Optical characterization of materials deposited by different processes: the LaF_3 in the UV-visible region.

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ABSTRACT

The optical characterization of materials in thin film phase is a standard task in the field of coating technology. There are experimental circumstances where the accurate comparison between several deposition processes (for the same material) is important. In these cases, several sets of substrates are coated at the different deposition plants. The samples will be subsequently analyzed using, if the plants are at different locations, different spectrophotometers and finally the results of all the optical characterizations will be compared.
The aim of this work is to present the results of a global procedure for the optical characterization of LaF_3 in the UV-visible region, deposited at three different plants. We have used R and T spectrophotometric data and we have assumed the following model for the optical characterization: $n(\lambda)=n_0+ n_1/\lambda^2$, $k(\lambda)=k_0 \exp(k_1/\lambda)$. Our method characterizes all the samples from the same deposition process by a single set of parameters (instead of a set for each sample), using all the available measurements to determine them in a single numerical fitting, without a significant loss in the quality of the fittings. This procedure reduces the number of parameters and makes the comparison between different deposition processes more clear. By using similar results obtained for MgF_2, the optical characterization of stacks (manufactured using MgF_2 and LaF_3) is also presented.

1. INTRODUCTION

The optical characterization of thin film materials starts from reflectance (R) and/or transmittance (T) spectra of samples consisting of layers deposited on well-known substrates. The optical properties of a multi-layered structure are usually completely defined by the thickness and a set of parameters for each layer (according to the model that may be applied to it). The values for the parameters that define the stack are determined by fitting the available spectra. The fitting procedure requires:

- the definition of a merit function (MF),
- having approximate values for the parameters, and
- using an optimization algorithm that minimizes the merit function.

Numerical methods for the optical characterization are well developed [1][2] and many software packages implementing the different approaches are commercially available. New numerical procedures for the characterization of groups of identical layers, in the case of well-defined experimental conditions are also presented in this meeting [3]
The aim of this work is, fist, to summarize the results of the optical characterization of LaF_3 single layers, in the 200–800 nm spectral range, obtained by three different deposition procedures. These results, together with a similar characterization for MgF_2 (not presented here), are subsequently used for the analysis of stacks of alternate layers. Namely, we will address the optical characterization of:

- anti reflection (AR) coatings for 193 nm, consisting of 2 or 3 layers
- high reflection (HR) stacks, made of 51 and 63 layers (also designed for 193 nm)

These samples are manufactured with the two materials (LaF_3 and MgF_2), deposited by the same processes used for the corresponding single layers and will illustrate the differences arising in the materials when deposited as single layers or when belonging to a stack.

2. MODELLING THE MATERIAL. GENERAL COMPUTATIONAL SCHEME

The complete procedure for the optical characterization of our samples is developed in another communication at this meeting [3]. We present here a short summary of the method. We model the coating material by means of the Cauchy formula (with 2 terms), with exponential absorption, according to the dispersion formulae:

$$n(\lambda) = n_0 + \frac{n_1}{\lambda^2}\ ,\ k(\lambda) = k_0 \exp(\frac{k_1}{\lambda})\ . \qquad (1)$$

Thus, computationally, a single layer on a well-known substrate is defined by 5 parameters: the thickness plus n_0, n_1, k_0, k_1. In the space of all the unknown parameters, our MF is the chi-square function (χ^2) defined by the differences between measured and computed data [4] as follows. Suppose that our data consist of one spectrum (say, reflectance values y_i at normal incidence for wavelengths x_i). This is a set of n values y_i , $i=1,...n,$ corresponding to the independent variables x_i. Once all the defining parameters (say our 5 quantities: thickness, n_0, n_1, k_0, k_1) are assigned and assuming that we have an estimation of the error σ_i associated to each single data y_i, we can compute $y(x_i)$ and, subsequently,

$$\chi^2 = \sum_{i=1}^{n} (\frac{y_i - y(x_i)}{\sigma_i})^2 \qquad (2)$$

or, equivalently [5], $\xi^2 = \frac{1}{n-5-1}\chi^2$ (3).

The minimization algorithm we use is the 'Downhill Simplex' method [4] because is very easy to adapt to our situation where the number of unknowns and the range of their increments are quite variable. We start the optimization from the point in the parameter space defined by the estimated values (*guess*) of the unknown parameters.

