difficult because of the lower $pH$ of the Pt deposition solution ($pH2$ against $pH4.5$ in the anodization experiments). Indeed, the rate of $H$ incorporation into $Si$ is reduced at high $pH$ (low $[H^+]$) because diffusion towards the solution is favored [128].

To find out whether there is an enhancement of $H$ diffusion into $Si$ related to the presence of $Pt$, an additional experience was performed under comparable conditions: The shift of MS plots was followed in $p-Si(111)$
samples (1 Ωcm) during Pt deposition at the OCP (\(j_{\text{inj}} = 125 \mu A/cm^2\)) and during anodization (110 \(\mu A/cm^2\)), both in a fluoride solution of pH4.5. The results are shown in figure 4.18 and yield \(D_H = 7.0 \times 10^{-13} \text{ cm}^2/\text{s}\) during the Pt deposition process and \(D_H = 4.5 \times 10^{-13} \text{ cm}^2/\text{s}\) during anodic dissolution. The difference in the apparent H diffusion coefficient has somewhat reduced, but now it must be solely related to the Pt counterreaction. The possible reasons for this effect are discussed in the following section.

**4.4 Three-dimensional energy diagram of the interface**

After sketching the energy diagrams at the cathodic and anodic sites, they will be assembled in this section, in order to further discuss the mechanism of the overall process in the steady-state regime.

As deduced from measurements in Schottky electrodes, the energy bandgaps at the \(\text{Pt}|\text{Si}\) interface in the cathodic sites (Pt nuclei) are \(-E_{\text{cs}} = -0.35 \ V/SCE\) and \(-E_{\text{cs}}^{\text{F}} = +0.75 \ V/SCE\) (figure 4.9). The potential of the Si electrodes during deposition in the Pt(II)—fluoride solutions is \(U_{\text{OCP}}^{\text{n}} = -0.1 \ V/SCE\) and \(U_{\text{OCP}}^{\text{p}} = 0 \ V/SCE\), so the band bending at the cathodic sites is \(\Delta \phi_{\text{sc}} = U_{\text{OCP}}^{\text{n}} - U_{\text{FB}}^{\text{p}} = -0.1 - (-0.35 + 0.25) \ V = 0 \ V\) in \(n-Si\) and \(\Delta \phi_{\text{sc}} = 0 - (0.75 - 0.20) \ V = 0.55 \ V\) in \(p-Si\). This is shown in figure 4.19(a), which results directly from figure 4.9 at the values of OCP.
Figure 4.19: Electron energy diagrams of a Si electrode exposed to a fluoride solution containing a Pt$^{2+}$/Pt system. (a) Platinum deposits on the surface producing metal nuclei (cathodic regions). The energy diagram at these sites is deduced from figure 4.9. (b) Hydrogen permeation during the simultaneous oxidation of Si, results in the “warping” of the bands in the anodic regions. Diagram taken from the inset of figure 4.14, for $\Delta U_{FB} \sim 1\text{V}$.

given above.

The situation at the anodic sites (bare Si areas) is more complex, as a consequence of the dynamic process of doping compensation due to H permeation. If the Si bandedge energies are assumed to remain at the initial values, then the CB edge at the anodic sites is $-\frac{E_{cS}}{e} = -0.7 \text{V/SCE} (n-\text{Si})$ and $-\frac{E_{cS}}{e} = -0.5 \text{V/SCE} (p-\text{Si})$. The amount of the “double bending” of the bands in the SCR (inset of figure 4.14) depends not only on the hole injection rate set by the Pt(II) species in solution, but it also changes with the deposition time. For explanatory purposes, a shift in the FB extrapolation of $\sim 1\text{V}$ has been taken for both $n-$ and $p-\text{Si}$. The extrapolations are shown in figure 4.19(b) (dashed lines) together with the deduced band profiles (solid lines). Such band profiles give rise to a depth distribution of the carrier concentration that has local maxima and minima. The case of holes in the VB is qualitatively sketched in figure 4.19(b) using a grey scale:
The maximum hole concentration in \( n - Si \) occurs at a certain depth from the surface, which is the order of \( \delta \) (see table 4.18). In \( p - Si \), a local maximum is found at the surface despite the fact that the semiconductor is in depletion.

Considering the localization of the anodic and cathodic sites at the electrode surface during the deposition process, an alternative presentation of the band diagrams of figure 4.19 is given in figure 4.20. For both \( n - \) and \( p - Si \) (left and right respectively), the diagram axes are \( z \) the depth coordinate (distance to the surface), \( x \) is one spatial coordinate within the surface plane, and \( U \) is the electrode potential. Usual band diagrams are \( U \) vs \( z \) (one-dimensional), and since the \( x \) coordinate corresponds to either direction in the surface plane, the diagrams of figure 4.20 can be considered as three-dimensional. Both diagrams correspond to one \( Pt \) nucleus surrounded by two bare \( Si \) regions. The energy of the holes injected into the \( Pt \) nuclei is given by the redox level \( U^{\text{Pt}}_{\text{PCl}} / Pt = +0.3 \text{ V/SCE} \) (not shown).

In view of the diagrams of figures 4.19 and 4.20, some questions arisen in the previous sections can be further discussed. For example, the enhancement of hydrogen incorporation into the \( Si \) electrodes can be explained by the presence of \( Pt \) nuclei on the surface. The \( H_2 \) molecules are a product of the

Figure 4.20: Electron energy diagrams in the surroundings of a \( Pt \) nucleus deposited on the \( Si \) surface. The center of each diagram corresponds to the \( Pt \) nucleus (cathodic site), as given by figure 4.19(a). The sides of the diagrams correspond to the bare \( Si \) regions (anodic sites, figure 4.19(b)).
Si dissolution reaction, and they are formed in solution at the anodic sites. Platinum is well known by its affinity to atomic hydrogen, which is adsorbed at the metal surface. It is thus possible that (reduced) H atoms remain as \( Pt - H(ads) \) at the nearby nuclei, instead of being released as \( H_2 \). This would explain the absence of gas bubbles during the reaction. Furthermore, since the potential of the Pt nuclei is more positive than \( U_{H^+/H_2} \), the \( H_2 \) molecules (or the adsorbed \( H \)) can be oxidized back to \( H^+ \) at the nuclei surface. Such process would produce an increase of the \( H^+ \) concentration near the surface (local \( pH \) increase), which acts as a “barrier” against proton diffusion towards the solution, and can enhance the hydrogen incorporation into \( Si \). This \( H_2 \) reoxidation mechanism is clearly not possible in the absence of Pt nuclei (anodic \( Si \) oxidation), so it can be expected that \( H_2 \) molecules show a slightly higher tendency to diffuse towards the solution [128].

Further experiments would be required in order to confirm the presence of such “stray” reaction in this particular case, but the enhancement of the \( H \) incorporation rate by the presence of metal nuclei on several substrates has been demonstrated in other studies: A thin layer of evaporated \( Pd \) (which has an even greater affinity for \( H \) than \( Pt \)) was shown to increase the \( H \) uptake rate during the cathodic HER in metals [130] as well as in \( Si \) [131].

As was explained earlier in this chapter, the overall deposition process can be envisaged as two simultaneous reactions, one cathodic (\( Pt \) reduction) and another anodic (\( Si \) oxidation) that exchange charge through the semiconductor substrate. It is therefore interesting to “trace” the trajectories of charge carriers between the anodic and cathodic reaction sites. Platinum ions in the solution reduce and deposit on the \( Si \) surface by withdrawing electrons from the VB, i.e. by injecting holes. Once a \( Pt \) nucleus has formed, the energy barrier for holes at the \( Pt|Si \) interface is as low as 0.35 \( eV \) and the deposition reaction can follow by hole injection through the \( Pt \) nuclei. This was sketched in figure 4.10. The injected holes are involved in the dissolution of \( Si \) (they are reactants in the anodic half-cell reaction) and they must travel to the anodic sites. At this point, it can be expected that some differences arise between \( p- \) and \( n- \) type substrates, because holes are minority charge carriers in \( n-Si \) and thus they are subject to recombination. In a similar way, the uneven concentration of holes pointed out in figure 4.19(b) can also have an influence on the morphologic distribution of the anodic regions. These aspects are difficult to study using electrochemical techniques and require a comparative microscopic study. It will be presented in chapter 7 and discussed using the diagrams developed here.
Chapter 5

Electrochemical Study of Nickel Deposition

The study of charge exchange processes between silicon and metal ions in fluoride solutions is complemented with the investigation of nickel deposition. As in the previous chapter, an electrochemical study is presented under idealized conditions, namely under potentiostatic control and in an electrochemical cell that exposes the polished side of silicon samples to the deposition solution. The choice of a redox system having an electron energy near the silicon midgap allows the study of electron transfer through mechanisms involving both the conduction and the valence band. The effect of illumination and solution pH is also investigated. After confirming the coupling between the silicon dissolution and the cathodic counterreaction, the focus is on the competition between two different cathodic processes: metal deposition and hydrogen evolution. Particular emphasis is put on the role of reaction intermediates.

5.1 Results

Silicon substrates were Si(100), both n- and p-type. Only the polished side was exposed to the solution (area 0.3 cm$^2$). The electrochemical experiments were carried out in the three-electrode configuration and in the dark unless otherwise specified. The electrodes were controlled using the computer-interfaced potentiostat and capacitance measurements were performed with a measurement signal of 10 mV at 25 KHz. All Si samples were electropolished prior to the experiments [115]. The remaining oxide was dissolved in HF 40% for a few seconds, until the surface showed an hydrophobic behavior (H-terminated).
Solutions were freshly prepared and were deoxygenated by bubbling with Ar for 30 min before starting each experiment. Deposition solutions were 50 mM NiSO$_4$·6H$_2$O and 5 M fluoride aqueous solutions of pH1 (solution I) and pH8 (solution II). Concentrated HF and NH$_4$F were respectively used. Occasionally, solutions 5 – 25 µM NiSO$_4$·6H$_2$O, 5 M NH$_4$F (pH8) were used.

The calculated value of the equilibrium potential of the redox couple Ni$^{2+}$/Ni is $U_{N_{i}^{2+}/Ni} = -0.53$ V/SCE, accounting for the 50 mM Ni$^{2+}$ concentration. It was experimentally verified by measuring the OCP of a clean and deoxidized Ni wire immersed in solution II.

When trying to deposit Ni at OCP from solution I (pH1), no visible change is observed on the surface of n- or p – Si even after 60 min of immersion. No deposition is either observed after negatively biasing the electrode (−1 V/SCE). Upon short anodic scanning of the potential, no oxidation peak is found near $U_{N_{i}^{2+}/Ni}$ that could be related to stripping of a Ni deposit, which was otherwise not visible to the naked eye.

In contrast to the above observations, if the n – Si electrode is immersed into solution II (pH8), a visible gray layer appears after about 20 min at OCP. EDX analysis during SEM imaging showed that this layer is formed by nickel nuclei. AFM imaging (figure 5.1) reveals a considerable increase in substrate roughness (16.1 nm RMS in image 5.1b) as compared to a surface in contact with a blank solution, free of Ni$^{2+}$ ions (1.7 nm RMS in image 5.1a). With p – Si, the same experiment led to quite different observations. After immersion into solution II, deposition could also be observed to the naked eye, but the substrate RMS roughness obtained by AFM remained practically unchanged (1.9 nm RMS in image 5.1c). The surface had a more homogeneous appearance than n – Si, with a small density of cluster-like features.

These strong differences in morphology suggest that Ni deposits much faster on n – Si than on p – Si. In order to verify this point, the deposition rates were independently estimated by means of voltammetry in both n- and p – Si in solution II.

Complete voltammograms for p – Si in the fluoride solution at pH8 with and without nickel are shown in figure 5.2. Curves 5.2ab and curves 5.2c-f correspond respectively to the anodic and cathodic branches in different situations. In the absence of Ni$^{2+}$ ions, the diode behavior of the interface is shown in figure 5.2c (reverse bias corresponds to negative potentials). After adding 5 µM Ni$^{2+}$, stirring the solution resulted in a significant change in the slope of the cathodic branch: The stronger the stirring, the more negative the current (curves 5.2d-f). In the absence of stirring, rising nickel concentration from 5 µM to 25 µM produced a similar increase of the reverse
5.1. RESULTS

Figure 5.1: Tapping mode AFM images of Si electrodes immersed during 20 min in NH$_4$F 5M solutions at pHS: (a) n – Si in a “blank” solution (no nickel added); (b) n – Si in solution II (50 mM Ni$^{2+}$); (c) p – Si in solution II; and (d) p – Si in solution II under illumination. The silicon surface RMS roughness has been indicated in every case.

current. Further increase of nickel concentration (e.g. 50 mM in solution II) saturates the effect. In contrast, in solution I (pH1) the dark current in a p–type electrode was neither altered by the increase of Ni$^{2+}$ concentration nor by solution stirring.

After keeping the p – Si sample at the OCP (−0.42 V/SCE) and in the dark for a few minutes, Ni is found to deposit at the surface. This is demonstrated by the anodic (stripping) peak observed in figure 5.2a. The OCP deposition rate was calculated as follows: the p – Si electrode was kept at OCP for different times and the anodic peaks were recorded afterwards (see figure 5.3). The potential axis was then converted into time ($t = \frac{\Delta V}{v}$ using the scan speed $v = 25$ mV/s), and the charge corresponding to the area under the peak was used to determine the amount of Ni deposited.
Figure 5.2: (a) Nickel oxidation current peak on a p–Si electrode in solution II (pH8) after 3 min at OCP in the dark. (b) Nickel oxidation peak after 3 min at the same potential but under illumination. (c) Cathodic branch of the current-potential plot in a p–Si electrode immersed in the dark in a “blank” 5M NH$_4$F solution (pH8). (d, e, f) Effect of increasing solution stirring on a p–Si electrode immersed in the dark in a 5M NH$_4$F, 5 µM Ni$^{2+}$ solution (pH8).

The resulting plot (deposited Ni vs. time at OCP) is shown in the inset of figure 5.3 and the linear fit yields a deposition rate of 0.02 ML/s. The same value was found if the sample potential was kept at more negative potentials, instead of at OCP.

The effect of light on the Ni deposition rate on p–Si was also briefly investigated. Under illumination, the photopotential shifts the OCP to −0.29 V/SCE. Setting again the sample potential at −0.42 V/SCE in order to have the same band bending during deposition, the amount of Ni can also be obtained from the stripping peak (figure 5.2b). The calculated deposition rate is 0.18 ML/s and therefore, illumination enhances Ni deposition on p–Si.

The results for n–Si are presented in figure 5.4: In the blank fluoride solution at pH8 (curve a) the n–Si electrode displays the basic diode behavior, although the reverse (positive) leakage current is higher and more potential-dependent than at low pH. Its value is ~100 µA/cm$^2$, against ~10 µA/cm$^2$ at pH1 (not shown in figure 5.4). This anodic current is due to electron injec-
Figure 5.3: Procedure employed for the calculation of deposition rates (see text). Deposition conditions: 1, 2 and 3 min at the OCP in the dark (p–Si electrode in solution II, pH8).

...ation into the CB, a process related to the Si dissolution mechanism [4]. After addition of Ni ions (solution II), a cathodic peak was found at −1.2 V/SCE clearly differentiated from the hydrogen evolution wave (figure 5.4b). Keeping the electrode potential at −1.2 V/SCE for increasing times, the anodic stripping peak increases its intensity. The cathodic peak was thus attributed to Ni$^{2+}$ reduction. In the absence of stirring, and using the same procedure described above, the calculated deposition rate was 0.76 ML/s. At the OCP, the rate is 0.19 ML/s, which is about 10 times greater than on p–Si under the same conditions.

The energy diagrams of the interface Si | electrolyte were constructed using the values of OCP ($U_{OCP}$) and FB potential ($U_{FB}$) measured on both n– and p–type silicon in solutions I and II. In every case, the band bending is given by the difference $\Delta \phi_{sc} = U_{OCP} - U_{FB}$ (upwards band bending when $\Delta \phi_{sc} > 0$). The energies of the CB ($n - Si$) and VB ($p - Si$) were deduced from $U_{FB}^{n,p}$ knowing that the Fermi level $E_F$ is located at about 0.25 V of the corresponding band [28]. Figure 5.5 deals with the energy diagrams corresponding to solutions I and II (pH1 and pH8 respectively). The concentration of majority carriers at the surface can be estimated from the band bending in each case, using the expressions:

$$n_{S} = n_{bulk} \cdot e^{-\frac{e\Delta \phi_{sc}}{kT}}$$  \hspace{1cm} (5.1)
Figure 5.4: Cyclic voltammogram of a n – Si electrode immersed in the dark in a “blank” solution (a: NH₄F 5M, pH8, no nickel added) and in solution II (b), showing the nickel reduction and oxidation current peaks.

\[ p_S = p_{bdk} \cdot e^{\frac{\Delta \phi_{oc}}{n}} \] (5.2)

where \( n_{bdk} = 5 \cdot 10^{15} \text{ cm}^{-3} \), \( p_{bdk} = 10^{16} \text{ cm}^{-3} \), and \( n \cdot p = n_i^2 = 2 \cdot 10^{20} \text{ cm}^{-6} \) yields the minority carrier concentration.

5.2 Discussion

The first question raised by the observations is why nickel deposits much faster at pH8 than at pH1, despite a nearly identical energetic situation (figure 5.5 shows that the relative energies of the Si bandedges and the Ni²⁺/Ni redox level are very similar at pH1 and pH8). The second important question is why Ni deposition from solution II at the OCP is faster on n – Si (0.19 ML/s) than on p – Si (0.02 ML/s).

The behavior observed in figure 5.2d-f indicates that the reduction of Ni²⁺ ions on p – Si in the dark occurs through hole injection into the VB [76]. The experimental deposition rate derived from stripping measurements (0.02 ML/s) is rather independent of the applied potential, and is closely related to the hole injection current derived from figure 5.2d-f (0.03 ML/s). The dependence of the cathodic current with solution stirring shows that
for \(Ni^{2+}\) concentration below 25 \(\mu M\), the deposition process is diffusion-controlled. The same VB deposition mechanism described for \(p-Si\) can be expected in \(n-Si\), because hole injection involves \(Si\) bonding electrons and is not affected by the presence of charge carriers at the electrode surface.

Nickel deposition may also be achieved through CB (free) electrons on \(n-Si\) in the dark (figure 5.4) and on \(p-Si\) under illumination (figure 5.2a). In \(n-Si\), the deposition rate depends on the band bending. Thus, the deposition process may involve either of the two bands.

In the case of \(n-Si\), EDX analysis, and in particular AFM results (figure 5.1), show that \(Ni\) deposition has occurred with a simultaneous increase of the \(Si\) substrate roughness: 16.1 \(nm\) RMS after 20 \(min\) in solution II (figure 5.1a) against 1.7 \(nm\) RMS for the same time in 5\(M\) \(NH_4F\) at \(pH8\) (figure 5.1b). This suggests that \(Ni\) deposition enhances the dissolution rate of \(n-Si\). On the contrary, the results obtained with \(p-Si\) indicate no enhancement of \(Si\) dissolution: the surface remains smooth during \(Ni\) deposition and the hole injection current derived from figure 5.2d-f is close
to the experimental deposition rate derived from stripping measurements.

