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Optical characterization of ns-SiN:H in the infrared by spectroscopic ellipsometry

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Abstract

The optical properties of thin films of amorphous silicon nitride with embedded nanoparticles are determined in the infrared using spectroscopic ellipsometry. In the spectral range of study (950–3500 cm^{-1}), the material presents a considerable number of absorption bands, and consequently, a large number of parameters are necessary for the complete description of its optical behaviour. This fact enhances the possibility of reaching good numerical solutions without or with incomplete physical meaning. Particularly, we observe that the common approach consisting of optimising all the parameters in a single step may neglect some of the absorption bands that are evidenced by the experimental data. We propose a fitting strategy based on the progressive fitting of the data, introducing at each step new absorption bands and thus extending the fitted spectral range. This strategy is able to assure a good numerical solution with a correct description for all the absorption bands considered.
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Keywords: Spectroscopic ellipsometry; Lorentz oscillator; Plasma enhanced chemical vapour deposition (PECVD)

1. Introduction

Silicon nitride is a widely used ceramic due to its chemical, mechanical and optical properties. It can be used in microelectronics due to its high dielectric constant and large band gap. Similarly, hydrogenated amorphous silicon nitride (a-SiN_x:H) with embedded nano-particles (ns-SiN_x:H), also known as nanostructured hydrogenated amorphous silicon nitride, may also present a high chemical, thermal and mechanical stability. Thus, a significant research in the physical properties of these materials regarding its use in different applications has been recently performed [1–3]. Thin films of ns-SiN_x:H are usually produced by plasma enhanced chemical vapour deposition (PECVD) at low temperatures, and present a porous microstructure and a consequent spontaneous oxidization [4].

During the last years, infrared spectroscopic ellipsometry (IRSE) has appeared as a powerful technique for the precise optical characterization of materials due to its high sensitivity to the presence of chemical bonds [5]. Typically, the IRSE measurements are analysed considering the contribution of an oscillator for each of the absorption bands that the material presents in the spectral range under investigation [6,7]. Thus, when several absorption bands must be taken into account, a considerable number of parameters may be necessary for the correct description of the experimental data. In these cases, difficulties related to the non-uniqueness of solutions can arise in the numerical fitting of the data.

In this work, we present the methodology used for the accurate optical characterization of ns-SiN_x:H films in the infrared range using spectroscopic ellipsometry. The analysis of the measured data reveals the presence of a significant number of vibrational absorption bands. In order to overcome the above mentioned problems related to the high number of parameters, we test different fitting strategies: (i) a classical approach, consisting of fitting the entire range of the experimental data, optimising all the required parameters in a single step and (ii) fitting the data in a progressive way, introducing at each step new absorption bands and thus, extending the fitted spectral range until the complete range is

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fitted. The results achieved with both approaches are compared and the differences are discussed.

2. Experimental

A set of samples consisting of thin single layers of ns-SiN_x:H deposited on different substrates by radio-frequency plasma enhanced chemical vapour deposition (RF–PECVD) was obtained. The samples were obtained from gas mixtures of SiH_4, NH_3 and Ar. The differences among samples were the layer thickness, the deposition temperature, the flow ratio (defined as $R=[NH_3]/[SiH_4]$), and the wave mode of the radio frequency power (continuous or modulated). A more detailed description of the experimental conditions as well as of the ns-SiN_x:H material characterization can be found elsewhere [8]. In the present work, we focus on one of the samples deposited on a Cr substrate using a flow ratio $R = 6$ at room temperature (Sample C3 in reference [8]).

Ellipsometric measurements for both the bare substrate and the thin film deposited on the substrate were performed in the spectral range from 900 to 3500 cm^{-1} with an FTIR phase modulated ellipsometer [9]. The measurements were done following a calibration procedure based on the multiple harmonic modulation model that also takes into account the effect of the multiple reflections of the beam between the modulator faces [10]. The IR spectra were recorded with a resolution of 8 cm^{-1} and by integrating of 500 interferograms. Using this procedure, the average estimated error for the ellipsometer angles was $\delta\Delta = 0.36^\circ$ and $\delta\Psi = 0.29^\circ$. The angle of incidence was fixed to 72.5°. We performed the measurements just after the deposition of the sample and later at different time intervals. The analysis of the measurement revealed a homogenous oxidization of the sample reported in [11]. The measurements analysed in this work were obtained one week after the deposition.