Our numerical approach allows three non-standard computation capabilities:

- C1) the ability to perform the minimization of the χ^2 defined by several spectrophotometric and/or ellipsometric spectra corresponding to one sample.
- C2) the ability to perform the minimization of the χ^2 defined by several spectrophotometric and/or ellipsometric spectra corresponding to several samples, so that the parameters of each sample are considered independent.
- C3) the ability to perform the minimization of the χ^2 defined by several spectrophotometric and/or ellipsometric spectra corresponding to several samples, so that the parameters defining the samples are forced to be equal.

These features may be attained by including in the sum (2) the terms corresponding to all the spectra, affected by their respective error estimations σ_i, and by linking together the parameters during the optimization (for capability C3). It is worth noting that these important capabilities are only possible by using the χ^2 estimator for the MF, since each term in the sum (2) is a dimensionless number that allows mixing any kind and any number of measured data into a single merit function. It is important to note the practical difference between χ^2 and ξ^2: they both provide the same minimae but χ^2 is to be used for computing the curvature matrix whereas ξ^2 gives a better idea of the 'goodness' of a fitting (since the final value has to be around 1 for ξ^2). In our results we will use ξ^2 for defining our MF since it is also useful for interpreting the confidence limits for the parameters [5].

3. OPTICAL CHARACTERIZATION OF LAF_3 SINGLE LAYERS

Three sets of samples were obtained by three different manufacturing processes, at three different laboratories: 6 samples were manufactured by boat evaporation (PVD1), 5 samples were obtained by a similar procedure (under different conditions, PVD2), and 5 other samples were obtained by ion beam sputtering (IBS). Two different substrates were used: fused silica and CaF_2 (their optical constants were taken from Ref. [6]). The deposited layers were designed to be 6-quarter-wave thick @ 193 nm (optical, QWOT). To represent the optical properties of the materials, we have used the Cauchy model, with exponential absorption, defined by expression (1). We have assumed a constant error for T (0.0015) and for R (0.003). In the following we present the results corresponding to the 200-600 nm range for PVD1 and to 200-800 nm for PVD2 and IBS.

For each set (PVD1, PVD2, IBS) of samples deposited in the same batch process (apart from the individual sample-by-sample characterization) we have performed the two kinds of global fittings introduced in the previous paragraph as non-standard capabilities:

- option C2, i.e., a global fitting for all the samples together, with independent parameters for each sample,
- option C3, i.e., a global minimization constraining the layers of the samples to be identical.

As explained in detail in Ref. [3], the results of both methods are different, but the final values for the MF are of the same order of magnitude. Since the second procedure allows defining a single group of optical parameters for the whole set of samples, we present here the results given by this option C3:

LaF_3	MF	Th (nm)	n_0	n_1 (nm2)	k_0	k_1(nm)
PVD1	3.57*	172.5	1.55	3400	0.	0.
PVD1	0.91*	5 x 34.5	1.56 (-2%)	3501.	0.	0.
PVD2	1.03	158.0	1.571	4347.	0.	0.
IBS	0.91	175.0	1.588	4590.	1.1e-5	1205.

Note that we have presented two rows for the first set. The samples prepared by the procedure PVD1, when considered to be homogeneous layers (in depth), reach a final MF quite high (3.57). If one assumes in-depth inhomogeneity by modeling with the layer by 5 sub-layers with linear profile in the refractive index n, the fitting procedure ends with a MF of 0.91 and an inhomogeneity around -2% (this is a refractive index n decreasing from inside to outside). Thus, when assuming inhomogeneity for PVD1 samples, we get final values for the MF (in all characterizations) around 1, as expected for the ξ^2 estimator [5]. Fig. 1 illustrates the agreement between the experimental data and the global fitting for two of the IBS samples (on a CaF_2 substrate). Fig 2 compares the dispersion data obtained from the global optimization applied to the three deposition processes.