These results can be explained by considering the different processes occurring on Si electrodes immersed in fluoride solutions [4]. The Si surface is very reactive and easily oxidizes in aqueous media. In the presence of fluoride species (HF, F\(^-\), HF\(_2\)\(^-\)), the oxidation products are readily dissolved and corrosion continues, keeping the surface permanently terminated by Si – H bonds. The Si electrode achieves a rest situation (OCP) in which the anodic (corrosion) current is balanced with a cathodic current (hydrogen evolution if no other reaction is available). In the absence of an applied potential, these two currents are equal and have opposite sign. The OCP of the system is thus the potential leading to the same rate for the anodic and cathodic reactions (mixed potential). Both processes can be described in a n – Si electrode by reactions 5.3 - 5.5 and 5.6 - 5.7 respectively (see reference [4] for the detailed mechanism):

\[
\begin{align*}
Si - H & \rightarrow Si^\bullet + H^+ + e^- \quad (5.3) \\
Si^\bullet + H_2O & \rightarrow Si - OH + H^+ + e^- \quad (5.4) \\
Si - OH + 3HF (or 3H_2O) & \rightarrow SiHF_3 (or SiH(OH)_3) \quad (5.5)
\end{align*}
\]

\[
\begin{align*}
2H^+ + Si^\bullet + e^- & \rightarrow Si - H + \frac{1}{2}H_2 \quad (5.6) \\
H_2O + Si^\bullet + e^- & \rightarrow Si - H + OH^- \quad (5.7)
\end{align*}
\]

The radical Si\(^\bullet\) corresponds to a silicon atom with an unpaired electron, as discussed in section 2.2.1. The two electrons in reactions 5.3 and 5.4 are injected into the CB from some antibonding states at the surface [3] and are responsible for the anodic current observed at pH8 under positive bias in darkness. A similar scheme holds with holes in p – Si, and in n – Si under illumination. The rate-determining step of the process is reaction 5.3. Reactions 5.3 - 5.4 correspond to the substitution of a hydrogen atom by a hydroxyl group, being their overall rate highly pH-dependent since the nearly unpolar Si – H group behaves as a weak acid. Indeed, the etching rate of silicon at the OCP is about ten times faster at pH8 (about 0.5 nm/min) than at pH1 (0.03 nm/min) [4]. Reaction 5.5 sketches that the silanol group is removed from the surface chemically, either with the help of HF molecules (at low pH) or molecular water (at high pH). On the other hand, reactions 5.6 - 5.7 stand for the cathodic hydrogen evolution reaction (HER), and involve the same Si\(^\bullet\) sites as reactions 5.3 - 5.5 [6]. The anodic and cathodic reactions are thus coupled through the formation of Si\(^\bullet\) sites.
5.2. DISCUSSION

The presence of \( Ni^{2+} \) ions in the fluoride solution may disturb the mixed potential of HER / Si dissolution in two ways, depending on the \( pH \) of the solution and the doping of the substrate. First, by promoting a hole injection current into Si (VB process) that results in \( Ni \) deposition. Second, by giving rise to a supplementary cathodic reaction that may compete with the HER. The VB and CB reduction of \( Ni^{2+} \) ions leading to \( Ni \) deposition can be respectively described by:

\[
Ni^{2+} + Si^* \rightarrow Si - N_i + 2h^+ \quad (5.8)
\]
\[
Ni^{2+} + Si^* + 2e^- \rightarrow Si - N_i \quad (5.9)
\]

In analogy with the HER (5.6 - 5.7), it is assumed that the above reactions involve the same \( Si^* \) sites as reactions 5.3 - 5.4.

Within the framework of the above set of reactions, it becomes clear why \( Ni \) may be deposited at \( pH8 \) and not at \( pH1 \). At low \( pH \) two facts are against \( Ni \) deposition: The \( Si \) dissolution rate is very small (\(< 0.1 \, nm/min\)), and dissolution is simply balanced by the HER. The rate of HER is actually faster that the reduction of \( Ni^{2+} \) ions due to the large \( H^+ \) concentration, and because the equilibrium potential \( U_{NP+/Ni} < U_{H+/H_2} \) (see figure 5.5). In other words, the weak dissociation of \( Si - H \) bonds and the strong proton concentration favor the HER as cathodic counterreaction at low \( pH \). The electrode mixed potential is thus established without contribution of the \( Ni^{2+} \) ions, which cannot even withdraw the bonding (VB) electrons of the \( Si - H \) bond (hole injection). Note that noble metals like platinum have \( U_{Pt^{2+/Pt}} > U_{H+/H_2} \) for all \( pH \) and thus can always inject holes [132].

In contrast, at \( pH8 \) the higher \( Si \) dissolution rate (\(~ 0.5 \, nm/min\)) and the lower HER rate (due to the lower proton concentration) seem to allow the participation of \( Ni^{2+} \) ions in the overall process. The situation at high \( pH \) must be discussed separately in \( n- \) and \( p- \) type electrodes.

In \( p - Si \) in the dark there are no electrons available in the CB, and the mixed potential is defined by \( Si \) dissolution and the \( Ni \) VB deposition (reaction 5.8). As was discussed above, this is supported by the fact that the \( Ni \) deposition rate obtained from the injection current (0.03 \( ML/s \)) is very close to the value calculated from the anodic peak (0.02 \( ML/s \)). The small deposition rate is consistent with the relatively low RMS roughness that is observed by AFM (figure 5.1c). Under illumination, an increase in the deposition rate is found in \( p - Si \) (figure 5.2ab). Light generates electron-hole pairs near the surface, which enables the CB deposition mechanism (photoelectrons can be transferred to the solution), but also results in a reduction of the band bending (see the subsection “The semiconductor electrode under illumination” in 1.3.2.2). At OCP, the lowering of the barrier favors emission
of holes towards the surface and gives rise to new $Si^\bullet$ states (reaction 5.3 is more properly written for a $p-Si$ electrode as $Si - H + h^+ \rightarrow Si^\bullet + H^+$). This, in turn, results in an enhancement of the $Ni$ deposition process through the VB.

If $Ni$ deposition on $n-Si$ at pH8 was occurring through the VB process as for $p-Si$, the same deposition rate should be expected. The increased rate at $n-Si$ must therefore be attributed to the CB process as counterreaction at OCP. The $n-Si$ electrode in figure 5.5 (right) is in weak depletion, and the electron surface density is indeed considerably greater than in $p-Si$ ($2 \cdot 10^{15} \text{ cm}^{-3}$ against $2 \cdot 10^7 \text{ cm}^{-3}$). On $n-Si$ the mixed potential is therefore mainly defined by the dissolution (anodic process) and $Ni$ CB deposition (cathodic process, reaction 5.9). The HER does not interplay because $U_{Ni^2+/Ni} > U_{H^+/H_2}$, as is indicated in figure 5.5. Numerically, the $Ni$ deposition rate (0.19 ML/s) is about 10 times the nominal rate of $Si$ dissolution in the corresponding solution (0.5 nm/min [4] is equivalent to 0.026 ML/s). This explains the large substrate roughness after immersion in solution II (figure 5.1b). The AFM image suggests indeed that the dissolution of $n-Si$ is enhanced by the presence of $Ni^{2+}$ ions (the cathodic current corresponding to $Ni$ deposition must be balanced by an enhanced anodic dissolution of the $Si$ substrate). This confirms the model in which metal deposition is coupled to dissolution, through the formation of $Si^\bullet$ sites. The process is seemingly autocatalytic.

In summary, while metal deposition on silicon from ions having very positive redox potential is expected to be a relatively simple VB process (hole injection) [132], charge exchange reactions with ions having their levels within the silicon bandgap are greatly affected by surface states. Those ions include nickel, copper, cobalt, iron, tin, etc. which often have a higher technological interest and wider application in the industry than noble metals. The study of the surface intermediate states involved in charge transfer reactions is therefore very important in order to understand and engineer deposition processes on silicon from metal ions solutions.
Chapter 6

Metal deposition overview

After studying in detail two model redox systems ($PtCl_4^{2-}/Pt$ and $Ni^{2+}/Ni$), this chapter aims to extend the discussion to other systems. A general deposition mechanism is indicated, and its different aspects are correlated with the results reported in the literature. The first part (6.1) gives a classification of redox systems under a thermodynamic approach, based on their oxidizing power relative to the $Si$ substrate. The possible reaction pathways are then described separately on $n$– and $p$–type electrodes using the concepts of the mixed potential theory introduced in 1.3.3. In the second part (6.2) the mechanism is refined considering the different competitive processes that define the rate of the overall reaction in every case.

6.1 Energetics of electron transfer

The physical process involved in charge transfer between an ion and the electrode is electron tunneling. This implies two requirements: Ions must be physically close to the electrode (less than $\sim 3$ nm for efficient tunneling) and the energy of the initial (filled) and final (empty) electron states must be very similar (isoenergetic transfer). At this point, it must be reminded that semiconductors can only exchange charge through the bandedges, i.e. at energies $E_{CS}$ or $E_{VS}$, which are approximately fixed (bandedge pinning). This is in contrast with metal electrodes, for which electrons are transferred at the Fermi energy and $E_F$ can be set to any value just playing with the applied potential. Thus in a semiconductor, the position of the bandedges relative to the redox level in solution gives rise to three essentially different situations. They are shown in figure 6.1:

- Redox systems having their Fermi energy close to the conduction band-edge ($M^+/M$ in the figure) can exchange electrons with the CB.
Figure 6.1: Depending on its redox energy, a redox system in the solution may interact with free electrons in the CB of the semiconductor ($M^+/M$), bonding electrons in the VB ($N^+/N$), or surface states (ss) if they are present at the interface.

- If the redox level is near the valence bandedge ($N^+/N$) the exchange can be done with the VB.

- Redox systems whose electronic levels lie within the bandgap ($P^+/P$) are in principle unable to exchange charge with the semiconductor, unless the transfer can be done through surface states near the redox level.

Of course, intermediate cases between these three are to be expected in practice. Note that the system $N^+/N$ interacts with bonding electrons, and the discussion is usually translated into holes as was explained in 1.3.2.2 for the dissolution of a semiconductor. For example, considering the transfer of electrons to the electrolyte, there is a substantial difference between the loss of an electron from the CB and from the VB: the former process requires both the existence of free electrons in the semiconductor (as in a $n$–type or an illuminated $p$–type) and downwards band bending such as to accumulate them at the surface. However, there are always bonding electrons in the VB to be withdrawn, regardless of the semiconductor type, band bending or illumination. Thus the “injection of a hole” is always possible from redox levels near the VB. The ions having such redox energies are termed, with good reason, oxidizing agents.

The presence of a redox system in the fluoride solution (e.g. due to the addition of metal ions) is associated with new electronic states that can exchange charge with the $Si$ electrode. The corresponding current adds a new
component to the total current through the interface, and can be treated using the electrode mixed potential (section 1.3.3). As was explained in chapter 2, the rest potential (OCP) of Si in fluoride media is the potential at which the rate of the HER equals the rate of Si oxidation, so that the total current through the interface is zero. The OCP is therefore defined by the mixed potential between the cathodic and anodic reactions. When metal ions are added to the solution, they disturb this current balance rather than achieving thermodynamic equilibrium with the electrode.

The discussion to follow will be focused on the interpretation of current-potential \((j - U)\) curves of Si in contact with a redox system in a fluoride solution. After sketching the electron energy diagram of the interface, the measurement of the voltammetric response is often used as the first experimental approach: The \(j - U\) curves for \(n-\) and \(p-\) type electrodes, in darkness and under illumination, and for slightly different electrolyte compositions, allow a qualitative discussion of the charge exchange processes with the redox system.

### 6.1.1 Conduction band processes in \(n - Si\) electrodes

The dark \(j - U\) curve of a \(n - Si\) electrode in a fluoride solution is equivalent to the general one described in figure 1.27. It has been plotted in figure 6.24 as the “blank” reference curve. Note that in the case of Si in fluoride media, the reverse current is due to the injection of electrons into the CB as a result of the etching reaction (see section 2.2.3 and figure 2.5).

The insets in figure 6.2 show that the potential applied to the electrode results in a change in \(E_F\). The semiconductor band bending and the electron concentration at the surface are modified, but the relative position of the band edges and the redox level remains constant in a first approximation. As the electrode potential is scanned towards negative values, \(E_F\) shifts upwards in the band diagram and electrons can be transferred to the electrolyte, thus promoting cathodic processes. Electrode potentials positive of OCP, shift \(E_F\) downwards and may give rise to anodic processes. At every potential value, the currents related to the different processes add up to give the total current measured in the \(j - U\) curve.

When a redox couple capable of exchanging electrons with the CB exists in the solution, the general form of the reduction current is:

\[
j_{\text{red,CB}} = k \cdot n_S \cdot [M^+]_{S,CB}\tag{6.1}\]

where \(k\) is the rate constant, \(n_S\) the electron concentration at the electrode surface, and \([M^+]_{S,CB}\) the concentration of metal ions having their redox
energy near the CB. At negative potentials in the dark, free electrons are accumulated at the surface of the $n-Si$ electrode and can be transferred to the solution, giving rise to a cathodic current peak (figure 6.2B). The metal ions that accept those electrons are reduced and will deposit on the surface if the reduced form of the couple is a solid (e.g. $Cr^{2+}/Cr$, but not $Cr^{3+}/Cr^{2+}$). Usually the current peak shows up before reaching the FB potential, because electrons can already overcome the relatively low barrier. The occurrence of a peak rather than a current plateau or an exponential function is the sign of a limitation in the solution: in the beginning the current does grow exponentially with potential at the expense of the ions situated near the electrode surface. But once these have been exhausted, other ions have to be supplied to the interface by slow diffusion in order to maintain the reduction reaction. A current decay as $\frac{1}{\sqrt{t}}$ and independent of potential $(U)$ is then observed, where the time $t$ is obtained from the potential scan rate $\nu$ as $t = \frac{U}{\nu}$ [133]. The decay of the current can be delayed by improving the mass transport conditions in the solution, e.g. stirring or increasing metal concentration. Note that the diffusion limitation is related to the fact that the bandedges are actually not pinned under accumulation: The band bending in the semiconductor saturates, and the applied potential is then mainly dropped within the Helmholtz layer (HL). The bandedges shift an amount

![Graph showing current density ($j$) vs. electrode potential ($U$)](image)
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\[ \eta = \Delta \phi_H(U) - \Delta \phi_H^{eq} \]

towards higher energies. In this range, the potential applied to the semiconductor results in a lowering of the reaction barrier \( \Delta G_{\text{cat}} \) (expression 1.72), thus increasing reaction kinetics and bringing on diffusion as the rate-limiting step. The situation is then analogous to metal electrodes (see section 1.3.2.2 for details).

Using the scan rate \( v \), the \( j-U \) curve can be turned into a \( j-t \) curve, the peak area now having units of charge. Subtracting the proper baseline, the total number of electrons involved in the reduction process can be calculated. This yields the amount of matter if the reaction is known (e.g. \( \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni} \) spends two electrons per \( \text{Ni} \) atom deposited).

As for the blank (fluoride-only) solution, at more negative potentials the onset of the HER is found. Sometimes the HER occurs at less negative potentials in the presence of a metal, which indicates a certain catalytic activity (e.g. \( \text{Ni}, \text{Pd}, \text{Pt} \)). Specially in these cases, the HER wave can also mask the deposition peak, although it can often be shifted to more negative potentials by rising solution \( p\text{H} \) (i.e. reducing \( H^+ \) concentration).

If the potential of the electrode (now covered with a metallic layer or scattered nuclei) is then scanned back towards positive values, the Fermi level of the electrode returns to a lower position than the redox couple energy. In a first approach, the electrons from the metal are regained as free charge in the silicon CB and the metal returns to the solution as oxidized species provided that a suitable complexing agent is present. This process gives rise to an anodic (“stripping”) current peak, whose shape is related to the oxidation rate and the area is now proportional to the amount of oxidized material. Note that semiconducting electrodes add another complication here: The deposited metal may build up a rectifying contact (reverse-biased at positive potentials) that prevents the flow of current needed to strip it. In this case the deposition process becomes irreversible [120]. However, several metals have been reported to deposit quite reversibly on \( n-Si \): \( \text{Zn} \) [134], \( \text{Pb} \) [135, 136], \( \text{Ni} \) [137] and \( \text{Sn} \) [138].

During CB processes in \( n-Si \) electrodes, holes are not involved and thus no illumination is required. The current that is measured is due directly to majority carriers (electrons). At negative potentials and in the dark, the dissolution of \( n-Si \) in fluoride media is stopped (at least at low \( p\text{H} \) where the chemical reaction is minimized). Deposition is thus carried out preserving the integrity of the silicon surface.

### 6.1.2 Conduction band processes in \( p-Si \) electrodes

In the dark and even at downwards band bending, there is only a small amount of thermally generated electrons in the CB of a \( p-Si \) electrode.
Electrons must be first photogenerated in order to transfer them to a redox system near the CB (photoreduction). In this case, the $j - U$ curve of a $p$–type electrode under illumination (dashed line in figure 1.26) has been taken as a reference in figure 6.3A. As in the $n - Si$ electrode (figure 6.2), cathodic processes are promoted at negative potentials. However, the HER wave (and possibly the metal reduction peak) saturate when all the photoelectrons are consumed, and a plateau is found instead of an exponentially growing current. As is shown in the inset, the cathodic current that is measured is due to the photogenerated holes (majority carriers in $p - Si$) that are separated from the photoelectrons at the SCR, and collected in the semiconductor bulk at negative potentials.

At positive potentials, and regardless of illumination, the deposit can be stripped by injection of electrons in the CB followed by recombination with holes, or directly injecting electrons in bonding levels (hole extraction). The actual mechanism probably depends on the height of the metal | $Si$ barrier formed after deposition, but in any case the measured current corresponds to majority carriers. Note that in this potential range, holes are accumulated at the surface and may produce the simultaneous electrochemical dissolution of the semiconductor (see section 2.2).
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Figure 6.4: Dark \( j - U \) curve of \( p - Si \) in a blank fluoride solution (A), and hole injection current due to the presence of an oxidizing agent (B). Curve C results from the superposition of A and B.

It must be mentioned that photodeposition onto \( p - Si \) electrodes involves several experimental difficulties, but it is interesting because of its applications to lithography, i.e. locally depositing a metal using selective illumination or scanning-probe techniques [139].

6.1.3 Valence band processes in \( p - Si \) electrodes

In this case, the “blank” reference curve is taken from the dark \( j - U \) plot of \( p - Si \) (figure 6.4A). A redox system overlapping the VB sets a hole injection current into the semiconductor regardless of its doping type, band bending (i.e. electrode potential) and illumination. The hole current \( j_{\text{inj}} \) is proportional to the concentration of ions with energy levels overlapping the VB, \( [N^+]_{s,VB} \):

\[
j_{\text{red,VB}} = k' \cdot [N^+]_{s,VB} \equiv j_{\text{inj}}
\]

It has been plotted in figure 6.4B as a constant cathodic current \( j_{\text{inj}} < 0 \). The resulting \( j - U \) plot (curve C in figure 6.4) is the superposition of curves A and B, and appears as a downward shift of the blank curve.

The injection current \( j_{\text{inj}} \) can be measured by collecting the holes, majority carriers in \( p - Si \), at very negative bias: The cathodic plateau of curve
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C in figure 6.4 gives approximately the value of \( j_{\text{inj}} \) (see left inset). If the measured \( j_{\text{inj}} \) depends on the mass transport conditions in solution (stirring and concentration of metal ions), the metal deposition process is limited by diffusion. It can be made kinetically-limited in certain cases, for instance if a maximum \( j_{\text{inj}} \) value is reached on increasing solution stirring or metal concentration. Under these conditions, the supply of ions to the electrode surface is no longer the limiting step, but the reduction reaction itself. Note, however, that the kinetic limitation would not be in contradiction with the large negative potentials applied to the electrode along the cathodic plateau: The \( p-Si \) electrode being in depletion, all the applied potential is dropped within the SCR, i.e. the semiconductor bandedges are pinned and the reaction barrier remains constant. In other words, the applied potential does not increase reaction kinetics in this range.

As can be seen in figure 6.4, after addition of the hole-injecting agent, the OCP of the electrode shifts towards positive potentials. This serves to balance \( j_{\text{inj}} \) with an anodic current of holes \( j_{\text{corr}} \) flowing to the interface (see right inset). In the presence of fluoride, such anodic current results in \( Si \) dissolution. The new OCP \( (U_{\text{max}}) \) is the mixed potential between the cathodic reaction (metal reduction by hole injection) and the anodic counterreaction (\( Si \) oxidation and dissolution). The current balance can also be seen as (a fraction of) the injected holes being captured at the surface, thereby resulting in \( Si \) oxidation. Note that the “corrosion” current \( j_{\text{corr}} \) may reach several mA/cm\(^2\) and seriously damage the \( Si \) substrate [140].

The positive shift in the OCP of \( Si \) electrodes as a result of a hole injection current has been reported by several authors [141, 142], both in \( p- \) and \( n-Si \). In particular, Chyan et al. [142] took advantage of this effect to fabricate a sensor for the detection of trace amounts of noble metals in fluoride solutions.

6.1.4 Valence band processes in \( n-Si \) electrodes

The \( j-U \) curve of a dark \( n-Si \) electrode in the presence of hole-injecting species (figure 6.5) can be built from a potential-independent cathodic current \( j_{\text{inj}} \), and the \( j-U \) curve of illuminated \( n-Si \) in fluoride media presented in figure 1.27. The curve under illumination is used because the effect of holes is analogous whether they are injected from the solution or photogenerated: the anodic current of figure 6.5A must be the “double” of the injection current. The sum of the “blank” curve \( (A) \) and the hole injection current \( (B) \) is given in curve \( C \). Before the HER wave expected for a \( n- \) type electrode, a cathodic plateau can be observed. It gives a measurement of \( j_{\text{inj}} \), through the recombination of electrons with the injected holes (see left inset). In some cases the plateau may be masked by the HER peak. On the anodic
branch, another plateau is found, roughly corresponding to a current \( -j_{\text{inj}} \) [143]. In this potential range, the hole injection current \( j_{\text{inj}} \) balances with a current of holes towards the interface, \( j_{\text{corr}} \), that results in Si oxidation. As was explained in 2.2.3, electrons are injected into the CB in the oxidation reaction (current doubling), and this is the net current of majority carriers that gives rise to the anodic plateau. Note that the anodic plateau provides a rather indirect measurement of \( j_{\text{inj}} \), because it involves the carriers produced in a reaction.

