Refractive index profiling of CeO2 thin films using reverse engineering methods

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Abstract

In some recent papers it was shown that ZrO_2 single films can be modelled using inhomogeneous models. A similar modelling approach to analyze CeO_2 layers has been used. Films have been produced using a standard reactive evaporation technique. Following the measurement results, obtained by normal incidence transmission and variable angle spectroscopic ellipsometry, reverse engineering of the monolayer with its sub-layers has been performed. Novel in this method is that no assumption of refractive index profile is needed. A very good fit of the experimental data with the reverse engineered multi-layers has been obtained, showing that it is possible to find a fine substructure of analyzed films.

Keywords: Optical coatings; Optical properties; Depth profiling; Oxides

1. Introduction

The refractive index of a thin film often varies through layer’s thickness. It can be seen that the transmittance of a simple single layer on a glass substrate could not be related to the known theory of homogeneous media. Instead of touching the substrate’s transmittance curve at the transmittance maximum (when $n_{\text{film}} > n_{\text{substrate}}$) it crosses it [1, 2]. The only possible explanation for this behaviour can be related to the inhomogeneities in the layer. Most dielectric films exhibit some degree of inhomogeneity.

Homogeneity of layers is a common approximation in the process of multi-layer design, introducing an error that cannot always be neglected. Unfortunately in the real world we have to accept inhomogeneity, which can be a source of error in production. Therefore, understanding of the refractive index profile is very important in the development of demanding multilayers, i.e. antireflective coatings for high power laser applications where the main contribution to the error we may expect from the first layer adjacent to the substrate, due to its inhomogeneity. The main causes of refractive index variation are modes of nucleation and growth during the deposition. The layer can then be represented by a multilayer stack [3, 4].

Numerous methods for optical characterization of inhomogeneous films have been developed. Some of them are based on transmittance $T(\lambda)$ analysis [1] or ellipsometric functions $\psi(\lambda, \theta)$ and $\Delta(\lambda, \theta)$ analysis [5], some on in-situ spectroscopic ellipsometry [6] or spectrophotometry [7] or their combination [8, 9].

For determination of optical constants of unknown homogeneous dielectric materials in multilayers the reverse engineering method has been successfully applied before [10]. Our approach was to divide a single inhomogeneous layer into several sublayers of unknown refractive indices and thicknesses and then find refractive index profile according to a measured transmittance spectrum at normal incidence and ψ spectra at several angles.

2. Experimental details

To illustrate the method we analyzed a cerium dioxide layer. Cerium dioxide has excellent operating properties such as high thermal and chemical endurance. It makes good high index optical coatings in the range between 500 nm and 14 mm (Merck–Patinal brochure). It is not very popular in the visible region due to its significant absorption bellow 500 nm, but is excellent for the infrared region. Due to their porous structure, which is growing using reactive evaporation, cerium dioxide layers are suitable also for gas sensors (Merck–Patinal brochure).

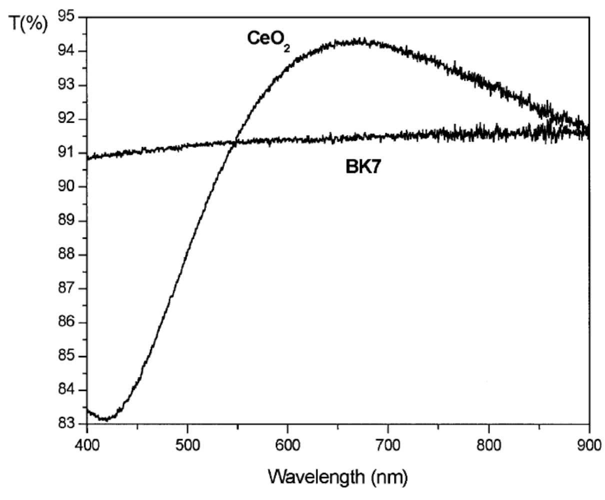

Fig. 1. Transmittance spectrum for the CeO_2 film and the bare BK7 substrate. CeO_2 curve crosses that of the substrate in a wide region of wavelengths showing considerable inhomogeneity.