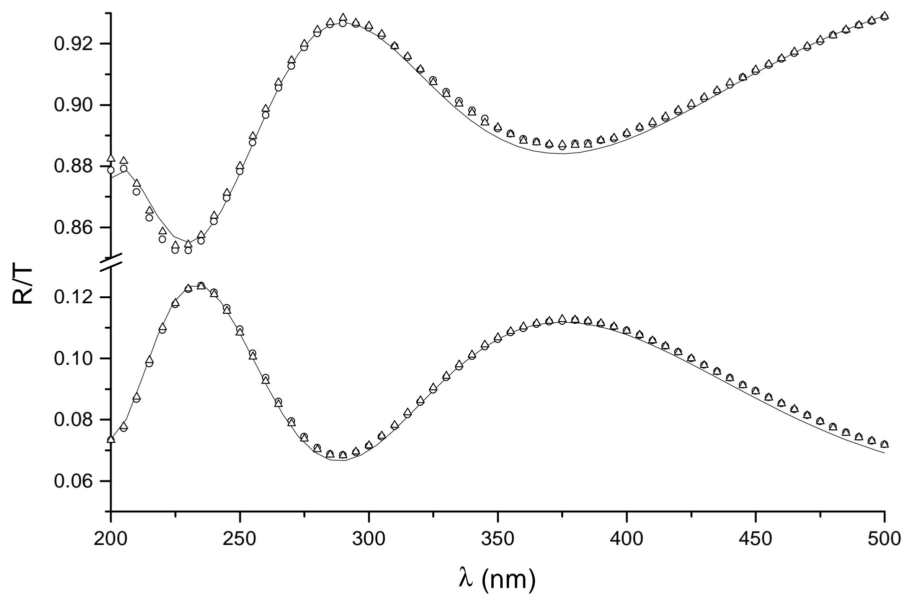

Fig. 1: Comparison between the global fitting (continuous line) and the measured R and T data of two samples (circles and triangles) corresponding to a single layer of LaF_3 (IBS deposition) on a CaF_2 substrate.

4. OPTICAL CHARACTERIZATION OF AR LAF_3/MGF_2 COATINGS

For the next step in the optical characterization process, several samples consisting of two (or three) layer stacks were deposited. We present here results corresponding to two AR coatings, one consisting of three layers (S/LHL/air) deposited by PVD1 and the other consisting of a V-coating (S/HL/air) deposited by PVD2. As a reminder, the following table summarizes the results for the optical characterization of MgF_2 single layers (performed elsewhere [3]). These values and those just presented for LaF_3 define now the starting point for the fittings. We also note that, for the rest of the work, there is no need of assuming inhomogenity in the LaF_3 layers manufactured by PVD1, since the thicknesses will be around the quarter-wave (less than 30 nm)

MgF_2	n_0	$n_1(nm^2)$	k_0	$k_1(nm)$
PVD1	1.375	2300	5.0e-6	1100.
PVD2	1.373	2056.	4.8e-6	1001.
IBS	1.379	1511.	7.2e-6	1112.

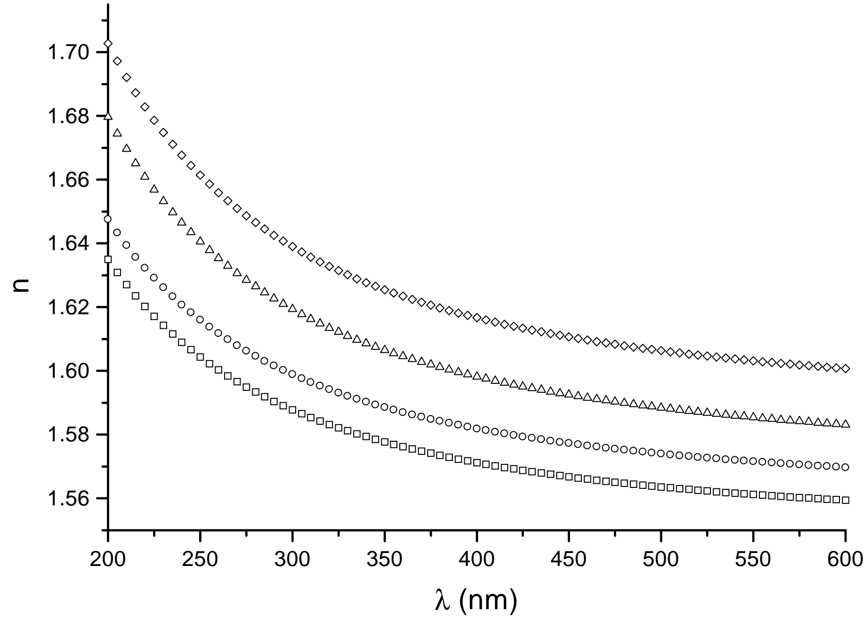

Fig. 2. Dispersion curves for LaF_3 deposited by thee different processes: PVD1 (homogeneous=squares, inhomogeneous mean values=circles), PVD2 (triangles) and IBS (rhombs).

