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Optical properties of SiO_2-TiO_2 sol-gel thin films

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The optical properties of thin SiO_2-TiO_2 sol-gel composite films were investigated using exact optical models and the Forouhi-Bloomer model, (Phys. Rev. B34, 7018 (1986)), which describes the optical dispersion of amorphous dielectrics. Films deposited on glass and silicon substrates, were characterized by optical transmission and reflection measurements. Theoretical spectra have been generated and fitted to the experimental ones via standard regression analysis techniques. The (five) adjustable Forouhi-Bloomer parameters describing the dispersion of the complex refractive index, as well as the film thickness were determined. The refractive index and absorption coefficient of the films were found to depend on the molar contents of the component oxides.

1. Introduction

The preparation of amorphous glasses through the sol-gel process in the past few decades has experienced remarkable growth and has found an increasing number of applications such as coatings, sensors, photocatalysts, precursors for preparation of ceramic materials, etc. [1–8]. Among them titania-silica composite oxides are noted for their interesting physical and chemical properties which include a very low or negative thermal expansion, a high refractive index, solid acidic properties, photocatalysis and alkali passivation mechanisms [9–15].

In the present work, we have studied the optical parameters of sol-gel SiO_2-TiO_2 composite films as a function of the various molar component concentrations. The experimental transmittance and reflectance spectra of the system, film-substrate-film, were fitted to theoretical ones, calculated using the Forouhi-Bloomer (FB) physical model [16] to describe the optical dispersion in the composite films.

2. Experimental

Thin composite films SiO_2-TiO_2 were produced via the sol-gel method by hydrolysis of the corresponding metal alkoxides in alcoholic solutions. The following compositions were prepared: $x\mathrm{SiO_2}\cdot(100-x)\mathrm{TiO_2}$, with $x = 0$, 25, 50 and 100 mol%. For the preparation of the 100 mol% SiO_2 film the precursor was silicon tetraethoxide ($Si(OC_2H_5)_4$, Merck) and was dissolved in absolut (99.8%) ethanol (C_2H_5OH, Merck), followed by the addition of HNO_3 (65 vol%, Farmitalia-Carlo Erba) as the acid catalyst and of distilled water. Then the mixture was stirred at 60°C for two hours to initiate the hydrolysis and polycondensation. Correspondingly, the 100 mol% TiO_2 film was produced through hydrolysis of titanium tetraethoxide ($Ti(OC_2H_5)_4$, Alfa Products, Germany) in absolut ethanol, with the addition of nitric acid, sealing the mixture from atmospheric air and stirring it at room temperature for about two hours as well. The composite SiO_2-TiO_2 films were made following the same procedure as for the SiO_2 films with the difference that, at the end of the stirring, $Ti(OC_2H_5)_4$ was added and the mixture was sealed from atmospheric air and left to stir for another half hour at room temperature. In all solutions the molar ratio of water to the TEOS alkoxide was kept equal to four. The amount of HNO_3 added to the solutions was enough to ensure that the pH values ranged between 0.5 and 2.

Amorphous uniform gel coatings were formed on both sides of substrates immersed in the above solutions, by dipping-withdrawing in an ambient atmosphere, a few hours after the sol preparation. The thicknesses of the highly uniform coatings, thus produced, are easily controlled through regulation of the withdrawal speed of the substrates from the solutions. For the cases of $x = 0$, 25 and 50 the substrates were 1 mm thick glass microscope slides and the withdrawal speed was set to 50 cm/min, and for the case of $x = 100$, where the sol-gel films would have a composition similar to that of the glass microscope slide and consequently similar optical properties, the substrate used, instead was a silicon wafer, withdrawn with a speed of 40 cm/min. All samples were heat treated after their formation for 30 min, at 400°C in a Carbolite RHF 1200 oven, in air, at a rate of 2°C/min, leading to oxide film structures. The temperature of 400°C was chosen so that it was high enough to ensure complete burning of the organic components, yet being within the range allowed by the glass substrate. The heating time of 30 min was selected to ensure sufficient time for densification and burning of organics, as well as to minimize the diffusion of alkali ions present in the glass substrate, as confirmed by references [17–19]. Transmittance spectra of the first three cases (Samples 1, 2 and 3), mentioned above, were recorded using a UV/VIS/NIR Lamda 19 spectrophotometer of Perkin Elmer. With the same spectrophotometer, specular reflectance spectra were taken for Sample 4, deposited on an opaque Si substrate. Doubly polished Si wafers were used as standards for the reflection. These wafers were covered with an oxide layer, approximately 50 nm thick, as determined by one wavelength (632.8 nm) ellipsometry. The reflection spectra of these mirrors were synthesized using refractive index data found in the literature for crystalline Si [20] and Malitson's formula [21], to describe the refractive index dispersion of the top oxide.