Due to the current doubling phenomenon, the mixed potential \( U_{\text{mix}} \) of the \( n-Si \) electrode corresponds to a somewhat complex balance of currents: The rest situation (OCP) is achieved when the hole injection current is cancelled with a positive current that corresponds (in equal parts) to the flow of holes towards the surface and the electrons injected into the CB.

### 6.1.5 Remarks

It must be mentioned that even if the relative energy of the semiconductor bandedges and the redox levels in solution have been measured or calculated with great accuracy, they must be taken just as a rough indication of whether
a charge transfer is *thermodynamically* favorable or not. Factors that are
harder to predict, like reaction kinetics or surface states may also play an
important role in the overall process. In most cases, if not all, the best proof
is experience.

Sometimes the aim of these electrochemical studies is to design or tune
a certain deposition process, e.g. by avoiding VB pathways that may in-
volve substrate corrosion. Two parameters may help in that way: First,
the semiconductor bandedges can be shifted along the energy scale by play-
ing with solution $pH$ (figure 2.1). Second, a metal can usually be de-
posited from several complexes, each of them having a hopefully very dif-
ferent redox energy. Thus it is possible to switch between a VB and a
CB process (cases $M$ and $N$ in figure 6.1) for a fixed metal/semiconductor
system. For instance, copper ions can be reduced to metallic copper from
$HCl$ solution ($U_{Cu^{+}/Cu}^{0} = +0.52 \, V/SHE$) and from $Cu(CN)_2^{2-}$ in alka-
line solution ($U_{Cu(CN)_2^{2-}/Cu}^{0} = -1.0 \, V/SHE$) [144]; or gold, which is a very
noble metal, can be deposited by a pure CB mechanism from $Au(CN)_2^{-}$
($U_{Au(CN)_2^{2-}/Au}^{0} = -1.1 \, V/SHE$) [145]. Of course, the stability of the complex
at the $pH$ of interest must be verified. Note that the kinetic properties can
vary strongly between different complexes of the same metal (“big” com-
plexes usually have a slower reduction kinetics), and this may give rise to
apparent contradictions. For example, the reduction of $Cu^{2+}$ is much faster
than $PtCl_4^{2-}$ despite the fact that $U_{PtCl_4^{2-}/Pt}^{0} > U_{Cu^{2+}/Cu}^{0}$, because the in-
ner solvation shell of $Cu^{2+}$ ions involves weakly bonded ligands ($H_2O$) as
compared to chloride ions in $PtCl_4^{2-}$.

6.2 Competitive processes and kinetic aspects

After discussing the energetics of charge transfer between $Si$ and a redox
system in the fluoride solution, and the coupling between the anodic and
cathodic half-cell reactions, this section will be concerned on the *rate* of
these processes. The cathodic reaction is given by a competition between
hydrogen evolution and the reduction of metal ions. On the anodic side,
either the formation of $Si$ oxide or its dissolution in the fluoride media can
be rate-limiting.

6.2.1 Cathodic half-cell reactions

The deposition of several metals on $Si$ will be compared, assuming an excess
fluoride in the solution. Under these conditions, the $Si$ surface is oxide-free.
6.2. COMPARATIVE PROCESSES AND KINETIC ASPECTS

This case has been of interest in several recent studies concerned on the effect of metal contaminants in oxide-etching solutions (i.e. relatively concentrated in fluoride).

Figure 6.6 shows the reduction potential of several redox systems as a function of pH. The lower the position of a redox system in the figure, the higher its tendency to gain electrons and reduce. The graph is based on Pourbaix diagrams in water [146], and although some values may be dependent on the presence of counterions like $Cl^-$, $SO_4^{2-}$ or $CN^-$, it will allow a qualitative discussion.

Redox systems whose electron energy levels lie close to the Si VB (located in the bottom of figure 6.6) act as oxidizing agents of Si. Usually the metal deposition rate controls the rate of the overall reaction. As it has been discussed in the previous section (6.1), bonding electrons are transferred from the VB to the redox levels in solution regardless of the Si doping type or the potential applied to the electrode. Under excess fluoride in the solution, a hole injection current has been measured for $Cu^{2+}/Cu$ [143, 147], $PtCl_4^{2-}/Pt$ [132] and $IrCl_6^{2-}/IrCl_6^{3-}$, $MnO_4^-/MnO_4^{2-}$, $Br_2/Br_-$ [76] ($U^0 = +0.87$, $+0.57$, $+1.1$ V/SHE respectively; not shown in figure 6.6). A positive shift of the OCP of Si electrodes has been detected for $Cu^{2+}/Cu$ [141] and $Ag^+/Ag$ [142], which provide an indirect verification of the hole injection process as discussed in section 6.1.3. In all these cases deposition was limited by the supply of metallic ions to the surface: The measured injection current was dependent on the concentration of metal ions [143] or on solution stirring [76, 132, 147], and the amount of the OCP shift was proportional to the logarithm of metal concentration [141, 142]. However, other processes can also be rate-determining, like the oxidation counterreaction in $n$ – $Si$ during $Pt$ deposition from $PtCl_4^{2-}$ (see chapter 4).

The presence of the redox system produces metallic nuclei on the surface when the reduced form of the couple is a solid (e.g. $Pt$, $Cu$, $Ag$ [148]), and results in an enhancement of the Si substrate etching. Besides the results presented in chapter 4 for $PtCl_4^{2-}/Pt$, this was verified in solutions 2 M fluoride containing 1 $mM$ $CuSO_4$, 1 $mM$ $AgNO_3$ and 100 $\mu M$ $AuCl_3$. In all three cases, a metallic layer was visible to the naked eye in a few minutes. Similar results were obtained using $Pd^{2+}$ salts [1, 149] and $BiCl_3$ [150] with somewhat longer deposition times.

When metal deposition is attempted from redox systems having a weaker oxidizing power (i.e. lying closer to the $Si$ CB and in the top or middle of figure 6.6), the rate of the overall reaction is in principle controlled by the anodic process (OCP etching rate). As was explained for $Ni^{2+}/Ni$ in chapter 5, the cathodic process can be regarded as the counterreaction that balances the anodic oxidation current. The rate of OCP etching is a function of $pH$
Figure 6.6: Simplified Pourbaix diagrams of several metals in aqueous solution. Redox systems are in its reduced form when the conditions are below the corresponding line. Data replotted from reference [146].
and varies between 1 $\mu$A/cm$^2$ at pH1 and 25 $\mu$A/cm$^2$ at pH14 (see chapter 2).

Depending on the specific conditions of the solution, the cathodic current can be the sum of several contributions, i.e. cathodic reactions involving different redox systems. In aqueous solutions containing metal ions, the electron-accepting species are protons and the metal ions, each reduction reaction having a different rate constant. The rate of every cathodic reaction depends on both the kinetic constant and the equilibrium potential. A qualitative comparison between the different reduction reactions can be made considering only the equilibrium potential, as is shown in the higher part of figure 6.6. In the case of Ni$^{2+}$/Ni, a competition is established between the reduction of $H^+$ and Ni$^{2+}$: At low pH the Si etching rate is very low and the cathodic counterreaction only involves the $H^+/H_2$ couple ($H_2$ evolution is faster than Ni deposition because $U_{H^+/H_2} > U_{Ni^{2+}/Ni}$). Despite being thermodynamically favorable (Ni$^{2+}$/Ni levels overlap the CB), nickel deposition does not occur at low pH. Increasing the pH results in an increase of the etching rate (anodic current) and a decrease in the equilibrium potential of the $H^+/H_2$ system. This combined effect allows Ni to be deposited at high pH. By comparison, all metals lying above the line tagged “$H^+/H_2$” in figure 6.6 are expected to have a lower reduction rate than protons, and they should not be able to deposit.

The results reported in the literature, together with some deposition experiments at the OCP, confirm these expectations quite well: No deposition was produced from HF 1 : 10 solutions containing 10 mM ZnSO$_4$, in agreement with previous studies [148]. The same results are obtained with Fe [148, 151], Cr [148] and Al [1, 151] for a wide range of pH (from concentrated HF to “buffered” HF : NH$_4$F mixtures). All these metals have a reduction potential considerably more negative than $H^+/H_2$. The system Co$^{2+}$/Co (having a reduction potential close to Ni$^{2+}$/Ni) was then studied in an attempt to reproduce the results obtained for Ni. However, no deposition could be obtained from 10 mM CoCl$_2$, 2 M fluoride solutions of pH1–8 at the OCP. Cobalt deposition under applied potential was not explored, but recent results [152] demonstrate that it is possible, even in the absence of fluoride when a thin oxide layer may be present. The system Sn$^{2+}$/Sn has a redox potential very close to $H^+/H_2$ at low pH. As expected, Sn could be deposited from 1 mM SnSO$_4$ 10 mM NH$_4$F both at pH1 and pH4, producing very adherent deposits [138]. The process is very reversible in n – Si and the deposition rate can be calculated as described in chapter 5 for Ni. The resulting surface was not inspected using microscopy techniques but it has been reported that Sn deposition occurs preferentially at surface flaws [1]. However, the case of Sn does not seem very representative because fluoride
ions may play an additional role as complexants of $Sn^{2+}$ species, probably in the form of $SnF^+$. This must particularly apply to the experiments at $pH4$, since otherwise $Sn(OH)_2$ is known to precipitate in aqueous solutions between $pH2$ and $pH12$ [153]. Similar to $Sn$, $Pb$ forms fluorocomplexes like $PbF_2$ and was not investigated, but $Pb$ electrodeposition on $n-Si$ from $HClO_4$ aqueous solutions has been reported [135, 154].

As was discussed above, for redox systems overlapping the CB (redox potential lower than $U_{H^+/H_2}$) the overall reaction is controlled by the $Si$ etching rate at the OCP. However, it was demonstrated in chapter 5 that $Ni^{2+}$ ions can set an “electron withdraw current” that results in an enhancement of $Si$ dissolution. Deposition is then auto-catalytic. This occurs under conditions where the metal deposition rate is higher than the HER (high $pH$) and in the presence of electrons in the CB ($n-Si$ or illuminated $p-Si$). This interesting effect was not further investigated with other systems, but $In^{3+}/In$, $Cd^{2+}/Cd$ and $Fe^{2+}/Fe$ are good candidates at high $pH$.

Some direct conclusions can be drawn from the above discussion, concerning the application to the $Si$ cleaning technology. Fluoride solutions are widely used in the microelectronics industry to etch $SiO_2$ from $Si$ wafers, and the process is carried out by simple immersion of the wafers in the etching solution, i.e. at the OCP. In that respect, fluoride solutions have a relatively high selectivity: While the etch rate of $SiO_2$ in buffered—HF at $pH5$ is 110 nm/min [148], the “overetch” rate of $Si$ at the same $pH$ is more than 1000 times lower [4]. This fact allows to achieve oxide-free $Si$ surfaces, flat to the nm scale, without a tight control of the wafer immersion time. However, the presence of trace amounts of metal contaminants in the etching solution may give rise to a number of electrochemical processes, even at the OCP. It has been shown in the previous chapters that all these processes severely modify the morphologic, chemical and electric properties of the semiconductor. When the aim is to obtain a clean, flat, $H-$terminated $Si$ surface, they must be prevented to the maximum extent. In view of figure 6.6, the most harmful contaminants lie below the $H^+/H_2$ level, including all noble metals; $Cu$, $Ni$, $Pb$, and probably $Sn$, $Cd$ and $In$. In addition, noble metals are difficult to remove from the wafer surface using standard cleaning procedures. When wafer processing involves these metals in certain steps, they are usually carried out in separate clean rooms: For example, copper metallization employed in advanced CMOS [155]. Other redox systems do not result in metal deposition, but can also act as oxidizing agents and must be equally avoided (e.g. $Cr^{6+}/Cr^{3+}$, $Fe^{3+}/Fe^{2+}$, $NO_2/NO_2^{-}$; not shown in figure 6.6).

The usual strategy is to reduce these contaminants well below the ppm range in the etching solutions [156], although other methods have been proposed for specific contaminants. A relevant example is the $O_2$ dissolved in
water, which gives rise to reactions like:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \] \hspace{1cm} (6.3)
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \] \hspace{1cm} (6.4)

at low and high \textit{pH} respectively. As can be seen in figure 6.6, \( O_2 \) can inject holes and enhance \textit{Si} dissolution, while its own reduction products remain in solution. The effect is usually minimized by purging the solution of \( O_2 \) using \( N_2 \) or \( Ar \) bubbling. Another very convenient option is adding \((NH_4)_2SO_3\) [95], which can be oxidized as:

\[ SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^- \] \hspace{1cm} (6.5)

and supplies the electrons for the homogeneous (in-solution) reduction of \( O_2 \). Note that the oxidation product of \( SO_3^{2-} \) is soluble in water and does not produce any precipitate on the surface.

### 6.2.2 Anodic half-cell reactions

As was explained in chapter 2, \textit{Si} etching can follow two different mechanisms, corresponding to the Porous Silicon (PS) and Electropolishing (EP) regimes. At a fixed concentration of holes at the \textit{Si} surface, the mechanism of etching depends on the dissociation of \textit{Si} – \textit{H} bonds (approximately given by the \textit{pH} of the etching solution), the fluoride concentration, and also on the different fluoride species present in the solution. The etching of \textit{Si} can also be regarded as a two-step process, the first of them being the oxidation \textit{strictu sensu} (loss of bonding electrons), followed by the complexation of the oxidation products. The reaction proceeds in the PS regime when \textit{Si} oxidation is the rate-determining step, and in the EP regime when oxide dissolution is the limiting process.

Given a solution with fixed fluoride concentration and \textit{pH}, the transition from the PS to the EP regime can be observed on increasing the \textit{Si} oxidation rate at positive potentials (hole accumulation). The sharp current peak \( j_{max} \) that appears in the \( j - U \) curve of figure 2.4 corresponds to the maximum oxidation rate that can be attained without the condensation of an oxide at the surface. At a fixed \textit{pH}, the value of \( j_{max} \) increases with the fluoride concentration [61].

Metal ions lying near the VB produce an enhancement of the \textit{Si oxidation} reaction (they withdraw VB electrons). Under these conditions, oxide dissolution can become rate-limiting depending on the complexation power of the fluoride solution. Recently, Martins et al. [143] have observed that the oxidation current of \( n - \text{Si} \) depends on the concentration of \( Cu^{2+} \) and
fluoride in the solution as is shown in figure 6.7. The experimental points correspond to the anodic current plateau described in section 6.1.4 (figure 6.5), which is due to the injection of electrons into the CB as a result of Si oxidation. Their results can be interpreted as follows: At the larger fluoride concentrations, the anodic current is independent of $[HF]$ and practically proportional to $[Cu^{2+}]$. The overall reaction is governed by the supply of $Cu^{2+}$ ions to the Si surface. The reduction of $Cu^{2+}$ to metallic $Cu$ is balanced by the oxidation of $Si$ atoms, which proceeds in the PS regime under excess fluoride. As the fluoride concentration is decreased in figure 6.7, the anodic current is proportional to $[HF]$ and virtually independent of $[Cu^{2+}]$. In this range, the oxide dissolution rate is lower than the supply of oxidizing agent and becomes the limiting step. The $Si$ oxidation reaction must then proceed in the EP regime, most likely with a thin oxide layer present at the surface. The oxygen that the authors detect by Rutherford backscattering spectroscopy [143] is consistent with this interpretation.

In addition, the transition between the PS and EP regimes is expected at a fluoride concentration such that $j_{inj} \sim j_{max}$. In figure 6.7 the plateau starts at about 120 $mM$ for 26 $mM$ $Cu^{2+}$, and own measurements in $p-Si$ samples yield $j_{max} \approx 500 \mu A/cm^2$ for the current peak in 120 $mM$ $HF$. If the current plateau of figure 6.7 is taken as a rough indicative of the hole injection current
set by the Cu$^{2+}$ ions, $j_{inj} \approx 170 \mu A/cm^2$ for the case of 26 mM Cu$^{2+}$. This value is not far from $j_{max}$, taking into account that the anodic current in $n-Si$ is not directly due to the injected holes, and thus it provides a lower limit rather than an accurate measurement of $j_{inj}$ (see section 6.1.4). At high enough fluoride concentration, $j_{max}$ is orders of magnitude larger than the Si oxidation current ($j_{inj}$). This guarantees that the oxide is readily dissolved and the anodic reaction proceeds in the PS regime. For example, in the 2 M fluoride solutions employed in chapter 4, $j_{max} \sim 20 mA/cm^2$ whereas the maximum injection current from the $PtCl_4^{2-}/Pt$ system was some hundred $\mu A/cm^2$ at the highest concentrations and stirring conditions employed.
Chapter 7

Technological aspects of metal deposition on silicon from fluoride solutions

In the previous chapters, attention has been focused to a large extent on metal deposition reactions proceeding under open-circuit conditions (i.e. in the absence of applied potential). In order to investigate the reaction mechanisms at the OCP, measurements of current density and faradaic impedance have been carried out under potentiostatic control. In a way, the success of these techniques lies on the availability of an electrode surface having a well-controlled area and very uniform reactivity: The more uniform the reactivity, the more accurate the microscopic interpretation, because the measurements of current density and impedance always correspond to an average over the electrode surface exposed to the electrolyte. For this reason the solution has been allowed to contact only the Si polished side in the experiments presented so far.

In practice, however, open-circuit processes are carried out by simple immersion (of the wafers in this case) without protecting the wafer edges or the rear side, and not controlling the sample OCP. It is therefore worthwhile verifying the applicability of the concepts discussed in the previous chapters to these particular —but widespread— conditions.

In the first part, the different reactivity of the Si samples in the polished and rear side is studied, and its effect during Pt deposition is discussed under both experimental conditions (in-cell, simple immersion). The structural and chemical characterization of Pt—deposited samples (corresponding to early experiments under simple immersion conditions) is presented in a second part. Finally the applications of these processes will be briefly discussed.
7.1 Inhomogeneities in surface reactions

As was described in chapter 3, the samples employed in this study were cut from Si wafers having only one polished side (“active” side, where microelectronic devices are usually fabricated). During the electrochemical measurements described in the precedent chapters, the active side (AS) was exposed to the solutions while the ohmic contact in the rear side (RS) was protected using the sample holder of figure 3.2. In order to extrapolate these measurements to the “simple immersion” situation (when both the AS and the RS are exposed to the solution), the OCP of the Si samples in a Pt—deposition solution was measured under the following conditions:

- AS: As usual, making an ohmic contact on the RS of the sample and exposing the AS to the solution through the sample holder window.
- RS: The ohmic contact was made on the AS, and the rough RS was exposed to the solution through the sample holder window.
- AS+RS: the InGa ohmic contact was made in one end of a rectangle-shaped Si chip, and the other end was immersed in the fluoride solution. In this way both sides can be exposed to the solution and contamination from the InGa is avoided.

The OCP measurements were carried out in solutions 2M HF, before and after addition of PtCl$_4^{2-}$ to a total concentration of 1 mM. The solutions were previously deoxygenated by bubbling with Ar for 15 min, and the bubbling was stopped during the measurements to avoid agitation. The OCPs of $p$—Si in 2M HF were:

\[ U_{OCP}^{AS} \simeq -0.4 \text{ V/SCE}, \quad U_{OCP}^{RS} \simeq U_{OCP}^{AS+RS} \simeq -0.5 \text{ V/SCE} \]

In the presence of the platinum ions, the OCP values obtained were:

\[ U_{OCP}^{AS} \simeq 0 \text{ V/SCE}, \quad U_{OCP}^{RS} \simeq U_{OCP}^{AS+RS} \simeq -0.1 \text{ V/SCE} \]

Using $n$—type samples, no systematic difference between the conditions AS, RS, AS+RS could be detected. The OCP in 2M HF was:

\[ U_{OCP}^{AS} \simeq U_{OCP}^{RS} \simeq U_{OCP}^{AS+RS} \simeq -0.3 \text{ V/SCE} \]

and in 1 mM PtCl$_4^{2-}$:

\[ U_{OCP}^{AS} \simeq U_{OCP}^{RS} \simeq U_{OCP}^{AS+RS} \simeq -0.1 \text{ V/SCE} \]
Figure 7.1: Surface of a $p - Si$ sample after immersion in the 2 $M$ HF, 1 $mM$ $Pt(II)$ solution during 10 min at the OCP. Both the active side and the rear side were exposed to the solution. The roughness of the Si substrate is 0.9 nm RMS.

The injection current from the $PtCl_2^-$ ions (in the absence of stirring) was evaluated at negative potentials in one $p - Si$ sample (AS): $j_{inj} \approx 300 \mu A/cm^2$.