4.1. 3-layer AR stacks (@ 193 nm) deposited by PVD1

Now, a sample will be defined by 15 values (5 for each layer) and this fact gives rise to multiple local minimae during the optimization process. There were four samples: two on CaF2 and two on fused silica. For each sample, two spectra (190-600 nm) were fitted simultaneously: R and T at 0 deg. The results of the global minimization, with the constrain of equal parameters for the two low index layers, are (see also Fig. 3, corresponding to a fused silica substrate)

PVD1 (MF=1.80)	Th (nm)	n_0	$n_1(nm^2)$	k_0	$k_1(nm)$
Layer 1	35.8	1.378	2335.	7.2e-6	0.8
Layer 2	26.0	1.550	3563.	0.	0.
Layer 3	35.8	1.378	2335.	7.2e-6	0.8

4.2. 2-layer AR stacks (@ 193 nm) deposited by PVD2

Now, a sample will be defined by 10 values (5 for each layer). There were three samples: one on CaF2 and two on fused silica. For each sample, two spectra (200-800 nm) were fitted simultaneously: R and T at 0 deg. The results of the global minimization are

PVD2 (MF=1.25)	Th (nm)	n_0	$n_1(nm^2)$	k_0	$k_1(nm)$
Layer 1	34.2	1.370	2010.	5.5e-6	1341.
Layer 2	27.2	1.579	4242.	0.	0.

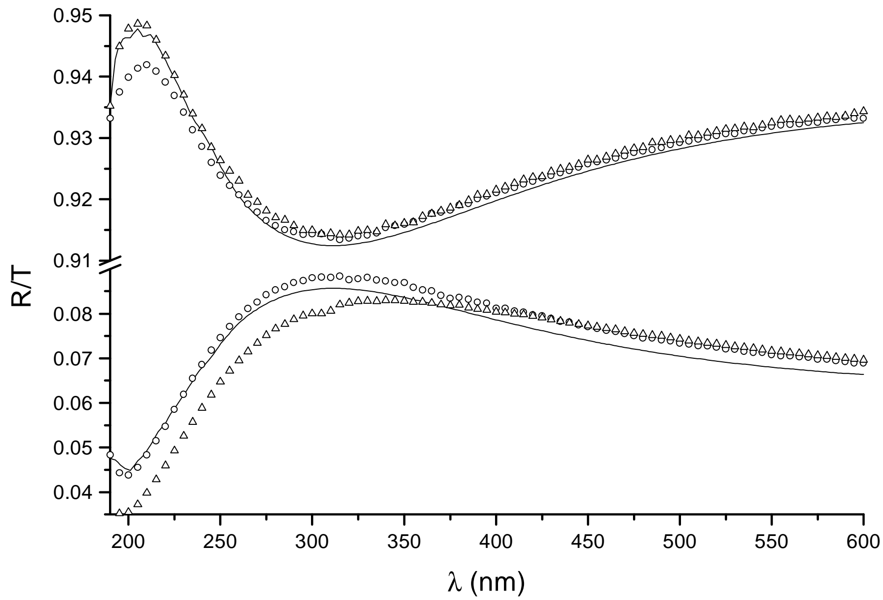

Fig. 3. Comparison between the global fitting (continuous line) and the measured R and T data of two samples (circles and triangles) corresponding to 3-layer stacks deposited by PVD1.

5. OPTICAL CHARACTERIZATION OF HR STACKS OF LAF_3/MGF_2 LAYERS

We consider now the fitting of experimental data for two HR stacks, designed for 193 nm. It is very difficult to obtain good fittings for the complete spectral range starting from the optical data obtained from the optical characterization of single layers of the two component materials. The main difficulties are in the sharp transitions of the spectra. The first key point of our fitting process is the definition of a ‘target’ on the X-axis, according to the following strategy. Instead of computing Rs and Ts for all the wavelengths, we define the ‘target’ as the only points on the X-axis effectively computed in all the fitting procedures. Thus, the choice of a suitable target may have the following advantages: i) avoid the sharp transitions in the spectra, and ii) produce faster calculations. By inspection of our R and T data, we have chosen as our target the 190 points 190...198, plus 219...399 (in 1 nm steps).
Besides the definition of the target, the second key point for our global characterization is forcing all the layers of the same material to be identical and restricting their range of variation. These arbitrary constrains will generate, of course, different final results as we will see.

