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Refractive index profile modelling of dielectric inhomogeneous coatings using effective medium theories

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Abstract

The coatings having refractive index changing with the thickness present interesting optical performance, improved mechanical properties and smaller light scattering in comparison with classical multilayer stacks. Lot of theoretical work and experimental advances have been done for designing and production of mixture layers with such particular performances. The effective refractive index of the mixture coatings can be calculated by the use of effective medium theories. The refractive index profile characterization of inhomogeneous films that are mixtures of SiO_2 and Nb_2O_5 is presented. The composition is linearly changed through the thickness of the layers. Ex-situ spectrophotometric measurements, i.e. reflectance and transmittance at different incidence angles, are used for the precise characterization of the refractive index profiles. Linear, Maxwell-Garnet, Bruggeman and Lorentz-Lorenz effective medium theories are applied and quality and differences of the results are studied and analyzed. It is shown that the Lorentz-Lorenz model is the most appropriate for the given mixture, suggesting components are well mixed and there are no separated phases.

Keywords: Composite thin films; Effective medium theory; Optical coatings; Optical characterization

1. Introduction

Progress in computer capabilities and advances in coatings process control has enabled design and deposition of gradient refractive index and rugate films with increasing complexity and precision. In this kind of coatings the variation of refractive index (*n*) varies through the depth of the film continuously, in contrast to the classical coatings with abrupt changes of refractive index. The coatings having smooth transition in refractive index, compared with classical quarter wave stacks, show better mechanical resistance [1,2], higher laser induced damage threshold [3] and less scattering losses, maintaining comparable or even better optical properties [4,5]. The variation of refractive index is obtained by variation of the composition through the thickness of the film. The standard techniques for deposition of such mixture coatings are sol–gel methods [6], changing the composition of the compounds by controlling the composition of reactive gas as in chemical vapour deposition [7] and co-deposition as in physical vapour deposition [8]. Calculation of optical constants of mixtures is important in design to predict the performance of the coating accurately. It is also important in analysis, i.e. optical characterisation, where model obtained by fitting of experimental spectra is compared with the targeted refractive index profile that was aimed to be deposited. Analysis of the differences between the two is crucial in detecting the errors of the deposition process and can be used for improvement of the manufacturing process.

2. Theory

Effective medium theories relate optical properties of the mixtures with their composition. The effective refractive index of a mixture is calculated from the refractive indices and volume fractions of the composing materials. The most frequently used and most successful theories are Maxwell-Garnett [9] (MG), Bruggeman [10] (BG) and Lorentz-Lorenz [11] (LL). The first two assume that the mixing materials are in separated phases. Typical dimensions of the constituent particles are supposed to be much smaller than the wavelength of the interacting radiation, but at the same time large enough to present their own electromagnetic behaviour. MG considers the mixture that has a separated

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two-material grain structure where particles of the first material are dispersed in the continuous host of the second material. On the other hand, BG assumes an aggregate structure being a space-filling random mixture of two material phases. In the limit of small volume fractions (f_v) the predictions of the two theories approach to each other. It is shown that in the case of higher filling factors, i.e. when volume fraction of one material is comparable to the volume fraction of another, the BG is valid up to the smaller particle radius than for MG [12]. LL model is based on the Clausius–Mossoti equation and takes an average of molecular polarisability of the components. In this case no phase separation is considered. Another possibility is to assume linear variation of refractive index with volume fractions of constituents (LIN).

Finally, depending on the level at which materials are mixed, one effective medium theory will be more appropriate than the other and will give more accurate prediction of the optical properties of the mixture. For example, in the case of SiO_2–TiO_2 amorphous mixture it has been shown experimentally [13,14] that LL model is more appropriate than BG, although not all the studies are in accordance [15].