After 10 min at OCP, the AS of the samples was inspected by AFM in order to evaluate the $Pt$ deposited and the etching of the Si substrate. Although some deposition can also be appreciated to the naked eye on the RS, this side is too rough to be imaged with the AFM. Figure 7.1a shows the surface of a $p - Si$ sample after 10 min immersion in the $Pt(II)$ solution exposing both the AS and the RS. As can be seen in the profile (figure 7.1b), the largest $Pt$ nuclei are $\sim 120$ nm high. The roughness of the Si substrate is $\sim 0.9$ nm RMS. When only the AS was exposed to the solution, deposition was observed to take place mostly in the center of the cell window (figure 7.2a) while the region close to the window edge was found to be strongly attacked, with almost no deposition (figure 7.2b). Similar results were obtained with $n - Si$ samples, although the etching reaction tends to be more localized (pitting): The sample of figure 7.3 was immersed in the $Pt(II)$ solution exposing both the AS and the RS (substrate roughness 2.5 nm RMS). When only the AS has been exposed, deposition takes place again in the center of the window (figure 7.4a, substrate roughness 1.9 nm RMS) while the edges are etched (roughness 3.5 nm RMS).
Figure 7.2: Appearance of a $p$–$Si$ sample after 10 min immersion in the $2\, M\, HF$, $1\, mM\, Pt(II)$ solution at the OCP. Only the active side was exposed to the solution through the cell window. Deposition occurs mainly in the window center (a, substrate roughness 1.0 nm RMS) and the regions near the window edge are strongly attacked (b, 9.8 nm RMS).

Figure 7.3: Surface of a $n$–$Si$ sample after 10 min at the OCP in the $2\, M\, HF$, $1\, mM\, Pt(II)$ solution (exposing both the active and rear sides). The substrate roughness is 2.5 nm RMS.
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Figure 7.4: Surface of a n-Si sample after exposing the active side to the 2 M HF, 1 mM Pt(II) solution for 10 min under OCP conditions. As for p-Si, deposition occurs in the window center (a, substrate roughness 1.9 nm RMS), while the region near the edges is mostly etched (b, substrate roughness 3.5 nm RMS).

The negative shift of the OCP can be interpreted in terms of the electrode mixed potential (1.3.3), taking into account the relative reactivities of the AS and the RS. As was explained in 2.1.2, the OCP of Si in aqueous fluoride media is the potential leading to a balance between the Si dissolution reaction (anodic) and the HER (cathodic). The current flowing in both directions at equilibrium (net current zero) was named the “corrosion current”, $j_{\text{corr}}$.

The OCP of p-Si in 2M HF is $U_{\text{OCP}}^{\text{RS}} < U_{\text{OCP}}^{\text{AS}}$, i.e. the band bending is larger when the RS is exposed to the solution (assuming that the bandedge energies are constant). This is shown in figure 7.5A and B (dashed lines). The larger band bending in the RS corresponds to a larger HER current, and indicates that $j_{\text{corr}}^{\text{RS}} > j_{\text{corr}}^{\text{AS}}$. In other words, corrosion kinetics is faster in the RS than in the AS (due to the higher roughness, density of kinks and defects) and a larger HER current is required to balance the dissolution at the OCP when the RS is exposed. When both sides are in contact with the solution, the situation is as for the RS alone, and $U_{\text{OCP}}^{\text{RS+AS}} \simeq -0.5 \text{ V/SCE}$ (figure 7.5C, dashed lines). Therefore the AS is more cathodic than it would be if the RS was protected (figure 7.5A).

In the presence of hole-injecting species ($PtCl_4^{2-}$), this behavior is maintained: The cathodic current imposed by the reduction of Pt(II) ions forces the electrode potential to shift towards positive values, in order to promote
Figure 7.5: Energy diagram of the interface between the Si samples and the fluoride solution (dashed lines), and after addition of PtCl$_4^{2-}$ (solid lines). **A:** exposing only the active side (AS) of p–Si. **B:** Exposing only the rear side (RS) of p–Si. **C:** “simple immersion” situation, where both the AS and the RS of p–Si contact the solution. **D:** Case of n–Si. (The FB potentials have been assumed constant and equal to the measurements of chapter 2, see figure 4.7).

an oxidation current that balances the situation. But if the RS is exposed (figure 7.5C, solid lines), the AS remains more cathodic in relation to figure 7.5A. In this case, the holes can be injected through the AS (Pt deposition) and be evacuated through the RS (Si dissolution). The AS acts as “cathodic side” and the RS as “anodic side”. Note, however, that the band bending in figure 7.5C (and thus the barrier for holes) is equal in both sides: The hole currents are only indicated to illustrate the faster kinetics of the RS.

This is in agreement with AFM results: The p–Si substrate is strongly etched in the samples deposited exposing only the AS, in particular at the window edges (9.8 nm RMS in figure 7.2b). When both the AS and the RS are exposed to the solution, the Si substrate is less damaged (0.9 nm RMS), especially considering that the amount of Pt deposited (about 0.2 μm$^3$ in figure 7.1) is much larger than the volume of etched Si (0.007 μm$^3$ taking a layer 3 × 3 μm$^2$ of thickness 0.9 nm as an approximation). Note that in n–type samples the polished side is strongly etched in all cases (exposure of the AS alone, figure 7.3; or AS+RS, figure 7.4), possibly because holes cannot be evacuated due to the upwards band bending, and the anodic/cathodic regions remain closer (see figure 7.5D).

Concerning the distribution of the deposited and etched regions (in the window center and edge respectively) when the samples are deposited exposing only the AS, it is most likely a diffusion-related effect: A characteristic feature of diffusion-controlled etching profiles is that the dissolution rate of
the solid is enhanced near the mask edge [118]. This is due to two-dimensional diffusion of the etching species, which is easier near the edge as is indicated by the arrows in figure 7.6 [118]. When deposition experiments are carried out using the sample holder, the enhanced mass transport conditions near the window edge may increase the reaction rates (both of Si dissolution and Pt deposition). It can be expected that the removal of material due to the etching process disturbs the deposition reaction, which may be progressively segregated towards the window center. Thus the window center becomes the cathodic site, even if the deposition reaction was initially slow in this region.

In summary, it has been shown that the corrosion rate on the RS is higher than on the AS, and that in certain cases the exposure of the RS makes the potential of the entire sample more negative when both sides are exposed to the solution. In this case, the net balance at the AS is cathodic, and reductive processes will mostly occur. When only the AS is exposed to the solution, anodic and cathodic regions are defined as a result of differential mass-transport conditions in the solution.

### 7.2 Characterization of Pt–deposited samples

The characterization was concerned on the ex-situ structural and elemental analysis of the Si samples deposited with Pt. For that purpose, samples were cut from a wafer and simply immersed in the deposition solution after oxide
etching, and therefore relevant electrochemical parameters like the potential of the silicon sample and the electrolyte, or the hole injection current into the silicon VB due to the platinum ions were not measured. The silicon area exposed to the solution was that of the sample chip in every case ($\sim 1 \text{ cm}^2$) but since the chip edges and the rough back side (more reactive due to the higher density of defects) were not protected, the measurements performed on the deposition rates are somewhat enhanced. However, the use of complementary microscopies (SEM, TEM, AFM) and elemental / chemical analysis (EDX, XPS) gave new insights on aspects that are difficult to investigate using electrochemical techniques. The main results are summarized in the present section.

Unless otherwise stated, the composition of the platinum deposition solutions was $\text{Pt(IV)}$ 1.0 mM in $\text{HF}(40\%) : \text{H}_2\text{O}$ diluted as 1 : 10 by volume (i.e. 2.2 $M$ fluoride and $pH2$). The solution employed to dissolve the silicon native oxide was 1 : 10 diluted $\text{HF}$ (DHF). When necessary, solution $pH$ was raised with $\text{NH}_3\text{OH}$.

7.2.1 First stages of deposition

In this case, $\text{Pt}$ deposits on $\text{Si}$ were investigated at low degree of coverage. No stirring was applied to the solution in order to keep the deposition rate low [157].

SEM and AFM images of the deposited samples on the $\mu$m scale showed that $\text{Pt}$ deposits are formed by hemispherical nuclei of different sizes, uniformly located over the surface (see figure 7.7). This distribution suggests a progressive nucleation process. The bare silicon areas are not unaffected, and AFM reveals a significant increase in roughness and the occurrence of etch pits: in the regions between the nuclei, an enhanced dissolution of silicon is occurring. These results fit well with the effect of a redox system whose energy levels overlap the silicon VB: $\text{Pt(IV)}$ ions reduce and deposit at certain sites on the surface by gaining electrons from the bonding levels of $\text{Si}$ (i.e. by injecting holes into the VB). Strictly, the loss of a bonding electron implies oxidation of that very atom, but in semiconductors the lack of an electron (the hole) is a free charge carrier that can move in the crystal. Thus oxidation does not actually occur until the hole is captured (i.e. the bonding electron is permanently lost), usually at a surface site away from the deposition region. In the presence of fluoride the oxidation products are readily dissolved, and the etching reaction is maintained in these regions (anodic sites). In the cathodic (deposition) sites, $\text{Pt(IV)}$ reduction continues and the nuclei grow.

The texture of the $\text{Pt}$ nuclei that is observed by AFM, corresponds to a
7.2. SAMPLE CHARACTERIZATION

Figure 7.7: Tapping mode AFM images (5×5μm², grayscale: 500 nm) showing that Pt deposition follows a progressive nucleation process: The samples have been immersed in 1 mM Pt(IV), 2 M HF during 3 min (a) and 30 min (b).

Figure 7.8: Cross-section TEM images of the same region in a Si sample after Pt deposition during 30 min. The sample was prepared by the cleavage method (no ion milling). In the bright-field image (a) a different contrast between Pt nuclei and the Si substrate can be observed. The dark-field (b) image shows bright spots in the nucleus contour, corresponding to crystals that give rise to a diffracted electron beam.
polycrystalline structure: This is confirmed by TEM imaging in dark field (figure 7.8b) and by electron diffraction. The crystalline domains have dimensions of about 5 nm, as demonstrated by the atomic-resolution TEM image of figure 7.9. Platinum nuclei have a very high purity, since no other elements can be detected by EDX during SEM/TEM imaging or by XPS. Besides carbon and oxygen contamination at the surface, XPS reveals the presence of a weak fluorine residue (most probably at the bare silicon areas) and a certain degree of silicidation at the Pt | Si interface, that will be discussed later.

7.2.2 Effect of Si doping type

The different behavior of $p$- and $n$-type Si samples during Pt deposition from fluoride solutions was studied at the first stages of the process [140] and in coalescent deposits [158] by SEM, TEM, and AFM. In general, $p$-type samples display a uniform etching on the surface while Pt deposits in a progressive nucleation process. Upon increasing solution stirring, a higher deposition (and hence etching) rate is obtained, and the Pt nuclei eventually coalesce in a continuous, cracked layer (figure 7.10a, b, c). As can be expected from the coupled Pt deposition / Si etching reactions, the existence of anodic regions where silicon can be continuously oxidized and dissolved is necessary to maintain the overall process. This requirement prevents the formation of a uniform, smooth Pt layer.

On the other hand, the process has a markedly local character in $n$-type substrates (figure 7.10d, e, f), in the sense that cathodic and anodic sites ($Pt$ nuclei and deep pits, respectively) are found very close to each other, leaving wide areas completely unaffected for relatively long deposition times. In addition, an “induction time” for the process is found, i.e. deposition is significantly delayed with respect to the $p$-type substrate. This behavior is not very surprising, since the carriers involved in the exchange of charge between the cathodic and anodic regions are holes, and these are minority carriers in $n$-type semiconductors (they have a limited diffusion length due to recombination). This is confirmed by the quenching of the “local” effect on illuminating the sample during deposition.

More puzzling is the growth of big (about 1 µm) nuclei several hundred nm underneath the silicon surface (figure 7.11). They nucleate presumably at the bottom of etch pits or pores, and grow at the expense of the surrounding silicon forming a buried layer. The strong modification of the Si structure in these regions is visible in the TEM cross-sections (see the high contrast regions in the substrate of figure 7.12, and a detail in figure 7.13). This is interpreted as the formation of a porous silicon (PS) layer and is the object
Figure 7.9: High-resolution TEM micrograph of a Pt-deposited Si sample (cross-section specimen prepared by polishing and nitrogen-cooled ion milling). The atomic planes are visible both in the substrate (bottom) and in the polycrystalline Pt nucleus (top).
Figure 7.10: Series of SEM micrographs showing the evolution of the Pt deposits on p – Si (abc) and n – Si (def). Magnification is the same for all images. Deposition times are 15 (a, d), 30 (b, e) and 60 min (c, e). The fuzzy white spots referred in the text can be observed in (e).
of the following section.

The distribution of $Pt$ nuclei and PS regions can be understood qualitatively using the 3-D diagrams developed in chapter 4 (figures 4.19 and 4.20). At the cathodic regions ($Pt$ nuclei), holes are injected by platinum ions into the $Si$ substrate. As was shown in figure 4.19b, the hole concentration at the anodic regions (bare $Si$) is different in $p$- and $n$–$Si$: In $p$–$Si$, holes are accumulated at the surface due to the upwards band bending, and can produce the oxidation of $Si$ in all the bare substrate regions in contact with the solution. On the contrary, the double band bending in $n$–$Si$ results in a “well” for holes, and the maximum hole concentration is found at a certain depth from the surface. This suggests that dissolution of $n$–$Si$ is enhanced at these sites, and allows the PS layer to grow thicker.

### 7.2.3 Porous silicon formation

The porous appearance of the $n$–$Si$ substrate after $Pt$ deposition (figures 7.11a, 7.12 and 7.13), and most of all, the fact that the deposited samples display photoluminescence (PL) in the visible range, prompted a more detailed and accurate analysis of the silicon half-cell reaction [132]. Indeed, despite being an indirect-gap semiconductor, silicon can be rendered photoluminescent by anodization in fluoride media, a process that results in the formation of a PS layer at the sample surface. PS is usually fabricated passing large anodic currents (up to 100 m$A$/cm$^2$) through the $Si$ sample immersed in concentrated $HF$ solutions, which are conditions quite distant from those employed in the deposition of $Pt$ (diluted $HF$, OCP).

In order to establish a correlation, it was compulsory to study the system under well-defined electrochemical conditions (see section 4.3.1): A sample holder was used to expose to the solution only a controlled area of the $Si$ active side, providing at the same time an electric contact to the electrode. A reference electrode and a counter electrode connected to a potentiostat completed the classical “three-electrode configuration”, allowing to control simultaneously the sample potential and the current passing through. Using this experimental setup, the maximum current density for PS formation in the diluted $HF$ solution employed for $Pt$ deposition, was precisely located at 20 m$A$/cm$^2$ (figure 4.12). On the other hand, the $Si$ oxidation current that balances $Pt$ deposition was determined from the measurement of hole injection at negative potentials in $p$–$Si$, and turned out to be of some hundreds of $\mu$A/cm$^2$, well below the maximum PS current. This confirmed that during $Pt$ deposition at the OCP, the $Si$ oxidation reaction taking place at the anodic sites of the surface is analogous to the one employed for the fabrication of photoluminescent PS layers.
Figure 7.11: Appearance of the Pt–deposited n–Si samples by SEM (a, b) and TEM (c). At low accelerating potentials (a), the SEM image is obtained from secondary electrons and is essentially topographic. On increasing the imaging potential (b), the contribution from backscattered electrons allows to visualize the Pt nuclei underneath.
**7.2. SAMPLE CHARACTERIZATION**

Figure 7.12: TEM cross-section of a n–Si sample deposited with Pt. The metal nuclei grow underneath the surface plane and the substrate regions exposed to the fluoride solution display a different contrast.

PL in the Pt–deposited samples was visible to the naked eye as a red-orange glow when putting them under an ultraviolet lamp. The PL spectra could be measured using a 6 W argon laser (λ = 457 nm, blue). As an example, the PL spectrum of a p–Si sample deposited with Pt (hole injection rate of 50 μA/cm² during 60 min) is shown in figure 7.14.

X-ray diffraction results (figure 7.15) also indicate the presence of a layer on the Pt–deposited samples that is similar to the surface of anodized PS.

The visible PL of the Pt–deposited samples points out a possible application of the process. As was explained above, radiative recombination in Si is hindered by the fact that it is an indirect bandgap semiconductor. In addition, its bandgap energy (corresponding to 1.1 μm, infrared) lies below the visible light spectrum. However, the discovery of the photoluminescent properties of PS [78] aroused the interest on the possible optoelectronic applications of Si. The formation of PS displaying intense PL in the visible range has been widely studied ever since, and extensively reviewed very recently [159]. One of the major technical difficulties that must be solved in PS-based electroluminescent devices is the buildup of high-quality electric contacts, because the PS material is considerably fragile and the pores surface is difficult to access. Physical vapor deposition of gold, aluminum and indium-tin-oxide glass (ITO) is usually employed to fabricate electric contacts on PS, although this technique provides little penetration of the conducting material into the pores. Several attempts have been also done to deposit metals by electroless or electrochemical means on PS layers that had been previously grown using a different process [160, 161, 162]. In contrast, the process presented
here allows to \textit{simultaneously} produce a PL layer and deposit metal nuclei on the surface, which may improve the performance of subsequent electric contacts to the porous layer. Interestingly, this process works in \textit{p– and} \textit{n–Si} in the dark and both substrates yield similar PL spectra, whereas intense illumination is required to anodize \textit{n–Si} using the standard procedures.

\textbf{7.2.4 Effect of solution pH}

As was shown in figure 2.8, the \textit{pH} of the fluoride solution has a great influence on the silicon etch rate at the OCP, as well as in the relative importance of the chemical and electrochemical etch mechanisms. In the presence of platinum ions, however, both the deposition and the (enhanced) etch rates are
7.2. SAMPLE CHARACTERIZATION

Figure 7.14: Photoluminescence spectrum of a p–Si sample after immersion in the Pt deposition solution at the OCP for 60 min. The injection current was 50 μA/cm².

governed by the current of holes injected from the Pt ions, rather than by the fluoride. And this is a diffusion-limited current that can be increased with the metal concentration or with solution stirring. Thus the effect of changing the pH of the Pt deposition solution is to be expected not on the rate of the process but on the character of the reaction.

The platinum deposition solution, as-prepared from HF 1 : 10 has pH2, and the deposits obtained have been discussed in the previous sections. For comparison, solutions of pH3.5 (after addition of NH₄OH) and pH < 1 (using HCl) were tested under the same deposition conditions as early studies (Si chips of 1 cm² were simply immersed in the deposition solution after oxide etching in diluted HF; no stirring was applied during deposition). Solutions of pH > 3.5 were found to be unstable and could not be investigated in those experiments. At pH < 1 deposition is completely prevented and, consistently, no enhanced etching can be noticed on the Si surface: Samples are apparently unaffected by the deposition solution. These results were initially attributed to simple displacement of the complexation equilibrium of PtCl₆²⁻ ions (in a very coarse approach, PtCl₆²⁻ → Pt⁺ + 6Cl⁻ displaces to the left on addition of a strong HCl concentration) and were therefore disregarded [19]. Although this effect cannot be ruled out, the results are also consistent with the discussion to come, and hence they have been included here. At pH3.5, the Pt nuclei density and the total amount of metal is similar to those obtained at pH2, and the enhanced etching of the Si substrate produces a similar roughness in both solutions. This result is in agreement with the expectations, as was explained above. However, a different arrangement of
the nuclei on the substrate is found at the higher pH: AFM images show that Pt nuclei are “nailed” into the silicon, and have a wedge shape that is clearly visible in TEM cross-sections (figure 7.16). The interface between Pt and Si in figure 7.16b reminds of a preferential (anisotropic) etching in the \{111\} crystallographic direction. Fluoride solutions of alkaline pH are known to etch Si anisotropically, producing similar pyramidal pits in Si(100) that result in a great increase in surface roughness [96]. This effect is attributed to the local or chemical mechanism of Si etching, which is the prevailing one beyond pH8 (see figure 2.8 and reference [4]). Indeed, an increase of the Si – H monohydride termination (associated to (111) facets) was detected by electron energy loss spectroscopy during the deposition of copper on silicon from HF solutions [163].

With these ideas in mind, the fact that Pt does not deposit on Si from very acidic solutions (pH < 1) can be explained by the low Si etching rate, about 0.02 nm/min: the anodic current that corresponds to this reaction is as small as 500 nA/cm^2 (see section 2.2.2) and can be easily balanced by the HER. Platinum ions do not even participate in the current balance and are thus unable to enhance the Si etching through hole injection. In a sense, the autocatalytic behavior of Pt deposition is hindered at low pH. Under another point of view, the fact that the chemical path of Si dissolution is practically stopped at pH < 1 could also play a role: This chemical dissolu-
Figure 7.16: Appearance of the Pt deposits from solutions of pH2 (a) and pH3.5 (b): the wedge shape of the nucleus of figure b is probably related with the relatively more anisotropic etching of silicon at higher pH.