5.1. 51-layer HR stacks (@ 193 nm)

This case corresponds to LaF_3 films deposited by PVD2 (and MgF_2 films deposited by e-beam). The coating consists of a 51-layer structure S/HL...H/Air. There are three samples: one on a fused silica substrate and two on a CaF_2 substrate. We present the details for one sample on CaF_2, using only T data at 0 deg. As mentioned our target included the 190-198 and 219-399 nm zones. Regarding the starting points for minimizations and the ranges of variation allowed, we have considered the following three variatios:
v1) Starting point defined by data from single layers of MgF_2 and LaF_3, and allowing the variation ranges: 27-30 nm, 1.574-1.580 (for LaF_3) and 34.0-34.7 nm, 1.37-1.39 (for MgF_2).

MF=12.1	QWOT	Th (nm)	n_0	$n_1(nm^2)$	k_0	k_1(nm)
MgF_2	1.042	34.7	1.390	2178.	1.8e-6	1085.
LaF_3	0.949	27.3	1.574	3818.	0.	0.

v2) Starting point defined by data from 2 and 3-layer stacks and allowing the variation ranges: 27-27.4 nm, 1.577-1.581 (for LaF_3) and 34.0-34.4 nm, 1.368-1.372 (for MgF_2).

MF=60.8	QWOT	Th (nm)	n_0	$n_1(nm^2)$	k_0	k_1(nm)
MgF_2	1.018	34.4	1.372	2063.	5.4e-6	867.
LaF_3	0.963	27.4	1.581	4248.	0.	0.

v3) Starting point defined by data from 2 and 3-layer stacks and allowing the variation ranges: 1.577-1.581 (for LaF_3) and 1.368-1.372 (for MgF_2) , leaving thicknesses free.

MF=20.3	QWOT	Th (nm)	n_0	$n_1(nm^2)$	k_0	k_1(nm)
MgF_2	1.030	34.5	1.368	2777.	2.5e-6	80.1
LaF_3	0.960	27.8	1.577	3301.	0.	0.

The graphical comparison is presented in Fig. 4.