3. Modelling

We model the sample under investigation as a homogeneous layer deposited on a Cr substrate. The optical constants of the substrate were determined for each wave number from the direct inversion of the ellipsometric measurements of the substrate, prior to the deposition of the ns-SiN_x:H film. Regarding the optical constants of the ns-SiN_x:H, we represent each of the absorption bands with the contribution of one oscillator. Typically, Lorentz oscillators are considered for this aim. However, this model fails when the material is amorphous, since there is no long-range order. An alternative approach for amorphous materials is the so-called Gauss model, proposed by Brendel and Bormann [12]. The approach consists of the assumption of a Gaussian distribution of classical oscillators (each one with a width γ) centered in a characteristic frequency ω_0 and with a distribution width σ_0. The square of the plasma frequency, ω_p, is proportional to the oscillator concentration. Then, the dielectric function can be expressed as:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{1}{\sqrt{2\pi}\sigma_0}\int_{-\infty}^{\infty} \exp\left[-\frac{(x-\omega_0)^2}{2\sigma_0^2}\right]\frac{\omega_p^2}{x^2-\omega^2+i\gamma\omega}\,dx \quad (1)$$

In the limit where $\sigma_0 \to 0$ the model is equivalent to the classical Lorentz oscillator. For the computations we have used an approximation to the integral proposed by the same authors [13]. The fitting of the data is performed by optimizing the parameters of the Gauss model (4 for each band: ω_0, ω_p, γ and σ_0) plus the thickness of the layer. The optimal value of these parameters is found via the minimisation of the following merit function:

$$\xi^2(P_1, P_2, \ldots, P_{N_p}) = \frac{1}{2n_{meas} - N_p - 1}\sum_{i=1}^{n_{meas}}\left[\left(\frac{\Delta_i - \Delta(x_i; P_1, P_2, \ldots, P_{N_p})}{\sigma_{\Delta_i}}\right)^2 + \left(\frac{\Psi_i - \Psi(x_i; P_1, P_2, \ldots, P_{N_p})}{\sigma_{\Psi_i}}\right)^2\right] \quad (2)$$

where n_{meas} is the number of measured wavelength points (x_i), P_1, P_2,..., P_{N_p} are the N_p parameters that define the sample, Δ_i and Ψ_i are the ellipsometric angles for each wavelength, while σ_{Δ_i} and σ_{Ψ_i} are respectively their experimental errors and $\Delta(x_i; P_1, P_2, \ldots, P_{N_p})$ and $\Psi(x_i; P_1, P_2, \ldots, P_{N_p})$ are the calculated values of the ellipsometric angles at each x_i. The use of this merit function allows a direct evaluation of the quality of the fitting, as values of ξ^2 close to 1 indicate that the differences between the simulation and the experimental data are around the value of the experimental error. For all the computations, the NKD software has been used [14].

4. Results

Some of the absorption bands can be inferred by direct observation of the ellipsometric spectra shown in Fig. 1, as they are easily identified by the presence of maxima or minima in the Ψ spectra due to the so-called ‘‘weak’’ oscillators. It is the case of the minima observed at approximately 1450 cm^{-1} (attributed to the Si–N=O bound), 1620 cm^{-1} (H_2O bending) or 3340 cm^{-1} (N–NH stretching). However, other absorption bands that are involved in the spectral range under study correspond to ‘‘strong’’ oscillators and in this case the minima and maxima in the Ψ spectra may be related to other causes, like the Berreman effect [15]. For these cases, the presence of the absorption bands has to be more carefully assessed. Thus, the absorption bands corresponding to the Si–N stretching (850–900 cm^{-1}), Si–O stretching (1070 cm^{-1}), N–H bending (1175 cm^{-1}) and H_2O stretching (2800–3700 cm^{-1}) were also identified.