3. Theoretical procedure

The spectra obtained were analyzed using exact optical models [22, 23] for the transmittance and reflectance of a stack of films, combined with the physical model of Forouhi-Bloomer [16], for the optical constants of amorphous materials. The calculation principles of the optical models have been presented in earlier publications [24–26]. The optical models include five phases: air-composite film-substrate-composite film-air and the transmittances and reflectances of the composite system are calculated using the "effective" reflection and transmission Fresnel coefficients described in detail in reference [24]. These coefficients are functions of the real, n, and imaginary, k, part of the complex refractive index of the films and the substrate, and also of their respective thicknesses. The FB model, which has been extensively described in previous papers [24–26], assumes electronic transitions only between two parabolic bands, the valence and conduction bands, originating from superposition of molecular orbital states, the valence from bonding and the conduction band from antibonding states. These bands are separated by an energy gap E_g while the energy distance between bonding and antibonding states equals to $B/2$. The dispersion relations $n(E)$ and $k(E)$, which are Kramers-Kronig related, are then derived to be [16]:

$$n(E) = n(\infty) + \frac{B_0 E + C_0}{E^2 - BE + C} \tag{1}$$

$$k(E) = \frac{A(E - E_g)^2}{E^2 - BE + C} \tag{2}$$

where

$$B_0 = \frac{A}{Q}\left[-\frac{B^2}{2} + E_g B - E_g^2 + C\right],$$

$$C_0 = \frac{A}{Q}\left[\left(E_g^2 + C\right)\frac{B}{2} - 2E_g C\right] \quad \text{and}$$

$$Q = \frac{1}{2}(4C - B^2)^{1/2}$$

Except $n(\infty)$, which is the refractive index at high energies, A is related to the position matrix element and the lifetime of the electronic transitions involved and C is related to B and the lifetime. This rather simple mathematical model describes well the excitations near the absorption threshold in disordered dielectrics [25–28] and the results are physically meaningful provided that [25]: (i) E_g, as defined by the FB model, takes smaller values than $B/2$, (ii) E_g takes values close to those obtained using other physical models (e.g., Tauc's [29] model), and (iii) Q is positive. Under the above conditions, the FB model relates n and k to parameters pertaining to the dielectric's electronic structure, unlike other formulas (e.g., Cauchy's formula). It should be emphasized at this point that although the crystallinity of the samples of this investigation is unclear, the FB model for disordered dielectrics can be applied, even in the case of their being polycrystalline. This is possible because the model is being applied within the low energy domain, where the existence of sharp structures in the dielectric constants of the samples is not expected. Moreover, the model permits the determination of n and k from one and only measurement. We have used a modified version of the FB model which demands that the extinction coefficient, k, vanishes for energies below the energy gap E_g. This version has been previously used to describe optical dispersion in silicon oxynitride [28], tin oxide [25, 26], silicon nitride [27], amorphous [25] and polycrystalline Si thin films [30].

4. Results and discussion

In Table I are presented the values of the five FB model parameters and the corresponding 90% confidence intervals which are estimated by fitting the calculated transmittance and reflectance spectra to those experimentally recorded, minimizing the quantity (unbiased estimator):

$$f = \frac{1}{N}\sum_{N}\left(\frac{T_{\mathrm{exp}}(\lambda) - T_{\mathrm{calc}}(\lambda)}{\sigma(\lambda)}\right)^2 \tag{3}$$

by standard regression analysis techniques [31]. N represents the number of points used for the minimization process (about 800 points), T_{exp} (λ) the experimental, $T_{\mathrm{calc}}(\lambda)$ the calculated values of the transmittance and $\sigma(\lambda)$ the uncertainty of the measurement at each wavelength. The uncertainty $\sigma(\lambda)$ varied with each wavelength in an unknown way so, an uncertainty equal to $0.05T_{\mathrm{exp}}$ has been attributed to each value. A corresponding estimator is defined for the reflectance spectra. The thicknesses d, of the films are also estimated

TABLE I Forouhi-Bloomer model parameters, film thicknesses d, and unbiased estimators f for the four samples studied. The corresponding 90% confidence intervals are also shown