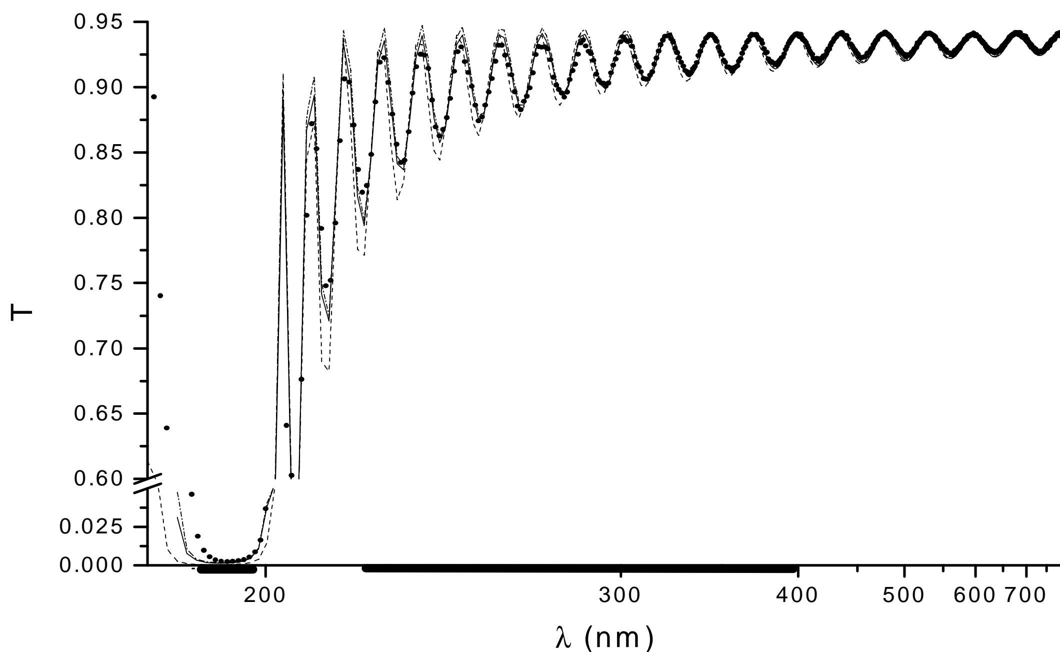

Fig. 4. Comparison between the three global fittings (v1, continuous line; v2, dashed; v3, dash-dot) and the measured T data for one 51-layer sample. The 'target' zone is indicated on the X-axis (see text for a full description).

The X axis has been re-scaled in the figure for better clarity and the zones corresponding to the target are indicated by a thick line. It is very interesting to note that much of the discrepancies in the 200-210 nm zone may be interpreted in terms of insufficient spectrophotometric resolution (slit too wide). The variations on the spectral data, clearly observed to be weaker than the computed ones, can also be interpreted in terms of slit width. The T data of the other sample on CaF_2 lead to similar results.

5.2. 63-layer HR stacks (@ 193 nm)

This second case corresponds to LaF_3 films deposited by PVD1 (and MgF_2 films deposited by boat). The coating consists of a 63-layer structure S/HL...H/air. There are four samples: one on fused silica and three on CaF_2. For all the samples R and T spectra in the 190-600 nm range were available. As before, to avoid the sharp transitions we have used the same

optimization strategies. We present the details for one sample on CaF_2, using the R and T of the 190-600 nm range simultaneously. We used the same target for the fittings, allowing several starting points and variation ranges.

v1) Starting point defined by data from single layers of MgF_2 and LaF_3, and allowing the variation ranges: 27-30 nm, 1.54-1.57 (for LaF_3) and 33-36 nm, 1.365-1.385 (for MgF_2).

MF=77.	QWOT	Th (nm)	n_0	$n_1(nm^2)$	k_0	k_1(nm)
MgF_2	0.974	33.0	1.365	2225.	5.8e-6	163.
LaF_3	1.009	29.2	1.570	3634.	0.	0.

v2) Starting point defined by data from 2 and 3-layer stacks and allowing the variation ranges: 25-27 nm, 1.54-1.56 (for LaF_3) and 35-37 nm, 1.37-1.39 (for MgF_2)

MF=116.	QWOT	Th (nm)	n_0	$n_1(nm^2)$	k_0	k_1(nm)
MgF_2	1.063	35.8	1.370	2312.	6.1e-6	151.
LaF_3	0.922	26.9	1.560	3479.	0.	0.

v3) Starting point defined by data from 2 and 3-layer stacks and allowing the variation ranges: 1.54-1.56 (for LaF_3) and 1.37-1.39 (for MgF_2), leaving the thicknesses free

MF=77.	QWOT	Th (nm)	n_0	$n_1(nm^2)$	k_0	k_1(nm)
MgF_2	1.013	35.3	1.384	0.44	1.7e-5	0.2
LaF_3	0.961	27.3	1.547	5610.	0.	0.

These values correspond to the following fittings in the 190-300 nm range (v1, continuous line; v2, dashed; v3, dash-dot)