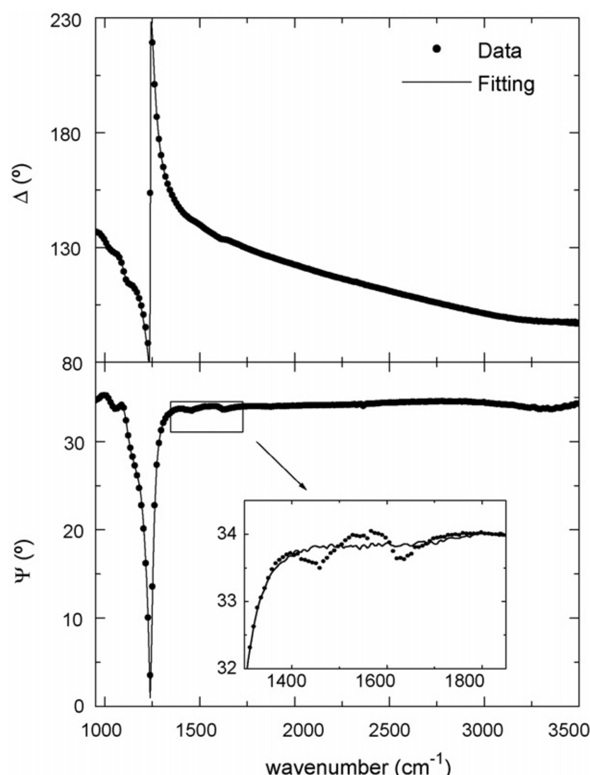

Fig. 1. Best fit obtained with the simultaneous optimisation of all the parameters (Section 4.1).

4.1. Simultaneous fitting of all the absorption bands

In order to fit the experimental data, our first approach consists of considering simultaneously the contribution of each of the seven absorption bands listed above. Since each absorption band is represented by a 4-parameter Gauss oscillator, a total of 30 parameters are required for the complete description of the data (28 parameters for the absorption bands plus the value of ε_∞ and the layer thickness). This methodology is the most widely applied approach in optical characterization of materials, usually available in commercial software and it is implemented in the NKDSoftware as a standard routine [16].

The optimisation procedure leads to a merit function of 1.07, indicating the good quality of the fitting. The best fit obtained is shown in Fig. 1. Although the final value of the merit function indicates the good quality of the fit, one must notice that in the spectral region compressed between 1350 and 1800 cm^{-1} (as shown in the inset of Fig. 1) the simulation qualitatively differs from the experimental data. Actually, it can be seen that the obtained optical constants do not include the two absorption bands corresponding to the Si–N═O and the H_2O bending (inset of Fig. 3). Thus, the optimisation procedure has overlooked the presence of these absorption bands.

4.2. Progressive fitting of the absorption bands

In order to obtain a correct description for all the absorption bands, we apply the following methodology: the absorption bands are introduced in a progressive way, fitting the spectral range where they have a significant weight. Thus, the procedure begins considering the absorption bands of highest intensity, fitting that spectral region where the other absorption bands have a smaller influence. At each new step, new oscillators are introduced, extending the spectral region until all the spectral range of the measurements is enclosed. The implementation of this routine has been done through the specific capabilities of the software that allow choosing, at each step, the spectral range that is currently fitted and what parameters are optimized.

In the first step (Step 1) of the procedure, we consider the Si–N bending, Si–O stretching and N–H bending absorption bands, and the fitting is restricted to the range between 950 and 1350 cm^{-1} and between 1800 and 2100 cm^{-1}. The value of the parameters resulting from the fitting are listed in Table 1 (ε_∞ = 2.05, layer thickness 196 nm), and the value of the merit function is 6.22. In the following step (Step 2), we include the oscillators representing the absorption bands H_2O stretching and N–NH stretching and extend the spectral range to the region between 2100 and 3500 cm^{-1}. Nevertheless, we do not optimise all the parameters in a single step: as first, we consider the parameters corresponding to the newly introduced absorption bands. In this way, we work with a reduced number of parameters, what allows us to find out their appropriate initial values. Once we obtain these values, we refine the fitting optimising all the parameters (including those optimised in Step 1). Now, the merit function drops to 1.14, and the parameters values are listed in Table 2 (with ε_∞ = 2.02, layer thickness 197 nm). In the final step (Step 3), we include the two weakest absorption bands (Si–N═O and H_2O bending) and extent the fitted spectral region to the whole spectral range of the measurement. Same as in the Step 2, first we optimize the parameters corresponding to the newly introduced absorption bands, obtaining appropriate initial values and then refine the fitting optimizing simultaneously all the parameters. The values of the parameters are listed in Table 3 (with ε_∞ = 2.02, layer thickness 197 nm). Fig. 2 shows the best fit obtained that