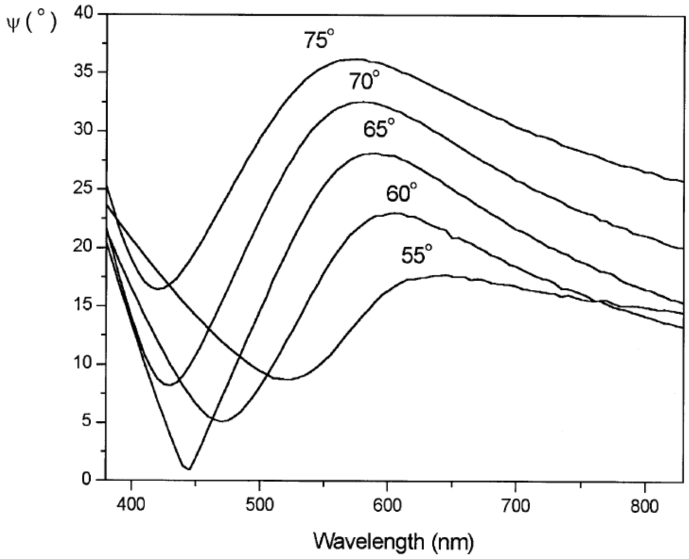

Fig. 2. Ellipsometric spectra for the CeO_2 film at different angles.

The film was prepared by reactive electron beam evaporation. The starting material was CeO_2 in tablets (Balzers, purity 99.9%). The BK7 glass substrate was heated to 225°C. Temperature of substrate was measured by bimetal maximum thermometer (PTC instruments, model 575 CM). Residual gas and reactive gas pressures were 2×10^{-6} torr and 4×10^{-6} torr, respectively. The rate of deposition and layer thickness were controlled by an oscillating quartz crystal. According to the assumed cerium dioxide density of 7.1 g/cm^3, the rate of deposition was 0.2 nm/s and the layer thickness was 150 nm. The substrate was rotated during deposition to improve uniformity and minimize optical anisotropy of the film.

We expected that measuring the transmittance and c function at different angles would give enough data to obtain a unique and reliable solution. Transmittance measurements have been done using a Cary 50 spectrophotometer. Transmittance has been taken each 1 nm between 400 and 900 nm at the 0° incidence angle. Ellipsometric ψ function measurements have been done using a Jobin Yvon UVISEL DH10 spectroscopic ellipsometer at five different angles between 55° and 75° and each 5 nm between 380 and 830 nm. The film was relatively thin so the transmittance curve had only one maximum. The measurements are represented in Figs. 1 and 2.

The commercial TFCalc^{TM} version 3.4 software has been used for reverse engineering calculations. The measured data were defined as target values. The initial design was a stack consisting of 10 sublayers of equal thicknesses and unknown refractive indices. Total thickness was set at 150 nm. Transmittance and ellipsometric data were restricted to a narrow region, 40 nm wide, including the transmittance maximum. In this way the error due to not yet introduced dispersion of sublayer's refractive indices could have been reduced. Then, the software was let to find indices and each sublayer's thickness. The profile having decreasing refractive indices has been obtained. Significant changes of initial thickness all led to the same result. The next step was introduction of dispersion in the whole range of measured data. Due to cerium dioxide absorption, *k* index had to be introduced as well. All the layers were given the same Cauchy shape of dispersion, each layer having some shift in refractive index. Sublayers with refractive indices slightly different from the initial layers, were introduced and optimized, decreasing the deviation from target function. As long as it has been so, the model could have been improved. To test the reliability of the method simplex and variable metric optimization methods have been used and results compared.

3. Results and discussion

Comparison of the results obtained by simplex and variable metric optimization method is presented in Table 1. The refractive index profile preserved its shape while decreasing towards air. Both obtained models are very similar, as illustrated in Fig. 3.

Table 1

Comparison of models of refractive index profile obtained by simplex and variable metric optimization methods

	Thickness (nm)	Mean refractive index at 500 nm $\bar{n}$	Deviation	Number of sublayers	Deviation of refractive index from the mean value for each sublayer $(n-\bar{n})/\bar{n}$ (%)			
					1	2	3	4
Variable metric	211.24	1.619	0.375	4	47.52	4.91	1.21	−24.73
Simplex	205.68	1.635	0.365	4	49.54	3.98	0.31	−22.63

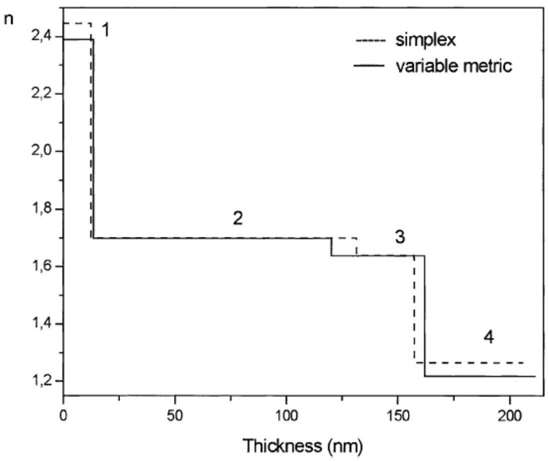

Fig. 3. Comparison of models of refractive index profile for the CeO_2 film obtained by variable metric and simplex methods. Layer 1 is adjacent to the substrate.