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Figure 7.17: XPS spectra profiles (Pt and Si peaks) of a p – Si sample after 30 min Pt deposition. The first two spectra (bottom) are acquired before sputtering the sample with an argon ion beam. The spectra above are acquired after successive sputtering cycles (depth profile).

silicide and metallic bonds are approximately equal. On the other hand, samples deposited at pH3.5 have an almost constant metal / silicide signal ratio of 2.5 along a depth twice as high as samples of pH2 [19]. As can be seen in figure 7.19, no relevant difference is found between the XPS spectra profiles in n- and p-type samples, besides a factor 2 in the intensity of the peaks (due to the higher deposition rate in p – Si) and the presence of about 5% atomic concentration of Pt – O and Si – O bonds in p – Si samples [140]. These results seem to suggest that the silicide is mainly found at the nucleus | substrate interface at low pH, while it is more steadily produced during the deposition at higher pH. A morphologic artifact in the XPS data cannot be discarded, though, in view of the different shape of the Pt | Si interfaces (figure 7.16). In addition, the XPS spectra were acquired in non-coalescent platinum deposits during the studies of the first stages of deposition. Therefore they contain data mixed from the Si substrate and the Pt nuclei, and the information that can be drawn is limited: For instance, the silicide peak that is always detected corresponds to a formal valence of Pt$_2$Si, but this proportion cannot be confirmed from the atomic concentration data due to the intense contribution of the bare Si areas.

Platinum silicide layers on p – Si provide a low Schottky barrier height, and have technological applications as infrared detectors. These layers are
usually obtained by Pt evaporation in vacuum, annealing at $\sim 450^\circ C$ to form a silicidated interface, and removal of the unreacted Pt with selective etching solutions. The chemical formation of a silicide should be very interesting in microelectronics because it would avoid the many drawbacks of furnace annealing on chip devices: Doping diffusion, thermal stress, materials interaction, etc. Note that, although quite surprising, the reaction of Si with metals during vacuum deposition at room temperature is well documented: Ti [164], Ni [165] and especially Pt [166, 167, 168, 169, 170] are known to form intermixed metal-silicon layers of a few nm after evaporation or sputtering at room temperature. In particular, XPS [168] reveals that Pt layers 2 nm thick evaporated on Si are fully reacted to PtSi at room temperature, which has been confirmed by own measurements. Of course the silicidation can be helped by an increase in the sample temperature due to the evaporation / sputtering process, but the results at least point out the relatively high reactivity of Pt and Si. More recently, Donaton et al. [170] speculated that the transformation of the intermixed Pt $- Si$ layer into PtSi in samples that had not been annealed could be due to a short-range diffusion during the selective etch step. In particular, the Pt—etching aqueous solutions employed in [170] are based in $HNO_3$ (a strong oxidizing agent) and $HCl$, which acts as a complexing agent of the Pt oxidation products. When the intermixed layer is reached, $HNO_3$ oxidizes Si but $HCl$ cannot dissolve it: The etching stops and the diffusion of Si caused by the oxidation process promote the
formation of a thin $PtSi$ layer. This could be a more relevant mechanism for the samples deposited with $Pt$ from fluoride solutions: $Pt$ ions themselves oxidize the $Si$ during deposition. But since fluoride is a complexing agent of silicon, the reaction is not stopped and result in great amounts of both platinum silicide (near the interface) and metallic platinum in the nuclei outer shell.

The study of fluoride solutions of $pH > 3.5$ would be very advantageous in order to verify these interpretations. For that purpose, buffered $HF$ solutions (i.e. $NH_4F$ solutions acidified with $HF$) must be employed to overcome stability problems. Preliminary measurements on samples deposited at $pH6.5$ indicate an increase in the silicide ratio, further confirming this point.

To finish, it must be added that deposition of $Pt$ from fluoride solutions is
always preferential at coarse surface flaws such as intentional scratches, even not visible to the naked eye. At a more microscopic scale, $Pt$ deposition solutions of $pH$3.5 yield different deposition rates on samples that have been damaged with several doses of argon ion implantation [19]. This defect-revealing behavior is favored at high $pH$ due to the local character of the reaction, and was the original object of the study presented in reference [19].

### 7.2.5 Effect of the oxidation state of $Pt$ ions

Besides $pH$, another relevant parameter of the deposition solution is the oxidation state of the metal ions. In order to investigate its effect on the deposition process and other closely-related aspects like ion solvation, two different $Pt$ ions were employed to prepare the solutions: $PtCl_2^- \ (\text{which corresponds to oxidation state (IV) of } Pt \text{ and } PtCl_2^- \ (Pt(II))$. The first visible effect is the higher deposition rate of $Pt(II)$ solutions, as well as the improved uniformity and reproducibility of the deposited layers. This made $Pt(II)$ preferable for most of the subsequent studies (e.g. the fabrication of Schottky diodes or the study of hydrogen incorporation during $Pt$ deposition, see chapter 4), but also evidenced that controlled electrochemical conditions (namely, injection rate) were required in order to correlate $Pt(II)$ and $Pt(IV)$ solutions. Silicon samples deposited using both solutions under comparable conditions (1 mM $PtCl_2^-$ and 100 $\mu$M $PtCl_4^-$ in HF 1 : 10, and adjusting the stirring such as to obtain $\sim 70 \ \mu A/cm^2$ in every case) were inspected by SEM and displayed qualitatively the same features: A comparison between $p - Si$ and $n - Si$ substrates deposited from the $Pt(II)$ solution show again the local deposition and etching in $n - Si$, including the “nailed” nuclei, while the process is more uniform in $p - Si$. However, the detailed appearance of the samples deposited from $Pt(II)$ and $Pt(IV)$ under equivalent conditions is not identical: The density of $Pt$ nuclei is larger in figure 7.20 (top, $Pt(II)$ solution) while the nuclei size is much smaller, suggesting that nucleation is easier from $Pt(II)$ solutions and that growth is more favored in $Pt(IV)$.

In an attempt to account for this difference, the electrochemical reduction of $Pt(II)$ to metallic $Pt$ is written as given in the tables [171]:

$$PtCl_2^- + 2e^- \rightarrow Pt^0 + 4Cl^- \quad E^\circ = +0.5V/SCE \quad (7.1)$$

The reduction of $Pt(IV)$ to $Pt$ (reaction 7.4) can be expressed as the sum of two steps, a previous one comprising $Pt(IV) \rightarrow Pt(II)$, followed by the reaction written above (7.1):

$$PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^- \quad E_1^\circ = +0.5V/SCE \quad (7.2)$$
Figure 7.20: Appearance of the deposits obtained on p – Si from fluoride solutions containing Pt(IV) (top) and Pt(II) (bottom) under comparable conditions (electrochemically controlled in the cell).
\[ \text{PtCl}_4^{2-} + 2e^- \rightarrow \text{Pt}^0 + 4\text{Cl}^- \quad E_2^o = +0.5V/SCE \quad (7.3) \\
\text{PtCl}_6^{2-} + 4e^- \rightarrow \text{Pt}^0 + 6\text{Cl}^- \quad E_3^o = +0.5V/SCE \quad (7.4) \]

The calculated potential for the total reduction of Pt(IV) ions is again +0.5 V/SCE, which can be explained intuitively as follows: Since the two tabulated steps (a, b) have the same reduction potential, whenever this potential is applied, both reactions can occur successively. This means that, in a coarse approach, the reduction of platinum from either PtCl\(_6^{2-}\) or PtCl\(_4^{2-}\) is energetically the same. The difference, of course, concerns the amount of charge that they take (twice as much for Pt(IV) than for Pt(II)), i.e. every Pt(II) ion injects two holes to reduce and deposit as Pt on the surface, while four holes are injected from every Pt(IV) ion.

The higher deposition rate displayed by Pt(II) ions must then be due to kinetics, in agreement with the notion that the PtCl\(_6^{2-}\) complex is “heavier” than PtCl\(_4^{2-}\). A more detailed analysis reveals an even greater difference, because the most abundant form of Pt(II) ions is actually PtCl\(^{+}\). Considering the complexation equilibria of PtCl\(_4^{2-}\) and PtCl\(_6^{2-}\) and their corresponding equilibrium constants [172]:

\[ \text{PtCl}_4^{2-} \leftrightarrow \text{PtCl}_5^- + \text{Cl}^- \quad K_1 = \frac{[\text{PtCl}_5^-] \cdot [\text{Cl}^-]}{[\text{PtCl}_4^{2-}]} = 0.0126 \quad (7.5) \]
\[ \text{PtCl}_5^- \leftrightarrow \text{PtCl}_2 + \text{Cl}^- \quad K_2 = \frac{[\text{PtCl}_2] \cdot [\text{Cl}^-]}{[\text{PtCl}_5^-]} = 0.0011 \quad (7.6) \]
\[ \text{PtCl}_2 \leftrightarrow \text{PtCl}^+ + \text{Cl}^- \quad K_3 = \frac{[\text{PtCl}^+] \cdot [\text{Cl}^-]}{[\text{PtCl}_2]} = 0.0001 \quad (7.7) \]
\[ \text{PtCl}_6^{2-} \leftrightarrow \text{PtCl}_5^- + \text{Cl}^- \quad K_4 = \frac{[\text{PtCl}_5^-] \cdot [\text{Cl}^-]}{[\text{PtCl}_6^{2-}]} = 0.3846 \quad (7.8) \]

Neither the complexation equilibrium of PtCl\(^{+}/\text{Pt}^{2+}\), nor those below PtCl\(_6^{2-}/\text{PtCl}_5^-\) were found in the literature, and thus they have been neglected. Equations 7.5-7.8 must be rewritten as a function of the ion added with the corresponding salt (PtCl\(_4^{2-}\), PtCl\(_6^{2-}\)):

\[ \text{PtCl}_4^{2-} \leftrightarrow \text{PtCl}_3^- + \text{Cl}^- \quad K'_1 = \frac{[\text{PtCl}_3^-] \cdot [\text{Cl}^-]}{[\text{PtCl}_4^{2-}]} = 0.0126 \quad (7.9) \]
\[ \text{PtCl}_4^{2-} \leftrightarrow \text{PtCl}_2 + 2\text{Cl}^- \quad K'_2 = \frac{[\text{PtCl}_2] \cdot [\text{Cl}^-]^2}{[\text{PtCl}_4^{2-}]} = K_1K_2 \quad (7.10) \]
\[ \text{PtCl}_4^{2-} \leftrightarrow \text{PtCl}^+ + 3\text{Cl}^- \quad K'_3 = \frac{[\text{PtCl}^+] \cdot [\text{Cl}^-]^3}{[\text{PtCl}_4^{2-}]} = K_1K_2K_3 \quad (7.11) \]

Given an initial concentration of PtCl\(_6^{2-}\) and PtCl\(_4^{2-}\), numerical resolution of the above equations yields that the most abundant forms of Pt(IV)
and \( Pt(II) \) are \( PtCl_5^- \) and \( PtCl^+ \) respectively. It is thus clear that, besides the charge necessary for the reduction to the metal form, \( PtCl_5^- \) complexes must get rid of five \( Cl^- \) ions in relatively complicated steps, whereas the release of one \( Cl^- \) from \( PtCl^+ \) complexes is likely to be a much faster process. In addition, \( PtCl^+ \) is more electrophillic, because its net charge is positive. This is probably at the origin of the different behavior displayed by \( Pt(II) \) and \( Pt(IV) \) solutions (figure 7.20): While \( PtCl^+ \) ions can continuously give rise to new nuclei on the Si surface, the reduction of \( PtCl_5^- \) is preferential at the existing nuclei, and result in a slow, well-ordered growth (note the crystalline appearance of the deposits of figure 7.20, top).

### 7.3 Applications

Although the main objective of this thesis has been to elucidate the mechanisms of metal deposition, the findings that have been exposed allow to envisage several applications.

Deposition of metals on silicon from fluoride solutions (and its consequences, like enhanced substrate etching), has been found to occur spontaneously when the reduction potential of the metal redox system is more positive than \( U(H^+/H_2) \). Another key parameter is solution \( pH \), which plays mainly on the OCP etching rate of Si. When the aim is to keep the Si surface as flat and clean as possible, the electroactive contaminants to be avoided are those having a redox potential more positive than \( U(H^+/H_2) \). Cleaning solutions must then be purified with special attention to these contaminants, which include noble metals but also redox systems like \( Cr^{6+}/Cr^{3+} \) or \( O_2/H_2O \), that do not produce deposits but are equally able to enhance substrate corrosion. On the other hand, species having a redox potential more negative that \( U(H^+/H_2) \) allow a higher tolerance.

Special caution is recommended on raising solution \( pH \), because the higher etching rate of silicon and the reduced availability of protons may allow the charge exchange with species that were ”inert” at low \( pH \). Keeping the \( pH \) as low as possible is thus advantageous for these applications, and in many cases it has the additional benefit of improving the stability of metal ions in solution. In this way, adding suitable complexing species can also help to tolerate trace amounts of potentially damaging metals.

These solutions can also be employed to deposit metal layers for several applications. In particular, the appearance of \( Ni \) and \( Cu \) deposits is shown in figure 7.21. They have been obtained by simple immersion at the OCP on \( Si \) samples having a \( Si_3N_4 \) mask. For comparison, layers prepared by the application of potential pulses using the same masked samples are shown in
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Figure 7.21: Ni and Cu layers (left and right respectively) deposited from fluoride solutions at the OCP on a p–Si substrate having a photolithographically patterned Si$_3$N$_4$ mask.

Figure 7.22: Pt and Cu layers (left and right respectively) electrodeposited on a n–Si substrate having a patterned Si$_3$N$_4$ mask. Note the larger nuclei size and the enhanced deposition rate at the mask edges.
Figure 7.23: The “sacrificial anode” concept applied to Si processing: A porous Si region (bottom of figure a) is formed by in-cell anodization while protecting the rest of the sample surface. When immersing the as-prepared sample in a Pt deposition solution (HF 1 : 10, 1 mM Pt(II), 5 min immersion at the OCP), the porous Si region is strongly corroded but produces an enhancement of the cathodic reaction in the flat Si regions (not exposed to the previous anodization, figure b). The deposition rate can be compared to those of figure 7.10.

The reported formation of porous Si during Pt deposition from relatively concentrated HF solutions can also have some advantages. Given the fragility of the PS material obtained using the standard procedures (anodization), the subsequent fabrication of good metallic contacts is difficult. These contacts are necessary for the fabrication of electroluminescent devices. The immersion of Si in Pt—containing fluoride solutions at the OCP can therefore be presented as an interesting method for simultaneously depositing a metal and producing a photoluminescent PS layer.

The room-temperature formation of Pt silicide by direct reaction can also be interesting to obtain the silicide without thermal processes, which have many disadvantages (doping diffusion, thermal stress and undesired aliasing).

The aspects of inhomogeneous reactivity treated in this chapter deserve at least two considerations: First, if a region with enhanced anodic reactivity is present in the sample, all cathodic reactions will be promoted on the other regions. In this case, special care must be taken that no potentially
damaging electroactive contaminants are present in the solution. On the other hand, this is interesting to enhance the cathodic reactions in a certain region, like in the example of figure 7.23. Of course the same principle can be employed to confine unwanted anodic processes by the pre-patterning of anodic/cathodic regions (concept of “sacrificial anode” used in the technology against corrosion). As another example, the atomic flattening of Si(111) surfaces by immersion in $NH_4F$ solutions, is greatly enhanced in the presence of anodic regions (e.g. the rough backside of the Si wafer): In this case, the only electrochemical process on the active side is cathodic (HER) and the anisotropic chemical etching proceeds more efficiently [173].
Chapter 8

Conclusions

The spontaneous deposition of metals on silicon from aqueous fluoride solutions has been investigated. The study has focused on the deposition mechanism of several metals as a function of the potential of the corresponding redox system, as well as on the effects of the deposition process on the silicon substrate.

In the introduction, the basic concepts of semiconductor electrochemistry have been summarized, with special emphasis on the potential distribution through the semiconductor | electrolyte interphase, and the coupling between two simultaneous electrochemical reactions occurring at the electrode surface.

The second chapter has reviewed the electrochemical behavior of silicon in aqueous fluoride media, and has outlined the recent advances in the understanding of the dissolution mechanism and the nature of the electrochemical equilibrium. Water molecules are able to react with silicon surface atoms, giving rise to an oxide layer. Fluoride species act mostly as a complexing agent of the oxidation products: They leave a hydrogen-terminated surface and allow the oxidation reaction to proceed. In the absence of externally-applied potentials, the response of the electrode to the oxidation reaction is to produce a cathodic reaction having the same rate and opposite current sign (hydrogen evolution in water). The open-circuit potential of silicon in aqueous fluoride solution is thus the electrode potential required to produce this counterreaction.

In order to electrochemically deposit a metal on the silicon surface (either applying an external potential or at open-circuit), electrons must be transferred from the semiconductor to the metallic ions in the solution. In the surface of hydrogen-terminated silicon, electrons are only available at energies near the valence bandedge (bonding electrons) or near the conduction bandedge (free electrons in $n$–type silicon under accumulation or in illuminated $p$–type). Metal deposition reactions involving bonding and free
electrons are studied separately in chapters 4 and 5:

The redox energy of the Pt(II)/Pt system in solution lies near the silicon valence band edge, and platinum ions can be reduced by the transfer of silicon bonding electrons. Under open-circuit conditions, the response of the electrode to this reductive reaction is an enhancement of the anodic oxidation reaction, until both processes have the same rate. The result is the simultaneous deposition of platinum and etching of the silicon substrate. Some details of the anodic and cathodic reactions are further investigated: The formation of porous silicon, the incorporation of hydrogen into the electrode and the potential distribution on the surface plane as a result of the distribution of metal deposits and bare substrate regions.

The redox energy of the Ni(II)/Ni system lies within the silicon bandgap, which allows the study of electron transfer involving both the conduction and valence bands. The focus in this case is on the competition between hydrogen evolution and nickel reduction as the cathodic counterreactions. It has been found that, under conditions where the silicon rate is low (namely, in acid solutions), hydrogen evolution prevails and nickel cannot be deposited. In other words, nickel reduction is not needed to balance the rates of the anodic and cathodic reactions. Increasing the silicon oxidation rate and decreasing the hydrogen evolution rate (e.g. in alkaline solutions) allows nickel deposition to participate in the overall process. A microscopic interpretation is presented taking into account the surface intermediates of the silicon dissolution reaction.

The studies of platinum and nickel deposition, together with some selective experiments with other metals and a review of the available literature, allow to generalize the deposition mechanisms to other cases and conditions. This has been presented in chapter 6. Anodic and cathodic reactions are simultaneously occurring at the electrode surface: They can be investigated using voltammetric experiments and playing with parameters like solution $pH$, mass transport conditions, sample type ($n$ or $p$) or illumination. At the open-circuit potential, anodic and cathodic reactions are balanced and there is no net current flow through the interface. On the cathodic side, a competition exists between hydrogen evolution and the reduction of metal ions. It appears to be governed by the oxidizing power of metal ions relative to the $H^+/H_2$ system. On the anodic side, either the condensation of silicon oxide or its dissolution in the fluoride media can be rate-limiting, and the relevant parameters in this case are solution $pH$, fluoride concentration and mass-transport conditions of the oxidizing agent.

The last chapter attempts to bridge the gap between the in-cell electrochemical studies and their technological applications. It is found that regions
having a different reactivity may affect the overall process in certain cases. In particular, the exposure to the solution of regions having a high corrosion rate, may enhance the rate of the cathodic reactions in the other regions. Ex-situ morphological and chemical studies are also presented in this chapter for the case of platinum deposition. These include the first deposition stages, the effect of the silicon doping type, the formation of porous silicon, the effect of solution $pH$ and of the oxidation state of platinum ions. Finally some applications in several fields are discussed.

Besides the specific conclusions outlined above, three major methodological conclusions can be drawn from this study:

- Electrochemical techniques are unique tools to investigate the charge exchange processes occurring at the semiconductor | solution interface: They provide in-situ, real-time information having monolayer resolution. The relatively simple experimental setup can be easily combined with other techniques. And more importantly, they give an insight into the mechanism of the reactions.

- The hydrogen-terminated surface of silicon in fluoride media is fairly ideal from an electrochemical point of view. In addition, the monocrystal surface can be made ideally (atomically) flat using chemical methods. It is therefore a very promising system for fundamental studies.