Table 1
Value of the parameters for the absorption bands after Step I of the progressive strategy (γ < 1.0E-2 means a numerical result that physically is zero)

Absorption band	ω_0 (cm^{-1})	ω_p (cm^{-1})	γ (cm^{-1})	σ (cm^{-1})
Si–N	932	286.8	<1.0E-2	34.8
Si–O stretching	1064	634.5	35.9	13.2
N–H bending	1153	316.3	<1.0E-2	50.2

Table 2
Value of the parameters for the absorption bands after Step II of the progressive strategy (γ < 1.0E-2 means a numerical result that physically is zero)

Absorption band	ω_0 (cm^{-1})	ω_p (cm^{-1})	γ (cm^{-1})	σ (cm^{-1})
Si–N	921	352.8	<1.0E-2	49.9
Si–O stretching	1063	606.4	24.3	17.7
N–H bending	1150	342.9	<1.0E-2	52
H_2O stretching	3270	536.0	17.75	903.1
N–NH stretching	3284	435.1	1.33E-2	231.8

Table 3
Value of the parameters for the absorption bands after the final step of the progressive strategy ($\gamma < 1.0E\text{-}2$ means a numerical result that physically is zero)

Absorption band	ω_0 (cm^{-1})	ω_p (cm^{-1})	γ (cm^{-1})	σ (cm^{-1})
Si–N	921	354.6	<1.0E-2	51.9
Si–O stretching	1063	598.5	17.8	23.2
N–H bending	1148	352.1	<1.0E-2	53.8
Si–N=O	1461	66.6	1.34	46.9
H_2O bending	1631	75.3	4.66	41.4
H_2O stretching	3300	507.9	14.9	890.2
N–NH stretching	3284	435.8	<1.0E-2	235.7

corresponds to value of the merit function of 0.81. From the inset one can realize that now all the absorption bands are well described, on the contrary to the results achieved by the strategy described in Section 4.1. Fig. 3 shows a comparison of the optical constants deduced using the two strategies considered.

5. Discussion

The modelling of the absorption bands with the Gauss model allows a very good description of the experimental data. Actually, this model allows a transition between Gaussian and Lorentzian line-shapes for the imaginary part of the dielectric function. Thus, some of the bands have values of the parameter γ close to zero, indicating a Gaussian line-shape, while others present a larger ratio of γ/σ, showing that the line-shape of the imaginary part corresponds to a convolution of Gaussian and

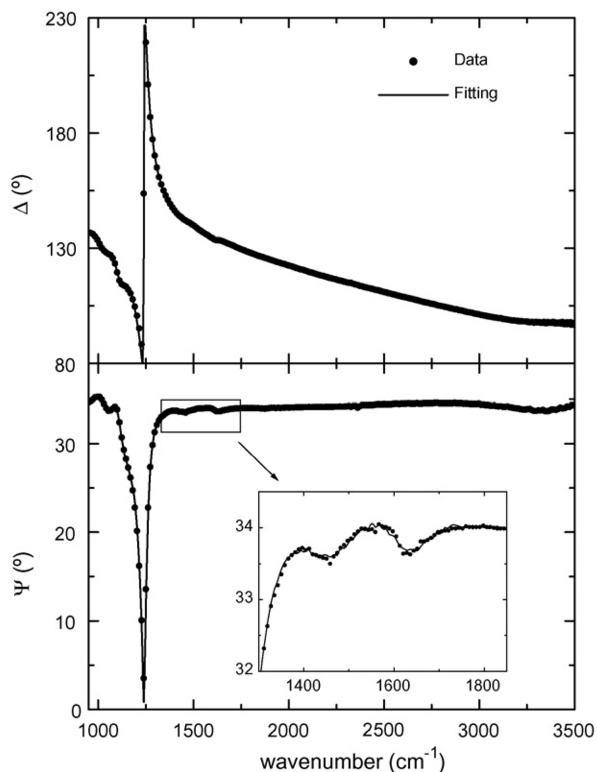

Fig. 2. Final fit obtained with the progressive optimisation of all the parameters (Section 4.2).