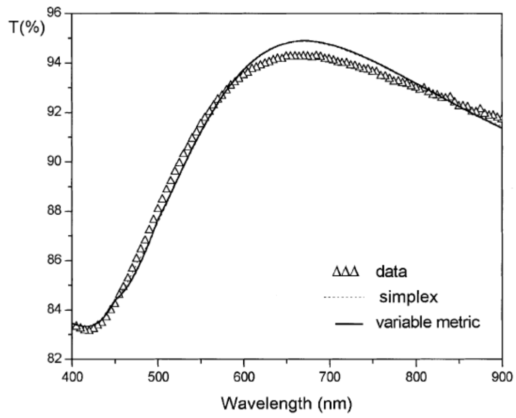

Fig. 4. Transmittance fits corresponding to the obtained refractive index profiles.

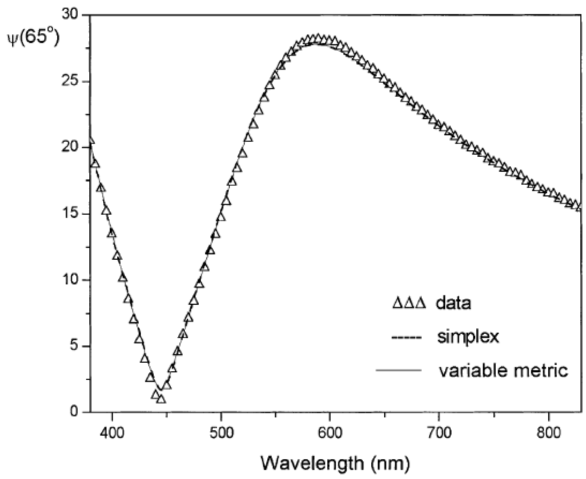

Fig. 5. Ellipsometric ψ function fits for 65° of the angle of incidence.

The transmittance curves calculated by the two methods match excellently, so they are almost indistinguishable one from another in Fig. 4. The same applied to ψ function fit. Only the fit for angle of incidence of 65° is presented in Fig. 5, and was similarly good for the other angles. Both, transmittance and ψ function, curves fit experimental data very well. Dispersion curves of all the sublayers are presented in Figs. 6 and 7 and comparison of mean refractive index dispersions obtained by simplex and variable metric methods is shown in Fig. 8. The comparison of *k* index dispersions is illustrated in Fig. 9. It can be seen the solutions obtained by two different optimization methods led to very similar solutions, so it can be said the results have good reliability. Although a multilayer structure, like the one obtained, has multiple local minima, we believe that the different ways of minimization starting with very thin layers, used by two methods, yield a reliable final solution. The reason for that is in the fact that local minima are very shallow and Simplex method can overcome such problems. If a simple gradient method only was used, than we may not make such a conclusion.

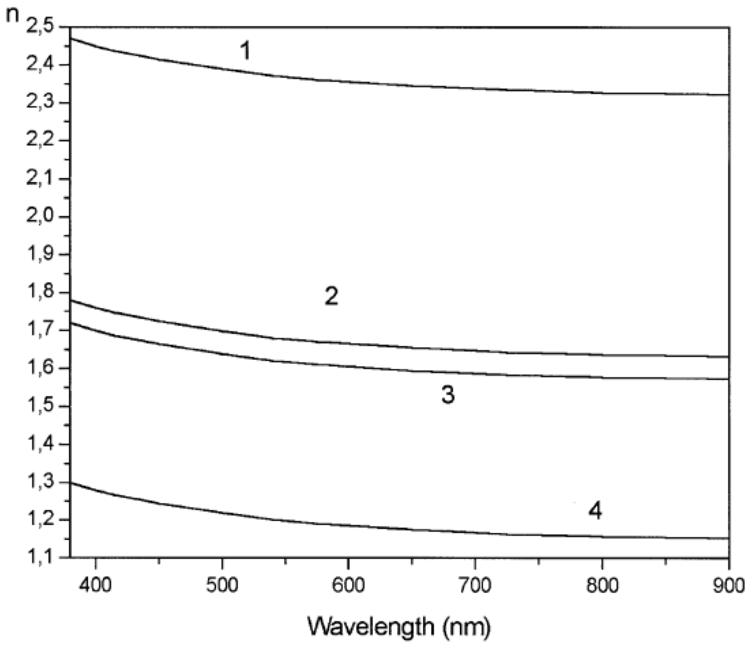

Fig. 6. Refractive index dispersions of all sublayers obtained by variable metric optimization method.