Layers with approximately linear gradient of refractive index (ramps) are the basic building elements of more complex hybrid [16] and good approximation for rugate coatings. They are deposited by linear variation in volume fraction f_v of constituents, from some minimum to maximum. Due to the above mentioned reasons it is important to check how much the different effective medium theories are capable to represent the refractive index profile of the layers obtained by linear change in volume fraction of the materials. For this purpose samples with linear variation of volume fraction of SiO_2 and Nb_2O_5 are prepared. Optical characterization from the measured reflectance (R) and transmittance (T) spectra is performed using MG, BG, LL and LIN effective medium theories. The quality of the fits to the experimental data are compared, also regarding the number of sublayers into each gradient was subdivided for the purpose of the calculations.

3. Experimental details

Layers of SiO_2–Nb_2O_5 mixtures with composition changing linearly through the thickness of the film were deposited onto suprasil substrates by reactive electron beam evaporation co-deposition technique in a Leybold Syrus Pro 1100 deposition system. The chamber was equipped with two electron beam guns. The change in the composition is achieved by a continuous modification in deposition rates (r) of individual materials. The rate of deposition is controlled and measured by two quartz crystal monitors one for each material, next to the source. The deposition process is controlled by computer software enabling simultaneous automatic measurements and acquisition of parameters (deposition rates, pressures, temperature etc.) during the deposition. Volume fraction f_{v1} of the material 1 in the mixture is related to the measured deposition rates of each material r_1 and r_2 by:

$$f_{v1} = r_1/(r_1 + r_2) \tag{1}$$

The minimum and maximum deposition rates (r_m and r_M) of each material, and therefore minimum and maximum volume fractions (f_{vm} and f_{vM}), were restricted due to the fact that it was not technically possible to achieve stable and reproducible arbitrarily low deposition rates for the given materials. Thus, r_m was set to 0.2 nm/s and r_M to 1.2 nm/s. The total rate of deposition, i.e. sum of the rates of the two materials, was kept constant during the process and set to 1.4 nm/s.

Three samples were deposited: one with content of niobia increasing from the substrate (Sample 1), another with content of niobia decreasing from the substrate (Sample 2) and the third with the content first increasing and then decreasing (Sample 3). The deposition rates vary continuously during the deposition, giving place to continuous change of the material composition. The thickness d of the first two samples was approximately 220 nm and 560 nm for the third.

Prior to deposition of the samples substrate and pure material layers have been characterized and their refractive indices determined. Spectrophotometric measurements were performed with a Perkin Elmer Lambda 900 spectrophotometer. A VN-attachment allowing absolute measurement of reflectance (R) without moving the sample after transmittance (T) measurement has been used. Reflectance and transmittance in the spectral range 400–900 nm were measured in steps of 2 nm at angle of incidence of 6° and s and p polarizations R_s, R_p, T_s and T_p at 45°.

4. Optical characterization

Optical characterization of the samples was done using thin film curve fitting software [17]. Fitting the experimental spectra allows determination of the optimal value of a set of parameters defining the sample. The variation of refractive index with thickness (inhomogeneity) of a ramp is taken into account by dividing it into a given number of homogeneous sublayers. For each ramp, all sublayers have the same thickness. Each sublayer has been modelled as a mixture of the two materials with refractive indices n_H and n_L and corresponding volume fractions f_H and f_L, where $f_H + f_L = 1$. Volume fraction of niobia in each layer is given by:

$$f_{H-i} = f_{H-\text{start}} + \frac{f_{H-\text{end}} - f_{H-\text{start}}}{N_{\text{sub}}}\left(i - \frac{1}{2}\right) \tag{2}$$

Here $f_{H\text{-}i}$ is volume fraction of niobia in the ith sublayer and $f_{H\text{-start}}$ and $f_{H\text{-end}}$ are niobia fractions at the beginning and the end of the ramp and N_{sub} is the number of sublayers. The

Table 1
Values of merit function obtained by use of different effective medium theories to the sample with refractive index decreasing from the substrate and division of the ramp into different number of sublayers

	3 layers	5 layers	7 layers	13 layers	25 layers
LL	0.2301	0.1390	0.1400	0.1404	0.1404
BG	0.4502	0.6244	0.6253	0.6198	0.6175
MG	–	–	–	–	0.8457
LIN	–	–	–	–	0.7844