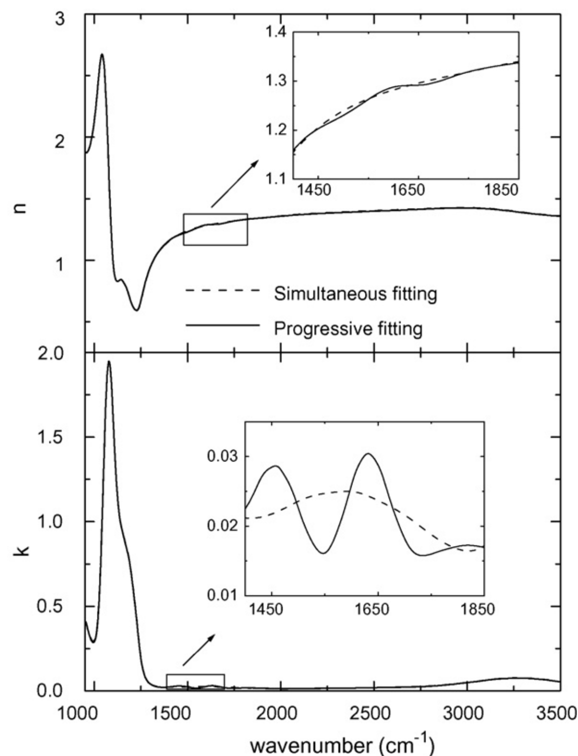

Fig. 3. Optical constants obtained from the fitting of the data using the simultaneous strategy (dotted line) and the progressive one (solid line).

Lorentzian curves. In any case, we do not obtain values of σ close to zero that would correspond to the classical Lorentz model. This evidences the inadequacy of the Lorentz model to describe the absorption bands of amorphous materials.

The two strategies proposed for the fitting of the data lead to numerically good results (the difference in the merit function is not very significant, 1.07 versus 0.81). However, the simultaneous strategy, described in Section 4.1, neglects the presence of absorption bands that are evidenced by the experimental data, while the progressive strategy, Section 4.2, is able to describe these absorption bands correctly. Thus, if the merit function is calculated only in the region 1350–1800 cm^{-1}, the value of the ξ^2 is 1.5 for the first strategy, while for the second is 0.15.

The progressive strategy allows guiding the optimisation process. At each step, we work with a reduced number of parameters, and in this way, we can decrease the multiplicity of solutions and obtain realistic values for each of the parameters. Hence, in the final refinement, when all the parameters are optimised simultaneously, the initial values of all the parameters are reasonably close to the final solution. In the simultaneous strategy, we introduce all the parameters simultaneously, but the initial guess has not been carefully chosen, increasing the possibility to find a good numerical solution but without adequate physical sense. We can expect that the parameters that will be more sensitive to attain wrong values, will be those ones that have less influence in the overall optical behaviour of the sample. In the present case, these parameters correspond to those ones describing the absorption bands of less intensity.

Finally, the robustness of the progressive strategy can be assessed analyzing the evolution of the parameters values. At

each step, the introduction of new parameters and the enlargement of the fitted spectral range do not change significantly the value of the parameters determined in previous steps, indicating their appropriateness (compare Tables 1–3).

6. Conclusion

We have accurately determined the optical properties of ns-SiN_x:H films in the infrared range using spectroscopic ellipsometry. As the optical behaviour of the material is determined by a large number of parameters, we have to deal with the problems related to the numerical inversion of the data (non-uniqueness of solutions). In order to overcome these difficulties, we have proposed a methodology based in the introduction of parameters in the optimisation procedure in a progressive way. This strategy allows the description of all the absorption bands present on the material, while a typical approach based in the simultaneous optimisation of all the parameters results to be inappropriate. In this way, the validity of the proposed methodology is confirmed.

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