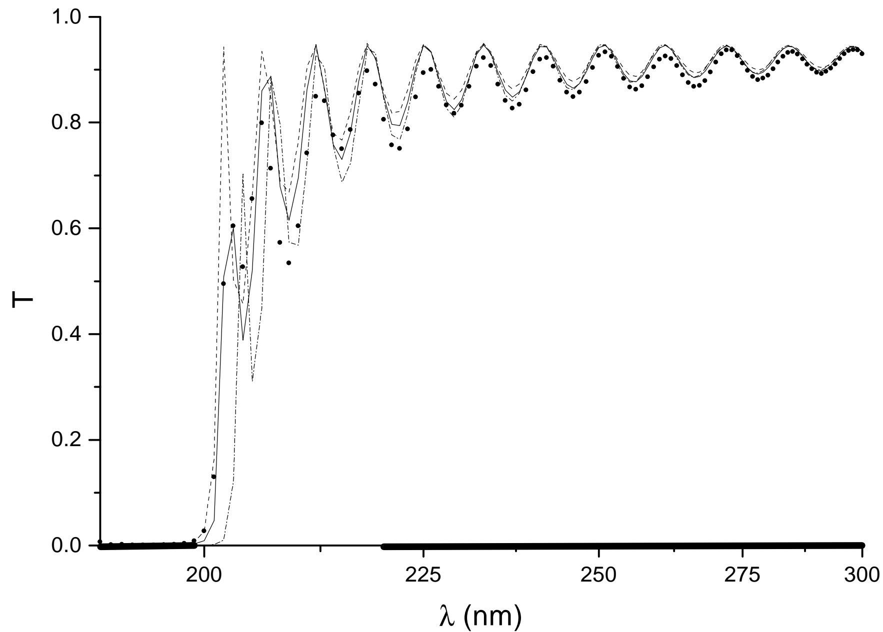

Fig. 5. Comparison between the three global fittings (v1, continuous line; v2, dashed; v3, dash-dot) and the measured T data for one 63-layer sample. The 'target' zone is indicated on the X-axis (see text for a full description).

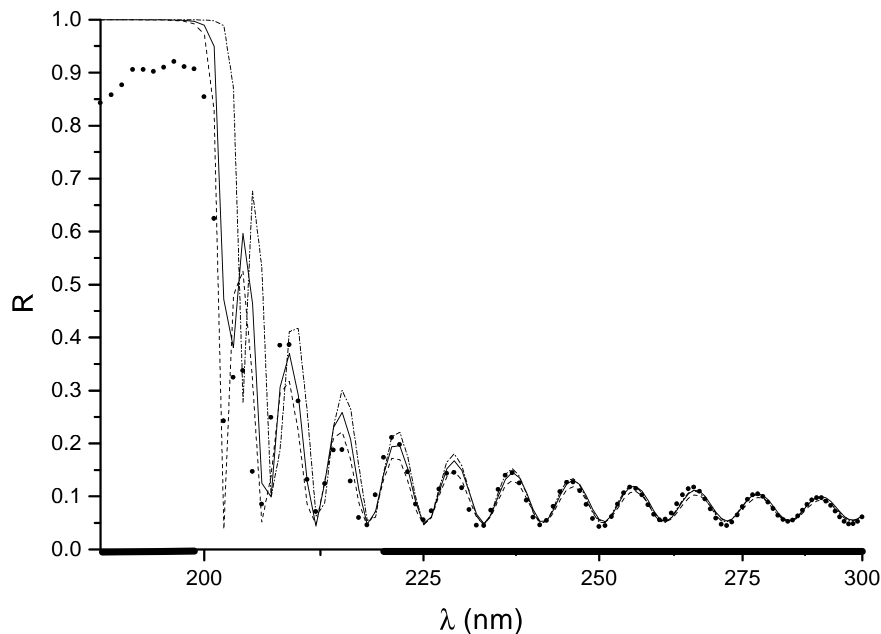

Fig. 6. Id as in Fig. 5, for the measured R data.

Now, the final values of the merit function (corresponding only to the 'target' zone) are higher than for the 51-layer samples, but share the same tendency for the three variations. This is due to the fact that we are optimizing now for R and T simultaneously. Although we have fitted for 190-600 nm, we show a re-scaled and reduced X-axis for better clarity. As before, much of the discrepancies in the 200-215 nm zone may be interpreted in terms of insufficient resolution.

6. CONCLUSIONS

The UV-visible optical characterization of LaF_3 films deposited by three different processes has been presented. Using these data (together with other for MgF_2), we have also performed the characterization of AR coatings (@ 193 nm), consisting of 2 and 3 layers. Using all the single layer and multi layer data, we have been able to obtain good fittings for HR (@ 193 nm) stacks consisting of 51 and 63 alternate layers.

In all the optimizations, many local minimae (having similar MF value) can be attained, even forcing the layers of the same material to be equal. In case of the multilayers, if the variation of the parameters defining the layers is not constrained during optimization, unrealistic optical constants and thicknesses can be obtained.

When fitting large wavelength ranges, to avoid the sharp transitions in the spectra that hinder the minimization procedures, it becomes necessary to define a 'target' (zone of the X axis actually fitted).

7. ACKNOWLEDGEMENTS

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