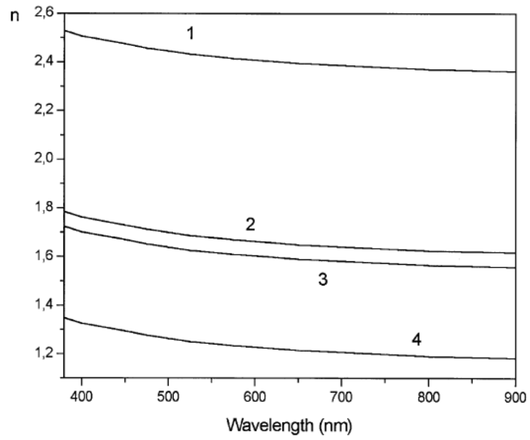

Fig. 7. Refractive index dispersions of all sublayers obtained by the simplex optimization method.

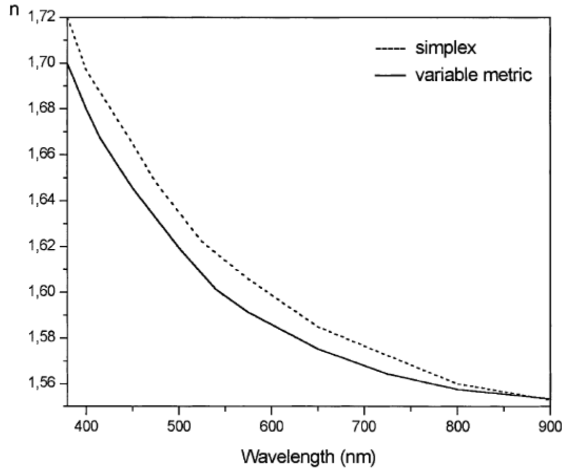

Fig. 8. Mean refractive index dispersions obtained by simplex and variable metric optimization methods.

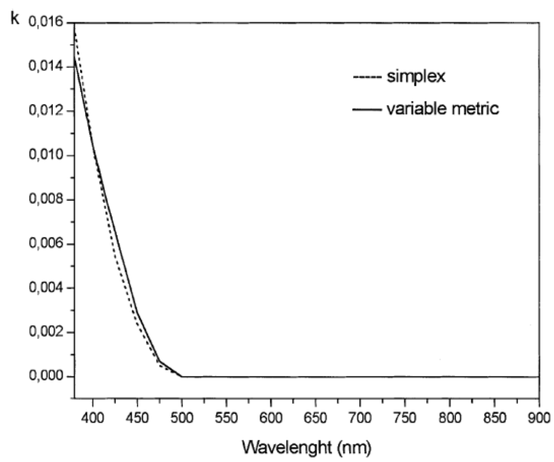

Fig. 9. Dispersions of *k* index determined by both methods.

It should be mentioned that during the optimization processes thickness of the sublayers were changed and particular sublayers have been replaced by others having even significantly different refractive indices. All of this again led to the same result. In just a few cases completely different design has been obtained, but was rejected for extreme thickness (300–600 nm) and very poor matching to the experimental data.

The obtained mean refractive indices are significantly lower than those usually found in literature. The reason for that is in the fact we applied a lower substrate temperature and deposition rate then recommended, to stimulate inhomogeneous growth. Therefore, the whole cerium dioxide film has a relatively low packing density and refractive index. Especially, looking at the Fig. 3, we can also notice that the surface layer has an extremely low refractive index what suggests that growth of the film yielded a very rough surface.

Processes of modelling and optimization gave two similar solutions. It means that the performed measurements provided enough data and boundary conditions (well known refractive indices of air and glass) were well defined. The used software had no option to optimize dispersion simultaneously with thickness. This is the reason why the shape of refractive index dispersion was the same for all the sublayers. Refractive indices were defined for discrete wavelengths and values between were linearly interpolated.

Still at the beginning of the study, we had to decide whether to make it on a thinner ($nd \approx \lambda/2$, $\lambda = 650$ nm) or a thicker ($nd > \lambda$) film. If we had a thicker film with more extremes, like in the ψ spectrum, this would enable the optimization process to run more smoothly. Several methods for determining refractive indices from the spectra of thicker films have already been published [1, 11]. In this paper we have shown that reverse engineering can also be successfully applied to thinner films.

The results of the presented study enable further improvements of many thin film components, especially those for which optical characteristics are strongly dependent on the layer adjacent to substrate. This layer can be simply replaced by a stack of layers, which can be predicted using the shown procedure. In this way one can obtain better agreement between designed and produced performances. It should be also mentioned that layers grown on already deposited layers surely have different profiles and this could be the subject of future research.

4. Conclusions

In the presented paper it has been shown that the reverse engineering method can be very successfully applied to relatively thin films of CeO_2. Both minimization methods led to the almost same solutions, i.e. the same refractive index profile. The results of this investigation can be applied to multilayers, the optical characteristics of which strongly depend on the layer adjacent to substrate.

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