- Ex-situ techniques provide complementary information regarding the chemistry and morphology of the samples. Once the basic mechanisms have been understood, these techniques help to deduce the details of a specific process with regard to its technological application in the fabrication of devices.
Appendix A

Electrochemical AFM study of silicon etching in NaOH media

A.1 Introduction

Electrochemical measurements under potentiostatic control have been employed in chapters 4, 5 and 7 to obtain in-situ information on the reaction mechanisms of several processes. However, they still provide data that is averaged over the entire sample area. Ex-situ imaging using scanning probe microscopy has proved to be a useful tool to investigate the details of these reactions at a local level with nanometer resolution. The disadvantage in this case is that all processes are stopped when the sample is withdrawn from the solution, rinsed, dried, and brought into the microscope.

Combining both techniques is therefore highly desirable, and several electrochemical studies have been carried out using in-situ scanning-probe microscopies. In particular, the Si surface has been investigated by scanning tunneling microscopy (STM) during immersion in several aqueous solutions under potentiostatic control: $H_2SO_4$ [174], $NaOH$ [5, 88] and $NH_4F$ [4, 175, 176, 177]. A review of the electrochemical applications of these techniques can be found in reference [178], and also in [134, 139] with special emphasis on semiconductor electrodes.

In-situ AFM studies are less abundant [95, 179] and all of them have been performed without controlling the sample potential in the solution. In this appendix, an electrochemical AFM study of Si etching is presented for the first time. The preliminary results are intended to demonstrate the capabilities of this technique as well as to describe the difficulties that are encountered in practice. The system chosen for this study (anisotropic etching of $n-Si(111)$ in aqueous $NaOH$ solutions at potentials negative of OCP) was
previously investigated using EC-STM [5, 88] and Monte-Carlo simulations [180], which will allow a comparison of the results.

A.2 Experimental details

The cleaning procedure employed in these experiments was slightly different from that described in chapter 3 for electrochemical measurements. The Si(111) samples (1 Ω · cm, Siltronix [106]) were introduced in the Piranha solution for a few minutes, then thoroughly rinsed with flowing MilliQ water and dried in a furnace at 60°C. This helped to improve wetting of the sample by organic solvents (not miscible with water) in the following cleaning steps. Organic contamination was removed in boiling trichloroethylene during 3 min, and the sample was subsequently dipped in acetone and methanol [4], prior to rinsing in MilliQ water. Metallic contaminants were removed in boiling chromic mixture (H₂SO₄ : H₂CrO₄, 1 : 1) or a commercial labware washing product [111]. This cleaning procedure was done immediately before the experiments, but the clean (oxidized) Si chips can also be stored in a MilliQ water for a few days until they are used.

Concentrated HF was used to dissolve of the SiO₂ layer (less than 1 min for native oxide), which leaves an H—terminated surface. Atomically-flat terraces were produced by immersion in concentrated NH₄F during 5 min. The hydrophobic sample was then mounted in the microscope cell without any further rinse, and the cell was filled with 2 M NaOH. The sample potential was previously set to a value negative of OCP (U_{OCP} = −1.0 V/SCE in 2M NaOH, pH13.5) in order to accumulate electrons at the surface and prevent the electrochemical dissolution reaction. As was explained in chapter 2, the electrochemical reaction is isotropic and damages the terrace structure, even at the OCP. In this way the chemical path of the dissolution reaction (anisotropic and independent of the applied potential) can be observed.

The AFM images were obtained in contact mode with a Molecular Imaging PicoSPM head [181] controlled with Nanoscope III electronics [103]. The AFM probes were OMCL-TR400PSA2 (nominal spring constants 0.02 N/m, 0.09 N/m) and occasionally TR800PSA2 (0.16 N/m, 0.68 N/m), manufactured in Si₃N₄ by Olympus [182]. The electrochemical cell and the cantilever holder were modified for optimum performance. The three electrodes (the Si sample (WE) and two Pt wires acting as CE and pseudo-RE) were controlled using the manual potentiostat described in chapter 3.

The choice of the experimental conditions had to meet several requirements, which were conflicting sometimes: Stiff cantilevers (spring constant ~ 0.68 N/m) provided the most stable AFM conditions, but often exposed
the sample to mechanical damage (e.g. due to an unnoticed drift in the force setpoint). Sometimes a “square” left by the previous scan could be observed on zooming out (figure A.1). On the other hand, softer cantilevers turned out to be more sensitive to instabilities and, more importantly, to the $H_2$ bubbles produced on the surface (due either to the HER reaction at negative potentials or to the simultaneous $Si$ dissolution reaction, see chapter 2): Hydrogen bubbles are progressively attached to the cantilever, thereby disturbing the laser optical path or pulling the tip off the surface. This effect was unavoidable in all cases, although it could be substantially delayed using stiffer cantilevers (at the risk of scratching the surface). An acceptable compromise could be achieved with 0.16 $N/m$ cantilevers, provided that the force setpoint (of a few $nN$) was frequently verified.

At the HER current employed in the experiments (see below), continuous
imaging at a fixed region of the sample surface was usually limited to \( \sim 5 \text{ min} \) at best (i.e. less than three 256 \( \times \) 256 pixel images at a scan frequency of 2 \( Hz \)). When such unstabilities occurred, the operation of the AFM could only be restored by withdrawing the cantilever from the cell (while keeping the sample under cathodic current flow), rinsing energically both the \( Si \) surface and the cantilever with the \( NaOH \) solution (in order to remove the bubbles) and bringing the AFM probe back into the cell after rearranging the laser alignment. Of course, the sequence had to be restarted in a new region.

The HER current can be reduced in order to minimize these problems, but then the surface remains flat for a shorter time. In figure A.2A (100 \( \mu A/cm^2 \)), the \( Si \) electrode was strongly pitted by the moment a stable image could be obtained. The \( Si \) steps are then too close to each other, and can barely be resolved with the AFM tip (10 \( \sim \) 20 \( nm \) diameter of the tip apex). Usually, currents around 300 \( \mu A/cm^2 \) allowed several attempts in different regions and gave better results. Note that the HER currents employed during EC-STM experiments are about three times lower \[180\], because the STM probe is not disturbed by \( H_2 \) bubbles.
A.3   RESULTS AND DISCUSSION

Figure A.3: EC-AFM image (500 × 500 nm², 3 nm vertical range) of the Si surface immersed in 2M NaOH under 300 µA/cm² cathodic current. All steps are ∼ 0.32 nm high, corresponding to one biatomic layer. Triangular etch pits have straight edges parallel to the [110] direction.

A.3   Results and discussion

Figure A.3 shows a 500 × 500 nm² image of the Si surface under 300 µA/cm² cathodic current. All steps are ∼ 0.32 nm high, corresponding to one biatomic layer (0.31 nm, see figure 2.6 for the crystallographic model). Triangular etch pits have straight edges parallel to the [110] direction.

Once the problems described above have been minimized, AFM imaging allows to record long-range images during reasonable periods of time, and even in the presence of small amounts of contamination on the surface. A time sequence of a 1 × 1 µm² region is shown in figure A.4. The anisotropic etching process can be observed as an apparent movement of steps towards the left, which is the result of a preferential attack at the kink sites and step edges. It corresponds to the chemical dissolution reaction described in chapter 2.

The etch rate during the sequence of figure A.4 can be derived directly from the loss of material between two frames [5]: this procedure is illustrated in figure A.5: The frames (500 × 500 nm²) have been enlarged from the upper central region of figures A.4C and A.4F, in order to ease the calculations. Taking 0.31 nm as the step height, the hatched area corresponds to an etched
Figure A.4: EC-AFM sequence of Si(111) in 2M NaOH, HER current 300 μA/cm². Original frames: 1 × 1 μm², 2 nm vertical range, 512 × 512 pixel. Imaging conditions: scan rate 7.2 lines/s (71.3 s per frame), 2 nN applied force. Video available at http://www.gf.ub.es/area4c/si-etch.html
Figure A.5: Procedure employed to measure the Si etch rate from EC-AFM sequences: The frames (500 \times 500 \text{ nm}^2, \text{ vertical range } 2 \text{ nm}) have been enlarged from the upper central region of figures A.4C and A.4F. The amount of Si etched can be calculated from the difference in terrace area (hatched area in the upper left part of the right image). Conversion to a vertical etch rate is made through the height of biatomic step and the time elapsed between frames.

depth of 0.15 \text{ nm}. The time elapsed between the frames is 3.6 \text{ min} (at a scan rate of 7.2 \text{ Hz}), which yields an etch rate of 0.042 \text{ nm/min}. Although slightly high, this value is comparable to the rate calculated from EC-STM observations (0.012 \text{ nm/min} at 200 \mu A/cm^2 [180]).

Another interesting measurement that can be obtained from figure A.4 is the nucleation frequency of etch pits on a terrace, \( F_p \) [180]. As an example, figure A.4E has been reproduced in figure A.6 and all the newly nucleated pits (i.e. not present in figure A.4D) have been marked with a circle. The average of the entire sequence (80 pits in figures A.4B through F) yields \( F_p = 2.3 \cdot 10^7 \text{ cm}^{-2} \cdot \text{s}^{-1} \). This value was not measurable in the EC-STM observations of reference [180], which covered an electrode area about 100 times smaller.

However, several facts indicate that there may be some errors involved in the measurement of \( F_p \): First, the nucleation frequency is not constant through the sequence, but it increases (25 pits have nucleated in frame F, against 8 in frame B). In addition, \( F_p \) is about 5 times larger than the value
expected from the nucleation frequency of isolated $\equiv Si-OH$ groups ($F_0 = 1.5 \cdot 10^8 \text{ cm}^{-2} \cdot \text{s}^{-1}$, with $F_0 \sim 30 \cdot F_p$ [180]). These facts, together with the slightly high experimental etch rate, suggest that the AFM imaging could be interfering with the Si dissolution reaction to a certain extent. Indeed, two major disturbances may be introduced by the AFM system: the forces applied during scanning (both normal and lateral, i.e. related to friction), and the illumination due to the laser, which can result in the photogeneration of holes. As was explained in chapter 2, holes are involved in the electrochemical (isotropic) reaction path, and could be related to the appearance of etch pits on the terraces. In any case, the results obtained are well within the orders of magnitude reported in the literature, and further refinements in the experimental procedure should allow more accurate measurements.
A.4 Conclusions

In summary, an electrochemical AFM study of the silicon dissolution reaction has been presented for the first time. The preliminary results are in agreement with previously reported data, and demonstrate that AFM is a useful tool for the characterization of chemical and electrochemical processes at the surface of an electrode.
Appendix B

Selected publications

This thesis is available in electronic form at:

http://www.qf.ub.es/area4c/publications.html

Other publications of the author related to the subject of this thesis are:

P. Gorostiza, M. A. Kulandainathan, R. Díaz, F. Sanz, P. Allongue and J. R. Morante

P. Gorostiza, R. Díaz, M. A. Kulandainathan, F. Sanz and J. R. Morante
Journal of Electroanalytical Chemistry, 469 (1999) 48

P. Gorostiza, R. Díaz, J. Servat and F. Sanz, J. R. Morante
Journal of The Electrochemical Society, 144 (1997) 909

P. Gorostiza, R. Díaz, F. Sanz and J. R. Morante
Journal of The Electrochemical Society, 144 (1997) 4119

P. Gorostiza, J. Servat, F. Sanz and J. R. Morante

P. Gorostiza, J. Servat, F. Sanz and J. R. Morante

P. Gorostiza, R. Díaz, F. Sanz and J. R. Morante,

P. Gorostiza, J. Servat, R. Díaz, F. Sanz and J. R. Morante
Electrochemical Synthesis and Modification of Materials
P. C. Andricacos, S. G. Corcoran, J. Delplancke, T. P. Moffat and P. C. Searson (eds.)

P. Gorostiza, J. Servat, F. Sanz and J. R. Morante
*Defect Recognition and Image Processing in Semiconductors*
A. R. Mickelson (ed.)

P. Gorostiza, J. Servat, J. R. Morante and F. Sanz
*Silicide Thin Films Fabrication, Properties and Applications*
R. Tung, K. Maex, P. W. Pellegrini, L. H. Allen (eds.)

Oral presentations in international meetings:

P. Gorostiza, M. A. Kulandainathan, R. Díaz, F. Sanz, P. Allongue
and J. R. Morante
*195th Meeting of The Electrochemical Society*
Seattle WA (USA), May 1999

P. Gorostiza, R. Díaz, A. Kulandainathan, J. R. Morante and F. Sanz
*Gordon Research Conference on Electrodeposition*
New London NH (USA), August 1998

P. Gorostiza, R. Díaz, F. Sanz and J. R. Morante
*190th Meeting of the Electrochemical Society*
San Antonio TX (USA), October 1996

P. Gorostiza, Y. Maniette, R. Díaz, J. Servat, F. Sanz and J. R. Morante
*3rd European Workshop on Electrochemical Processing of Semiconductors*
Paris (France), November 1996

P. Gorostiza, J. Servat, F. Sanz and J. R. Morante
*The European Materials Research Society Meeting*
Strasbourg (France), May 1995
Appendix C

Notation and units

As far as possible, the guidelines of the International Union of Pure and Applied Chemistry (IUPAC) have been followed for the quantities, units and symbols employed in this thesis. They are described in *Terminology in semiconductor electrochemistry and photoelectrochemical energy conversion*, Pure and Applied Chemistry 63 (1991) 569. A list of the main symbols and abbreviations is provided here for reference.

\[\begin{align*}
A & \quad \text{Electrode area} \\
C & \quad \text{Capacitance} \\
C_C & \quad \text{Compact layer capacitance} \\
C_d & \quad \text{Diffuse layer capacitance} \\
C_{GL} & \quad \text{Electrochemical double layer capacitance} \\
C_{GC} & \quad \text{Diffuse layer capacitance (Gouy-Chapman model)} \\
C_H & \quad \text{Compact layer capacitance (Helmholtz model)} \\
C_{sc} & \quad \text{Semiconductor capacitance} \\
d & \quad \text{Layer thickness} \\
D_H & \quad \text{Hydrogen diffusion coefficient in silicon crystals} \\
D_{ox} & \quad \text{Density of unoccupied electronic states in a redox system} \\
D_{red} & \quad \text{Density of occupied electronic states in a redox system} \\
\mathcal{D} & \quad \text{Diffusion coefficient of species in a solution} \\
e & \quad \text{Electron charge } (1.60 \cdot 10^{-19} \text{ C}) \\
E & \quad \text{Energy} \\
E_A & \quad \text{Electronic affinity} \\
E_B & \quad \text{Built-in barrier of Schottky junction (as “seen” from the metal)} \\
E_C & \quad \text{Conduction band energy} \\
E_{CS} & \quad \text{Conduction bandedge energy} \\
E_F & \quad \text{Fermi energy} \\
\epsilon E_F & \quad \text{Quasi-Fermi energy of electrons in an illuminated electrode}
\end{align*}\]
\( \psi E_F \)  Quasi-Fermi energy of holes in an illuminated electrode
\( E_g \)  Bandgap energy
\( E_i \)  Ionization energy
\( E_{ox} \)  Energy of the unoccupied electronic state of redox system
\( E_{red} \)  Energy of the occupied electronic state of redox system
\( E_V \)  Valence band energy
\( E_{vac} \)  Vacuum level
\( E_V S \)  Valence bandedge energy
\( F \)  Faraday constant \( (9.65 \cdot 10^4 \text{ C/mol e}^-) \)
\( F_0 \)  Force applied on the sample during AFM imaging
\( \Delta G_{att} \)  Activation energy of cathodic process
\( \Delta G_{an} \)  Activation energy of anodic process
\( h \)  Planck constant \( (6.63 \cdot 10^{-34} \text{ Js}) \)
\( j \)  Current density
\( j_0 \)  Exchange current density
\( j_C \)  Current density through the conduction band (free electrons)
\( j_{corr} \)  Corrosion (dissolution) current density
\( j_{inj} \)  Hole injection current density from oxidizing agent
\( j_{max} \)  Maximum anodic current density in the porous silicon regime
\( j_{ox} \)  Anodic current density (oxidation process)
\( j_{ph} \)  Photocurrent density
\( j_{red} \)  Cathodic current density (reduction process)
\( j_V \)  Current density through the valence band (free holes)
\( k \)  Rate constant
\( K \)  Equilibrium constant
\( k_B \)  Boltzmann constant \( (8.6 \cdot 10^{-5} \text{ eV/K}) \)
\( n \)  Electron density
\( n_b \)  Electron density in the semiconductor bulk
\( n_i \)  Intrinsic carrier density
\( n_S \)  Electron density at the semiconductor surface
\( N \)  Density of electronic states
\( N_A \)  Density of acceptor impurities
\( N_C \)  Effective density of states at the conduction band bottom
\( N_D \)  Density of donor impurities
\( N_{cl} \)  Concentration of redox species in solution
\( N_{ss} \)  Density of surface states
\( N_S \)  Doping of surface layer (different from bulk doping)
\( N_V \)  Effective density of states at the valence band top
\( p \)  Hole density
\( p_b \)  Hole density in the semiconductor bulk
\( p_S \)  Hole density at the semiconductor surface
\( Q \) Charge
\( Q_{\text{ads}} \) Specifically adsorbed charge
\( Q_{\text{el}} \) Electrolyte charge near the electrode
\( Q_{\text{sc}} \) Charge in the semiconductor
\( Q_{\text{ss}} \) Charge stored in surface states
\( R \) Etch rate
\( T \) Temperature
\( U \) Electrode potential
\( U_{\text{CS}} \) Electrode potential corresponding to the conduction bandedge
\( U_{\text{FB}} \) Flatband potential
\( U_{\text{OCP}}, U_{\text{mix}} \) Open-circuit potential, rest potential, mixed potential
\( U_{\text{Ox}/\text{Red}} \) Redox potential of the system \( \text{Ox}/\text{Red} \)
\( U_{\text{Ox}/\text{Red}}^\circ \) Standard redox potential of the system \( \text{Ox}/\text{Red} \)
\( U_S \) Band bending, surface barrier (as “seen” from the semiconductor)
\( U_{\text{VS}} \) Electrode potential corresponding to the valence bandedge
\( v \) Scan rate of current–potential curve
\( W \) Width of the space charge region in a semiconductor
\( x \) Distance to an interface
\( x_{\text{OHP}} \) Distance between electrode surface and outer Helmholtz plane
\( z \) Charge, number of electrons exchanged in a reaction
\( [\quad] \) Concentration of species in solution

\( \alpha \) Anodic transfer coefficient
\( \gamma \) Fraction of applied potential dropped in the semiconductor
\( \delta \) Polarity of atomic bond.
\( \epsilon \) Thickness of \( H \)–permeated \( Si \) layer
\( \epsilon_0 \) Permittivity of vacuum \((8.85 \cdot 10^{-14} \ \text{CV}^{-1} \text{cm}^{-1})\)
\( \eta \) Electrode overpotential
\( \eta_{\text{sc}} \) Semiconductor “overpotential”
\( \lambda \) Reorganization energy, Photon wavelength
\( \mu_C \) Energy between conduction band bottom and Fermi level \((n\text{-type})\)
\( \bar{\mu}_i \) Electrochemical potential of species \( i \)
\( \mu_V \) Energy between valence band top and Fermi level \((p\text{-type})\)
\( \nu \) Photon frequency
\( \phi(x) \) Electrostatic potential
\( \Delta \phi \) Potential applied over an interface
\( \Delta \phi_H \) Helmholtz layer potential
\( \Delta \phi_{DL} \) Electrochemical double layer potential
\( \Delta \phi_{ph} \) Photopotential of semiconductor electrode
\( \Delta \phi_{sc} \) Potential drop in the semiconductor, band bending
\( \Phi_m \) Work function of a metal
\( \Phi_0 \) Light flux
\( \omega \) Angular velocity of rotating electrode
Angular frequency of alternating electric potential

\[ \text{AFM} \] Atomic force microscopy
\[ \text{AS} \] Active side
\[ \text{CB} \] Conduction band
\[ \text{CE} \] Counter electrode
\[ \text{EC} - \text{AFM} \] Electrochemical atomic force microscopy
\[ \text{EC} - \text{STM} \] Electrochemical scanning tunneling microscopy
\[ \text{EDX} \] Electron dispersive X-ray spectroscopy
\[ \text{EIS} \] Electrochemical impedance spectroscopy
\[ \text{EP} \] Electropolishing
\[ \text{FB} \] Flat band
\[ \text{HER} \] Hydrogen evolution reaction
\[ \text{IHP} \] Inner Helmholtz plane
\[ \text{ML} \] Monolayer
\[ \text{MS} \] Mott-Schottky
\[ \text{OCP} \] Open-circuit potential
\[ \text{OHP} \] Outer Helmholtz plane
\[ \text{PL} \] Photoluminescence
\[ \text{PS} \] Porous silicon
\[ \text{RE} \] Reference electrode
\[ \text{RMS} \] Root mean-square
\[ \text{RS} \] Rear side
\[ \text{SCE} \] Saturated calomel electrode
\[ \text{SCR} \] Space charge region
\[ \text{SEM} \] Scanning electron microscopy
\[ \text{SHE} \] Standard hydrogen electrode
\[ \text{STM} \] Scanning tunneling microscopy
\[ \text{TEM} \] Transmission electron microscopy
\[ \text{VB} \] Valence band
\[ \text{WE} \] Working electrode
\[ \text{XPS} \] X-ray photoelectron spectroscopy
Dipòsit de metalls sobre silici en solucions fluorades

Introducció

Motivació

Quan aquest estudi va començar, hi havia al camp de la microelecètrònica un interès creixent en emprar mètodes electroquímics en el processat dels semiconductors. Una de les aplicacions més prometedoras era la de substituir les tècniques tradicionals d’obtenció de capes metàl·liques (evaporació i sputtering) per processos químics que puguessin satisfer les necessitats de la indústria: recobriment d’estructures tridimensionals complexes (interconexions multinivell a escala submicromètrica), altes velocitats de dipòsit (per aconseguir capes gruixudes en processos de microfabricació), i també l’atac anisòtròpic dels materials semiconductors. Alguns d’aquests processos són, a hores d’ara, una realitat a les plantes microelecètròniques, i ocupen bona part dels programes dels principals congressos d’electroquímica i de tecnologia de l’estat sòlid.

Amb la intenció d’abordar el camp multidisciplinar de l’electroquímica de semiconductors, els departaments d’Electrònica i Química-Física van endegar un projecte comú, i aquesta tesi n’és un resultat. La col·laboració ha permès introduir a la Universitat de Barcelona les tècniques electroquímiques de caracterització i processat de semiconductors, però els seus beneficis van més enllà d’aquest treball: Dos projectes al Departament d’Electrònica (dipòsit de metalls i aliatges de memòria de forma per microactuadors) i un al de Química-Física (propietats semiconductores dels òxids metàl·lics) donen continuïtat a la idea original, a més de les investigacions que es derivaran d’aquesta tesi en un futur immediat.

Els primers experimentes realitzats en aquest estudi es van centrar en el dipòsit de metalls nobles a la superfície del silici en dissolucions fluorades: platí, pal·ladi i or principalment. El dipòsit es produeix espontàniament per
DIPÒSIT DE METALLS SOBRE SILICI

simple immersió de les mostres en la dissolució, i és degut al “desplaçament” dels àtoms de silici pels d’un metall més noble [1]. Els dipòsits obtinguts amb aquest mètode es poden emprar també com a “llavor” per als següents processos, de cara a fer crèixer capes més gruixudes a la superfície del silici [2]. Els primers muntatges experimentals (simple immersió de les mostres en un recipient, per analogia amb els processos industrials) permetien només controlar la composició dels electròlits i el temps de dipòsit, i la caracterització de les mostres es va fer amb tècniques de microscòpia i anàlisi químic ex situ.

Aviat va resultar evident que la fenomenologia i les aplicacions d’aquests processos eren molt més àmplies que la seva utilització com a tècniques de pre-dipòsit, i requerien un estudi aprofundit sota un punt de vista més fonamental. El muntatge experimental va guanyar en complexitat (control de la superfície de la mostra exposada a la dissolució, estudi de la electroquímica de tres electrodos), alhora que va permetre esbrinar els diferents mecanismes de bescanvi de càrrega entre l’electròlit i el semiconductor. D’aquesta manera, la situació de “simple immersió” es va poder tractar posteriorment com a cas particular.

Simultàniament, la polèmica sobre la terminació química superficial del silici en dissolucions fluorades s’anava diluïnt a mida que es confirmava in situ l’existència d’enllaços Si – H. Basats en aquestes i en altres evidències, els estudis publicats per Gerischer i Allongue entre 1993 i 1996 van permetre aclarir el mecanisme de dissolució del silici en medi aquós [3, 4, 5, 6]. L’estada al laboratori de Philippe Allongue a la Universitat Pierre et Marie Curie el 1996 va ser doncs una oportunitat excel·lent per prendre els detalls del mecanisme i les tècniques experimentals relacionades. En el marc d’aquesta tesi, la comprensió dels processos d’oxidació del silici va permetre entendre el seu acoblament amb les reaccions de reducció (com ara el dipòsit de metalls), així com nombrosos aspectes fonamentals de l’electroquímica de semiconductors.

Objectius

El propòsit d’aquesta tesi és desenvolupar un mecanisme global per descriure els processos de dipòsit de metalls sobre silici a partir de dissolucions fluorades. Aquest mecanisme haurà d’ajustar-se als conceptes clàssics de l’electroquímica de semiconductors, i alhora tenir en consideració els avanços recents en la comprensió de la química del silici. Les eines principals d’aquest estudi són les tècniques electroquímiques in situ. Alguns aspectes es complementen amb caracteritzacions microscòpiques i espectroscòpiques ex situ.
RESUM

Estructura

La memòria està organitzada en tres parts:

Els dos primers capítols exposen els fonaments necessaris per a la interpretació dels experiments electroquímics.

- El capítol 1 és una introducció als conceptes bàsics de l’electroquímica de semiconductors. Un cop descrita la interfase semiconductor | dissolució des d’un punt de vista termodinàmic, la cinètica de transfereixió electrònica s’hi discuteix parant especial esment en les reaccions simultànies (teoria del potencial mixte). Aquest capítol té un propòsit didàctic i no requereix un coneixement aprofundit d’electroquímica o de física de l’estat sòlid.

- El capítol 2 pretén reunir els elements necessaris per a la comprensió de la química del silici en dissolucions aquoses i en presència d’especes fluorades. Tot i que el recull de dades correspon principalment a mesures electroquímiques, també s’hi discuteixen altres resultats obtinguts in situ amb tècniques espectroscòpiques i microscòpiques.

Els estudis electroquímics del dipòsit de platí i níquel corresponen al gruix dels experiments. Es presenten en els quatre capítols següents:

- El capítol 3 descriu els muntatges i les tècniques experimentals emprades, així com els procediments per a la preparació de mostres.

- El capítol 4 està dedicat a l’estudi del dipòsit de platí. Els nivells electrònics del sistema \(Pt^{2+}/Pt\) es troben superposats a la banda de valència del silici en medi fluorur, de manera que els ions \(Pt^{2+}\) actuen com a agent oxidant. La fenomenologia de les reaccions de dipòsit de platí i d’oxidació de silici és complexa i es presenta separatament.

- El capítol 5 descriu l’estudi electroquímic del dipòsit de níquel a dos valors extrems del \(pH\) de la dissolució. Aquest metall es va triar perquè els nivells electrònics del sistema \(Ni^{2+}/Ni\) es troben dins la banda prohibida del silici, i per tant podia donar lloc a una fenomenologia diferent de la del platí.

- El capítol 6 és una síntesi dels diferents mecanismes de dipòsit de metalls sobre silici en dissolucions fluorades. L’anàlisi dels dos capítols anteriors s’estén a altres sistemes i condicions, i les conclusions es contrasten amb dades bibliogràfiques i alguns experiments.
Finalment, els aspectes tecnològics es discuteixen al capítol 7. S’hi han agrupat dues sèries d’experimentes, realitzades en etapes molt diferents de la investigació: d’una banda, es presenta la caracterització ex situ de mostres preparades amb els primers muntatges experimentals. Aquests estudis són qualitatius a causa de les limitacions en el control dels paràmetres electroquímics durant la preparació de les mostres, però permeten discutir alguns aspectes no tractats en capítols anteriors. D’altra banda, les conclusions sobre els mecanismes de dipòsit de metalls en condicions controlades s’extenen al cas de “simple immersió” després d’un breu estudi electroquímic.

A l’apèndix A hi ha una selecció de les publicacions relacionades amb aquesta tesi. Com a demostració de les possibilitats de la microscòpia in situ, l’apèndix B presenta un estudi preliminar de la dissolució de silici en dissolucions de NaOH.

**Mecanismes de dipòsit**

Aquesta secció revisa, a tall de resum, els mecanismes de les reaccions de dipòsit de metalls sobre silici en dissolucions fluorades. És essencialment un extracte del capítol 6 de la memòria, i resulta de l’estudi detallat de dos sistemes model (PtCl\textsubscript{2}\textsuperscript{-}/Pt i Ni\textsuperscript{2+}/Ni) unit a l’analisi de la bibliografia en aquest camp. La primera part ofereix una classificació dels sistemes redox d’un punt de vista termodinàmic, basat en el seu poder reductor en relació al substrat de silici. S’hi discuteixen els possibles camins de reacció en elèctrodes de tipus n i p, utilitzant els conceptes de la teoria del potencial mixte introduïts a la secció 1.3.3. La segona part aprofundeix en els mecanismes, tenint en compte en cada cas els processos competitius que defineixen la velocitat de la reacció global.

**Aspectes energètics**

El procés físic implicat en la transferència de càrrega entre un ió en dissolució i l’elèctrode és l’efecte túnel. Per tal que es duguï a terme, els ions han de trobar-se apropiat de l’elèctrode (a menys de ~ 3 nm perquè l’efecte sigui eficient), i l’energia de l’estat inicial (ocupat) i el final (vacant) han d’ésser molt similars (transferència isoenergètica). Cal tenir present que els elèctrodes semiconductors només poden intercanviar càrrega a través de les vores de la banda de conducció (CB) o de valència (VB), és a dir a energies \( E_{CS} \) or \( E_{VS} \) (constants en una primera aproximació). En canvi, l’energia de transferència d’electrons en metalls és l’energia de Fermi, \( E_F \), i es pot ajustar a qualsevol valor tot variant el potencial aplicat. Per tant, l’energia de les
Figura C.1: En funció de la seva energia, un sistema redox en solució pot interaccionar amb electrons lliures a la banda de conducció del semiconductor (\(M^+ / M\)), amb electrons d’enllaç a la banda de valència (\(N^+ / N\)), o amb estats superficiais (ss) si aquests estan presents a la interfície.

Vores de banda d’un semiconductor en relació al nivell redox en dissolució dóna lloc a tres situacions fonamentalment diferents (figura C.1):

- Els sistemes redox amb energia de Fermi propera a la vora de la CB (\(M^+ / M\) a la figura C.1) poden intercanviar càrrega amb la CB.

- Si els nivells redox es troben prop de la vora de la VB (\(N^+ / N\)) la transferència pot efectuar-se amb la VB.

- Els sistemes redox amb nivells electrònics dins la banda prohibida (\(P^+ / P\)) en principi són incapaços d’intercanviar electrons amb el semiconductor. Aquesta transferència només és possible si l’energia dels estats superficiaus és propera al nivell redox.

A la pràctica, es donen casos intermedis entre aquests tres. Cal destacar que el sistema \(N^+ / N\) interacciona amb electrons d’estats enllaçants, i és més comú parlar d’intercanvi de forats (veieu la secció 1.3.2.2). Considerant, per exemple, la transferència d’electrons de l’elèctrode a l’electròlit, hi ha diferències substancials entre el procés de CB i de VB: pel primer cas, cal que existeixin electrons lliures al semiconductor (tipus \(n\), o tipus \(p\) sota il·luminació) i que les bandes estiguin corbades cap avall (acumulació d’electrons). Però la VB sempre és plena d’electrons d’enllaç que es poden transferir a l’electròlit, independentment del tipus de semiconductor, de la corbatura de bandes o de la il·luminació. Per tant la “injecció de forats” des de sistemes redox amb energia propera a la VB és sempre possible. És
per això que les formes oxidades del sistema redox reben el nom d’\textit{agents oxidants}.

La presència d’un sistema redox a la dissolució fluorada (per exemple en afegir-hi ions metàl·lics) està associada a nous estats electrònics que poden bescanviar càrrega amb l’èl·lerode de silici. El corrent corresponent a aquest bescanví afageix un nou component al corrent total que travessa la interfície, i es pot tractar amb la teoria del potencial mixte de l’èl·lerode (secció 1.3.3). Com es detalla al capítol 2, el potencial de circuit obert (OCP) del silici en una dissolució fluorada és el potencial d’èl·lerode al qual s’igualeix les velocitats de la reacció d’evolució d’hidrogen (HER) i d’oxidació del silici, i el corrent \textit{total} a través de la interfície és nul. Així, l’OCP és el potencial mixte entre les reaccions catòdica i anòdica. El balanç de corrents (i el potencial mixte) queda modificat quan s’afageixen ions metàl·lics a la dissolució.

La discussió que segueix està centrada en la interpretació de les corbes corrent-potencial \((j - U)\) del silici en contacte amb un sistema redox en medi fluorur. Després de plantejar el diagrama d’energies a la interfase (com es descriu a la secció 1.2.3.6), la mesura de la resposta voltàmètrica del sistema dóna informació de primera mà sobre els processos d’intercanvi de càrrega entre l’èl·lerode i l’electròlit.

**Processos de banda de conducció en elèctrodes de tipus \(n\)**

La corba \(j - U\) en foscor d’un elèctrode \(n – Si\) dins d’una dissolució fluorada es mostra a la figura C.2A (“blanc” o corba de referència). Malgrat que té l’aspecte general de les corbes d’èl·lerodes de tipus \(n\), cal notar que el corrent invers (a potencials positius) es deu a la injunció d’electrons a la CB com a resultat de la reacció d’oxidació del silici, i no només a les fuites a través de la barrera de potencial (veieu secció 2.2.3 i figura 2.5).

Els requadres inserits a la figura C.2 mostren que el potencial aplicat a l’èl·lerode produeix un canvi d’\(E_F\). Això modifica la corbatura de bandes al semiconductor i per tant la concentració d’electrons en superfície, però la posició relativa de les vores de banda i el nivell redox no varia en una primera aproximació. A mida que s’apliquen potencials més negatius a l’èl·lerode, \(E_F\) es desplaça cap a valors superiors en el diagrama d’energia i es poden transferir electrons a l’electròlit per promoure processos catòdics. A potencials de l’èl·lerode més positius que l’OCP, \(E_F\) es desplaça cap a valors inferiors i això pot donar lloc a processos anòdics. A cada valor del potencial, els corrents deguts als diferents processos se sumen per donar el corrent mesurat experimentalment a la corba \(j - U\).

Si existeix en dissolució un sistema redox capaç d’intercanviar electrons
Figura C.2: Corba $j - U$ en foscor d’un èlèctrode $n-Si$ dins d’un “blanc” de fluorur (A) i en presència d’un sistema redox que interacciona amb la banda de conducció (B).

amb la CB, la forma general del corrent de reducció és:

$$j_{\text{red,CB}} = k \cdot n_S \cdot [M^+]_{S,\text{CB}}$$  \hspace{1cm} (C.1)

on $k$ és la constant de velocitat, $n_S$ la concentració d’electrons a la superfície de l’èlèctrode i $[M^+]_{S,\text{CB}}$ la concentració de ions metàl·lics amb energia redox prop de la CB. A potencials negatius en la foscor, els electrons lliures (portadors majoritaris) s’acumulen a la superfície de l’èlèctrode de $n-Si$ i es transfereixen a la dissolució, donant lloc a un pic de corrent catòdic (figura C.2B). Els ions metàl·lics que reben aquests electrons són reduïts i, si la forma reduïda del sistema redox és un sòlid (per exemple $Cr^{2+}/Cr$, però no $Cr^{3+}/Cr^{2+}$), queden dipositats a la superfície. Sovint el pic apareix abans d’assolir el potencial de bandes planes de l’èlèctrode (FB), perquè els electrons poden superar una barrera d’energia relativament baixa. L’aparició d’un pic en lloc d’un corrent exponencial o d’un plateau, indica l’existència d’una limitació en la dissolució: al principi, l’aument del corrent és exponencial amb el potencial, i la reacció de reducció consumeix els ions situats a la vora de l’èlèctrode. Però a mida que es forma el dipòsit, aquests ions s’exhausteixen i d’altres han de difondre lentament a través de la dissolució. S’observa aleshores un decaiment del corrent com $\frac{1}{\sqrt{t}}$ i independent del potencial ($U$),
on el temps \( t \) pot obtenir-se de la velocitat d’escombrat del potencial \( v \) com
\[ t = \frac{U}{v} \] [133]. El decaliment del corrent de reducció es pot retardar millorant el
transport de matèria a la dissolució, per exemple augmentant la concentració
del metall o amb agitació. És important destacar que aquesta limitació per
difusió es deu a que l’energia de les vores de banda \( n_0 \) és constant en el
règim d’acumulació: la corbatura de bandes se saturat i aleshores el potencial
aplicat cau principalment a la capa de Helmholtz. Les vores de banda es
desplacen cap a energies superiors una quantitat \( \eta = \Delta \phi_H(U) - \Delta \phi_H^q \). En
aquest rang, el potencial aplicat al semiconductor resulta en una reducció de
la barrera de reacció \( \Delta G_{e} \) (expressió 1.72), cosa que augmenta la cinètica
de la reacció i permet que la difusió sigui, en últim extrem, el pas limitant
de la reacció. En aquest cas, la situació és anàloga als elèctrodes metàl·lics
(veieu la secció 1.3.2.2).

La corba \( j - U \) es pot transformar en una \( j - t \) fent servir la velocitat
d’escombrat \( v \), i l’àrea del pic permet calcular amb una gran precisió la
quantitat de metall dipositada. A potencials superiors al pic es produeix la
descàrrega d’hidrogen (HER).

Si el potencial de l’elèctrode (ara recobert de metall) es fa retornar a valors
més positius, el nivell de Fermi del semiconductor se situa per sota de l’energia
del sistema redox. Aleshores els electrons del metall poden ser “recuperats”
com a portadors lliures al semiconductor, suposant que la dissolució pugui
redisoldre els productes d’oxidació del metall. Aquest procés “arrenca” el
metall de la superfície de l’elèctrode i dóna lloc a un pic de corrent anòdic
que permet calcular la quantitat de material oxidada. Metaalls amb nivells
propers a la CB com el Zn [134], Pb [135, 136], Ni [137] i Sn [138] dipositen
reversiblement sobre \( n - Si \).

**Processos de banda de conducció en elèctrodes de tipus \( p \)**

En un elèctrode de \( p - Si \) en absència d’il·luminació només hi ha una petita
concentració d’electrons generats tèrmicament a la CB. Cal, doncs, foto-
generar electrons per dipositar un metall amb nivells energètics propers a la
CB (fotoreducció). En aquest cas, la corba \( j - U \) de referència és la d’un
elèctrode de tipus \( p \) il·luminat (figura C.3A). Com en el cas del \( n - Si \) (figura
C.2), els processos catòdics es promouen a potencials negatius, però el pic
d’hidrogen (HER), i possiblement també el de reducció del metall, presen-
ten una saturació quan es consumeixen tots els fotoelectrons (figura C.3B).
Com es mostra al requadre de la figura, el corrent catòdic es deu als forats
(portadors majoritaris en \( p - Si \)) fotogenerats junt amb els electrons, i dels
quals se separen a la zona de càrrega espacial del semiconductor (SCR).

A potencials positius, i independentment de la il·luminació, el dipòsit es
pot redissoldre mitjançant la immediació d’electrons a la CB (seguida de recombinació), o injectant directament els electrons a nivells enllaçants (extracció de forats). El mecanisme en cada cas depèn de l’alcàdà de barrera, però el corrent mesurat correspon a portador majoritaris. És important destacar que, en aquest rang de potencials, els forats s’acumulen a la superfície de l’elèctrode i poden produir la dissolució simultània del material semiconduct–tor (vegeu la secció 2.2).

**Processos de banda de valència en elèctrodes de tipus p**

En aquest cas la corba $j - U$ de referència és la de l’elèctrode $p - Si$ en foscor (figura C.4A). Un sistema redox amb nivells d’energia propers a la VB produceix un corrent d’immediació de forats al semiconductor, independentment del tipus ($n$ o $p$), de la corbatura de les bandes (és a dir, del potentencial de l’elèctrode) o de la il·luminació. El corrent d’inmediació $j_{inj}$ és proporcional a la concentració de ions, $[N^{+}]_{S,VB}$:

$$j_{red,VB} = k' \cdot [N^{+}]_{S,VB} \equiv j_{inj}$$  \hspace{1cm} (C.2)

i es mostra a la figura C.4B com un corrent catòdic constant $j_{inj} < 0$. La corba $j - U$ resultant (figura C.4C) és la superposició de les corbes A i B, i
apareix com un desplaçament cap a valors inferiors de la corba de referència.

El corrent d’injecció $j_{inj}$ es pot mesurar recollint els forats, portadors majoritaris en $p – Si$, a potencials negatius: a la figura C.4, la part plana de la corba $C$ dona aproximadament el valor de $j_{inj}$ (veieu el recadre esquerre). Si el corrent $j_{inj}$ mesurat depèn de les condicions de transport de matèria a la dissolució (agitació i concentració de ions), el procés de dipòsit del metall és limitat per difusió. En alguns casos es pot arribar a una limitació cinètica, per exemple si s’asseoleix un $j_{inj}$ màxim en augmentar l’agitació de la dissolució: en aquestes condicions, el subministrament de ions a la superfície de l’elèctrode ja no és l’etapa limitant sinó la reacció de reducció en si. Cal dir, però, que la limitació cinètica no estaria en contradicció amb el grans potencials negatius aplicats a l’elèctrode en aquesta regió de la corba: com que l’elèctrode de $p – Si$ és en depleció, tot el potencial aplicat s’empra en corbar les bandes, l’energia de les vores de banda és fixa i la barrera de reacció es manté invariant. És a dir, en aquest rang el potencial aplicat no actua sobre la cinètica de reacció.

Com mostra la figura C.4, en afegir un agent injector de forats l’OCP de l’elèctrode es mou cap a valors més positius. Això li permet cancel·lar el corrent $j_{inj}$ amb un corrent anòdic de forats $j_{anr}$ que flueixen cap a la
interfície (veieu el requadre dret). En presència de fluorur, aquest corrent anòdic provoca la dissolució del silici. El nou OCP ($U_{\text{mix}}$) és el potencial mixte entre la reacció catòdica (reducció del metal per injecció de forats) i la contrarreacció anòdica (oxidació i dissolució de silici). L’equilibri entre els dos corrents també es pot imaginar com una fracció del forats injectats que són capturats a la interfície i donen lloc a la reacció d’oxidació (veieu la secció 1.3.2). En qualsevol cas, el corrent de “corrosió” $j_{\text{corr}}$ pot assolir valors d’uns quants $mA/cm^2$ i deteriorar ràpidament la superfície de l’èlectrode [140].

**Processos de banda de valència en èlectrodes de tipus $n$**

La corba $j - U$ d’un èlectrode $n - Si$ en fòsfor i en presència d’espècies injectores de forats (figura C.5) es pot reconstruir amb un corrent catòdic $j_{m,j}$ independent del potencial, i la corba $j - U$ en dissolució fluorada d’un èlectrode $n - Si$ il·luminat (figura 1.27). És fa servir la corba sota il·luminació perquè en aquest cas l’efecte dels forats injectats o fotogenerats és anàleg; el corrent anòdic de la corba C.5A ha de ser el doble del corrent d’injecció (veieu la secció 2.2.3). La suma de la corba de referència $A$ i el corrent d’injecció $B$ donen la corba $C$, on s’observa una regió plana abans del pic corresponent a la HER. Aquest plateau permet mesurar $j_{m,j}$ a través de la recombinació d’electrons amb els forats injectats (veieu el requadre esquerra), tot i que de vegades pot estar emmascarat pel pic de la HER. A la branca anòdica apareix un altre plateau, que correspon aproximadament a $-j_{m,j}$ [143]. En aquesta gamma de potencials, el corrent d’injecció $j_{m,j}$ s’equilibra amb un corrent de forats cap a la interfície ($j_{\text{corr}}$) que resulta en la oxidació del silici. Com es detalla a la secció 2.2.3, en aquesta reacció s’injecten electrons a la CB, i aquest és el corrent net de portadors majoritaris a què correspon el plateau anòdic. La mesura de $j_{m,j}$ que proporciona és, per tant, bastant indirecta i involucra els portadors produïts en una reacció.

A causa d’aquest fenomen de multiplicació del corrent, el potencial mixte $U_{\text{mix}}$ de l’èlectrode $n - Si$ correspon a la cancel·lació entre tres corrents: a l’estat estacionari (OCP) el corrent d’injecció s’anul·la amb un corrent anòdic que correspon (a parts iguals) al flux de forats cap a la interfície i als electrons injectats a la CB.

**Aspectes cinètics**

Després de discutir els diferents processos d’intercanvi de càrrega entre un semiconductor i els sistemes redox en la dissolució, i l’acoblament entre les reaccions catòdica i anòdica, aquesta secció tracta la velocitat d’aquests processos. L’anomenada semireacció catòdica en realitat són dues semireac-
Figura C.5: Corba $j - U$ en foscor d’un elèctrode $n - Si$ dins d’un “blanc” de fluorur ($A$), i corrent d’injecció deguda a la presència d’un agent oxidant ($B$). La corba $C$ resulta de la superposició d’$A$ i $B$.

Cions que competeixen: l’evolució d’hidrogen (HER) i la reducció de ions metàl·lics. A la semireacció anòdica, tant la formació d’òxid de silici com la seva dissolució en medi fluorur poden ser etapes limitants.

**Semireaccions catòdiques**

Es pot fer una comparació entre el dipòsit de diferents metalls sobre silici, suposant de moment una concentració de fluorurs en excés. En aquestes condicions, la superfície del silici no té òxid i està terminada per àtoms d’hidrogen. La figura C.6 mostra el potencial de reducció de diversos sistemes redox en funció del $pH$ (diagrames de Pourbaix [146]): quant més positiu és el potencial al diagrama, més forta és la tendència del sistema redox a guanyar electrons i restar com a forma reduïda. Tot i que molts d’aquests valors depenen de la presència de contraiions com ara $Cl^-$, $SO_4^{2-}$ o $CN^-$, aquest gràfic permet una discussió qualitativa.

Els sistemes redox amb nivells electrònics propers a la VB del silici (situats a la part inferior de la figura C.6) actuen com a agents oxidants d’aquest semiconductor. La velocitat de la reacció global sovint està controlada per la velocitat de dipòsit del metall. Com s’ha discutit a la secció anterior, els electrons d’enllaç (VB) es transfereixen als nivells redox en la dissolució i és
Figura C.6: Diagrames de Pourbaix simplificats per diversos metalls en solució aquosa. Els sistemes redox es troben en la seva forma reduïda quan les condicions experimentals estan per sota de la línia corresponent. Dades obtingudes a la referència [146].
possible mesurar aquest efecte com un corrent d’injecció de forats. Aquest corrent ha estat mesurat en excess de fluor en la dissolució pels sistemes Cu²⁺/Cu [143, 147], PtCl₄²⁻/Pt [132] i IrCl₆⁶⁻/IrCl₆⁶⁻, MnO₇⁶⁻/MnO₆⁵⁻, Br₂/Br⁻ [76] (U° = +0.87, +0.57, +1.1 V/SHE, respectivament). Un desplaçament de l’OCP de l’electrode de silici cap a valors positius s’ha detectat pel Cu²⁺/Cu [141] i el Ag⁺/Ag [142], cosa que dona una verificació indirecta del proces d’injecció. En tots aquests casos, el dipòsit estava limitat pel subministrament de ions metà-llics a la superfície: el corrent d’injecció depenia de la concentració d’ions [143] o de l’agitació [76, 132, 147], i el desplaçament de l’OCP era proporcional al logaritme de la concentració de metall [141, 142].

La presència del sistema redox produeix nuclis metà-llics a la superfície si la forma reduïda del sistema és un sòlid (per exemple Pt, Cu, Ag [148]), i augmenta l’atac del substrat de silici. A més dels resultats que es presenten al capítol 4 per PtCl₄²⁻/Pt, això es va comprovar en dissolucions 2M de fluor i entre 100 μM i 1 mM de Cu²⁺, Ag⁺, Au³⁺, Pd²⁺ i Bi³⁺. En tots els casos es fa visible al substrat una capa metà-llica, després d’uns minuts d’immersió.

Quan s’intenta dipòsitar un metall a partir de sistemes redox amb un poder oxidant menor (més propers a la CB de silici i situats cap al mig de la figura C.6), la velocitat de la reacció global en principi és controlada pel procés anòdic (velocitat d’atac del silici a l’OCP). Com es discuteix al capítol 5 pel cas del Ni²⁺/Ni, el procés catòdic es pot imaginar com la contrareacció que permit cancèl·lar el corrent anòdic. La velocitat d’atac del silici a l’OCP és una funció del pH i varia entre 1 μA/cm² a pH1 i 25 μA/cm² a pH14 (veieu el capítol 2).

Depenent de les condicions específiques de la dissolució, el corrent catòdic pot ser la suma de diverses contribucions procedents de les reaccions catòdiques amb diferents sistemes redox. En dissolucions aquoses amb ions metà-llics, les espècies acceptores d’electrons són els protons i els ions metà-l·lics, i cada reacció de reducció té una constant de velocitat. La constant de velocitat de cada reacció catòdica depèn tant de la constant cinètica com del potencial d’equilibri, però aquest darrer ja permet una comparació qualitativa: en el cas del Ni²⁺/Ni, s’estableix una competició entre la reducció de H⁺ i Ni²⁺: a pH baix, la velocitat d’atac del silici és petita i la contrareacció catòdica només involucra el sistema H⁺/H₂ (l’evolució d’H₂ és més ràpida que el dipòsit de Ni, U_H⁺/H₂ > U_{Ni²⁺/Ni}). Tot i que és termodinàmicament favorable (els nivells del Ni²⁺/Ni són propers a la CB), el dipòsit de níquel no es dóna a pH baix. L’augment del pH resulta simultàniament en un augment de la velocitat d’atac a OCP (corrent anòdic) i en una reducció del potencial d’equilibri del sistema H⁺/H₂. Aquests efectes combinats fan que
el níquel dipositat a OCP i pH alt. Per comparació, és d'esperar que tots els metalls situats per sobre de la línia marcada “$H^+/H_2$” a la figura C.6 tinguin una velocitat de reducció menor que els protons, i no haurien d’ésser capaços de dipositar.

Els resultats reportats a la bibliografia i alguns experiments a l’OCP, confirmen aquestes expectatives força bé: no es produeixen dipòsits de zinc a partir de dissolucions $HF$ 1 : 10, 10 $mM \ ZnSO_4$, d’acord amb estudis previs [148]. El mateix resultat s’obté amb $Fe$ [148, 151], $Cr$ [148] i $Al$ [1, 151] per un rang ampli de valors del pH. Tots aquests sistemes tenen un potencial de reducció considerablement més negatiu que el $H^+/H_2$. El sistema $Co^{2+}/Co$ (amb un potencial de reducció proper al del $Ni^{2+}/Ni$) es va explorar en un intent de reproduir els resultats pel níquel, però no es van obtenir dipòsits a l’OCP a partir de dissolucions 10 $mM \ CoCl_2$, 2 $M$ fluorur a $pH 1 – 8$. Tot i així, resultats recents demostren que el dipòsit de cobalt és possible sota aplicació de potencial [152].

**Semireaccions anòdiques**

Com es detalla al capítol 2, la dissolució anòdica del silici pot seguir dos mecanismes diferents, corresponents als règims de silici porós (PS) i d’electropolit (EP). A concentració fixa de forats en superfície, el mecanisme de dissolució depèn de la dissociació dels enllaços $Si – H$ (donada aproximadament pel pH de la dissolució), de la concentració de fluorur, i també de les diferents espècies fluorades presents en la dissolució. La dissolució del silici es pot contemplar com un procés en dues etapes: l’oxidació en sentit estricto (pèrdua dels electrons d’enllaç), seguida per la complexació dels productes d’oxidació. En aquests termes, la reacció de dissolució transcorre en el règim de silici porós quan la oxidació és l’etapa limitant, i en el règim d’electropolit quan ho és la complexació.

Donada la concentració de fluorur i el pH d’una dissolució, es pot observar la transició del règim de PS al d’EP augmentant la velocitat d’oxidació del silici a potencials positius (acumulació de forats). El primer pic de corrent $j_{max}$ que apareix a la corba $j – U$ de la figura 2.4 correspon a la màxima velocitat d’oxidació que es pot assolir sense que condensi un òxid a la superfície. A pH fix, el valor de $j_{max}$ augmenta amb la concentració de fluorur [61].

Els ions metàl·lics amb nivells redox propers a la VB produeixen un augment de la velocitat d’oxidació del silici (n’extreuen electrons d’enllaç). Sota aquestes condicions, la dissolució de l’àcid pot esdevenir l’etapa limitant, depenent del poder de complexació de la dissolució fluorada. Recentment, Martins et al. [143] han observat que el corrent d’oxidació de $n – Si$ depèn
Figura C.7: Dependència amb la concentració d’HF, del corrent de corrosió d’un elèctrode n–Si en presència d’ions Cu$^{2+}$ a la dissolució (Martins et al. [143]).

de la concentració de Cu$^{2+}$ i fluorur en la dissolució, tal i com es mostra a la figura C.7. Els punts experimental corresponen al plateau anòdic de la figura C.5), que és degut a la injecció d’electrons a la CB com a resultat del l’oxidació del silici. Els seus resultats es poden interpretar així: a concentracions altes de fluorur, el corrent anòdic es fa independent de la concentració d’HF i pràcticament proporcional a la concentració de Cu$^{2+}$. La reacció global està dominada pel subministrament de ions Cu$^{2+}$ a la superfície del silici. La reducció de Cu$^{2+}$ a Cu metàl·lic està compensada per l’oxidació dels àtoms de silici, que té lloc en el règim de PS en excés de fluorur. A mida que la concentració de fluorur disminueix a la figura C.7, el corrent anòdic és més proporcional a [HF] i gairebé independent de [Cu$^{2+}$]. En aquest rang, la velocitat de dissolució de l’òxid és menor que l’aport d’agent oxidant, i esdevé l’étapa limitant. La reacció d’oxidació del silici ha de succeir en el règim d’electropolít, molt probablement amb una capa prima d’òxid present a la superfície de l’elèctrode. L’òxigèn detectat per espectroscòpia de retrodispersió de Rutherford [143] és consistent amb aquesta interpretació.

Aspectes tecnològics i aplicacions

Tot i que el principal objectiu d’aquesta tesi és aclarir els mecanismes de les reaccions de dipòsit de metalls sobre silici, és possible aplicar algunes de les conclusions a casos pràctics:
El dipòsit de metalls sobre Si a partir de dissolucions fluorades (i les seves conseqüències, com l’aument de l’atac del substrat), té lloc espontàniament quan el potencial de reducció del sistema redox del metall és més positiu que \( U(H^+/H_2) \). Un altre paràmetre clau és el \( pH \) de la dissolució, que actua principalment sobre la velocitat d’atac del Si a l’OCP. Quan l’objectiu és mantenir la superfície tan plana i neta com sigui possible, els contaminants electroactius a evitar són tots aquells que tenen un potencial redox més positiu que \( U(H^+/H_2) \). Cal purificar les dissolucions de neteja posant atenció especial en aquests contaminants, que inclouen els metalls nobles però també sistemes redox com ara \( Cr^{6+}/Cr^{3+} \) o \( O_2/H_2O \). Una estratègia alternativa és la d’afegir espècies en dissolució que proveeixin els electrons necessaris per a la reducció dels agents oxidants, impedint així l’oxidació del substrat (per exemple, \( SO_4^{2-}/SO_3^{2-} \) en el cas dels sistemes \( O_2/OH^- \) i \( O_2/H_2O \)). D’altres banda, les espècies amb un potencial redox més negatiu que \( U(H^+/H_2) \) permeten una major tolerança quant a la purificació de les dissolucions.

És recomanable tenir una precaució especial en dissolucions de \( pH \) alt, perquè l’atac més ràpid del Si i la reduïda disponibilitat de protons poden permetre l’intercanvi de càrrega amb espècies que eren “inerts” a \( pH \) baix. Mantenir el \( pH \) tan baix com sigui possible és doncs beneficiós en aquestes aplicacions. A més, té l’avantatge addicional de millorar l’estabilitat dels ions metàl·lics en dissolució. En aquest sentit, afegir agents complexants de metalls també pot ajudar a tolerar traces de metalls contaminants per la superfície del Si. Sota un punt de vista diferent, el desplaçament de l’OCP dels èlectrodes de Si com a resultat de la presència d’agents oxidants, es pot aprofitar per a fabricar sensors de contaminants en dissolucions fluorades [142].

Aquestes dissolucions d’agents oxidants també es poden fer servir per dipositar capes metàl·liques per a aplicacions diverses: com a exemple, la figura C.8 mostra l’aspecte de dipòsits de \( Ni \) i \( Cu \) sobre \( Si \) obtinguts per simple immersió en dissolucions fluorades.

Per una altra banda, la formació de silici porós durant el dipòsit de \( Pt \) en dissolucions d’HF relativament concentrades també té aplicacions potencials: a causa de la fragilitat de la capa porosa que s’obté amb els procediments habituals (anodització), es dificil fabricar bons contactes metàl·lics sobre ella. Aquests contactes són necessaris per a la realització de dispositius electroluminiscents. La immersió del \( Si \) en dissolucions fluorades que continguin platí es pot presentar com un mètode de creixement simultani de capes fotoluminiscentes i dipòsits metàl·lics.

Finalment, els aspectes de reactivitat inhomogènia tractats al capítol 7 mereixen com a mínim dues consideracions: la primera és que si a la mostra hi ha una regió amb forta reactivitat anòdica, totes les reaccions catòdiques
Figura C.8: Capes de Ni (esquerra) i Cu (dreta) dipositades a partir de solucions fluorades a l’OCP. El substrat és de p – Si i té una màscara de $\text{Si}_3\text{N}_4$ fabricada fotolitogràficament.

es veuran amplificades a les altres regions. En aquest cas cal posar especial atenció als contaminants electroactius que estiguin presents a la dissolució, perquè poden donar lloc a reaccions de reducció que no s’esdevindrien en mostres poc reactives. D’altra banda, aquest efecte és interessant de cara a promoure les reaccions catòdiques en una certa regió, com a l’exemple de la figura C.9. És possible aplicar el mateix principi al confinament de procésos anòdics indesitjats, mitjançant el pre-patterning de regions anòdiques i catòdiques (concepte d’“ànode de sacrifici” emprat en la tecnologia contra la corrosió).

**Conclusions**

S’ha presentat l’estudi del dipòsit espontani de metalls sobre silici a partir de dissolucions aquoses en presència de fluorur. La investigació ha estat centrada en els mecanismes de dipòsit de diversos metalls en funció del potencial del sistema redox corresponent, i també en els efectes del procés de dipòsit sobre el propi substrat.

A més de les conclusions específiques resumides en l’apartat anterior, d’aquest estudi es poden extreure tres conclusions metodològiques:

- Les tècniques electroquímiques constitueixen eines úniques per a investigar els processos d’intercanvi de càrrega que tenen lloc a la interfície semiconductor | dissolució: proporcionen informació _in situ_, en
Figura C.9: El concepte d’ànode de sacrifici aplicat al processat de silici: es fabrica una regió de silici porós (part inferior de la figura a) mitjançant l’anodització en una cel·la. En immagar la mostra preparada d’aquesta manera dins d’una dissolució de dipòsit de Pt (HF 1 : 10, 1 mM Pt(II), 5 min a l’OCP), la regió de porosa queda fortament atacada, però causa un augment de la reacció catòdica a les regions planes de la mostra (b). La velocitat de dipòsit es pot comparar amb la de la figura 7.10.

temps real, i amb una resolució de monocapa atòmica. El muntatge experimental és relativament simple i permet combinar-lo amb altres tècniques. I sobretot, donen una idea acurada del mecanisme de les reaccions.

- La superfície de silici terminada en hidrogen que s’obté en dissolucions fluorades és, des del punt de vista electroquímic, força ideal. A més, és possible preparar la superfície dels monocristalls perquè siguin idealment (atòmicament) planes. Es tracta, doncs, d’un bon sistema de referència per realitzar estudis fonamentals de comportament.

- Les tècniques ex situ proporcionen informació complementària sobre la química i la morfologia de les mostres. Un cop entesos els mecanismes bàsics de les reaccions, aquestes tècniques permeten deduir els detalls d’un procés particular amb vistes a la seva aplicació tecnològica en la fabricació de dispositius.
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Finalment, vull incloure aquí uns pensaments que em van impressionar per la seva profunditat [183] i que, en la meva opinió, expressen amb sublim claredat l'essència dels sistemes estudiats en aquest treball:

有機分子の吸着現象の原子レベルでの研究はほとんど未知の領域である。近年、STM、AFM及びその間連技術の発展は、分子のありのままの構造をその場で直接視覚化するという新たな可能性を切り開いた。特に原子解像度という点で大きなアドバンテージを有しているSTMは、固液界面での原子レベルの金属電析層3や吸着イオン4の構造を明確に可視化し、この分野を大きく進歩させた。しかし、現在でも有機分子を原子レベルの解像度で観察することは、容易なことではない。限られた系においては高真空下で観察された特殊な例を除いてあまり成功していない。溶液中での観察という事であればおおむね少ないのが実状である。

(水分子) \( H_2O \) (電子交換反応) (水和イオン)

(吸着イオン) (電子)

(水和イオン) (電気二重層)

(電極)
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