Composition x mol% SiO_2 y mol% TiO_2	$x = 0$ $y = 100$ Sample 1	$x = 25$ $y = 75$ Sample 2	$x = 50$ $y = 50$ Sample 3	$x = 100$ $y = 0$ Sample 4
n (∞)	1.9811 ± 0.0030	1.8012 ± 0.0042	1.6501 ± 0.0038	2.3759 ± 0.0365
A	0.1686 ± 0.0128	0.3015 ± 0.0205	0.2113 ± 0.0150	0.7083 ± 0.0095
B (eV)	8.5837 ± 0.0003	8.6740 ± 0.0206	9.1227 ± 0.0271	9.7520 ± 0.4735
C (eV^2)	18.685 ± 0.013	19.275 ± 0.0808	21.4690 ± 0.1253	91.5020 ± 2.8506
Eg (CV)	3.0020 ± 0.0235	3.3769 ± 0.0172	3.3372 ± 0.0217	10.0060 ± 0.2475
d (nm)	93.516 ± 0.237	100.430 ± 0.434	109.20 ± 0.91	104.09 ± 0.13
F	0.3797	0.2005	0.4456	0.2395

through the minimization process and are reported in the above table. It must be noted that the results from fitting to reflectance experimental values are less accurate than those obtained from fitting to transmittance values. This is related to the uncertainties pertaining to the calibration of the reference mirrors, as well as to the fitting procedure. Within this procedure data from the literature referring to the silicon wafer have been used, obtained for ultra pure silicon, cleaned at the moment of the measurement. These conditions were not fulfilled in this investigation.

It can be observed that for the first three samples the first of the previously mentioned, conditions ($E_g < B/2$) is fulfilled. On the contrary, this is not the case for the fourth sample composed exclusively of SiO_2. This is because SiO_2 starts to absorb at much higher energies than those in this study hence, the k is not involved in the calculation of the theoretical spectra, and consequently, the minimization program does not optimize E_g and B simultaneously (see Equation 2). Another observation that can be made concerning Table I, is that E_g and B do not vary appreciably with the molar content of the components. This is because E_g, within the FB model, is defined in such a way that the absorption threshold and the so-called Urbach's tail [29] are both described by this parameter (we return to this point further on).

In Fig. 1 are presented the experimental and the calculated transmittance spectra for Sample 3 and the good agreement between the two is apparent. In Fig. 2 are presented the experimental and calculated reflectance spectra for Sample 4. The good agreement between the two is also observed.

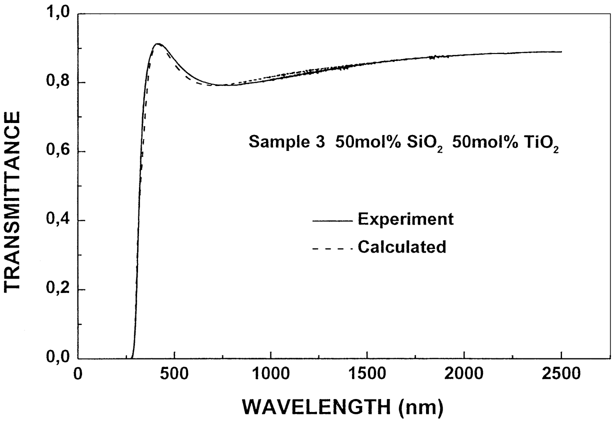

Figure 1 UV-Vis transmittance spectra, experimental (solid line) and calculated (dashed line) for Sample 3, with composition 50 mol%SiO_2· 50 mol%TiO_2.

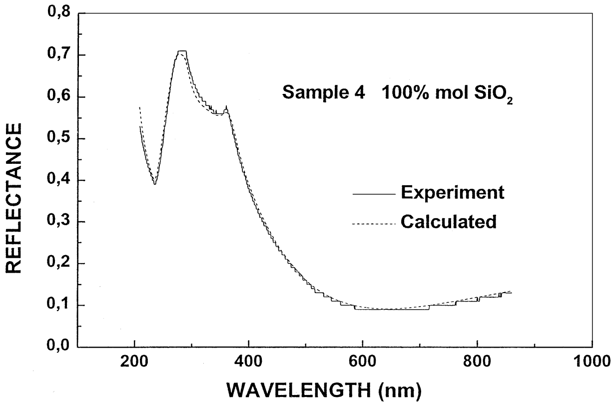

Figure 2 UV-Vis reflectance spectra, experimental (solid line) and calculated (dashed line) for Sample 4, with composition 100 mol%SiO_2.

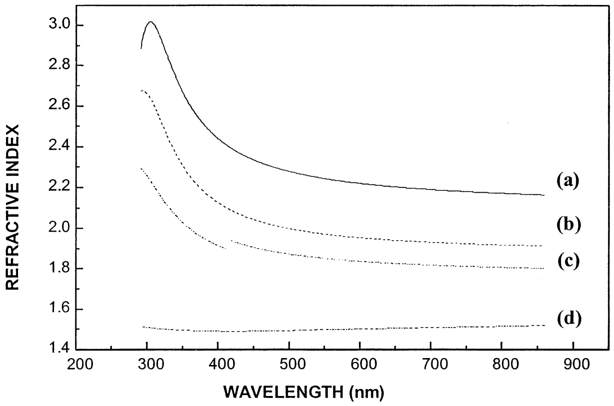

Figure 3 Wavelength dependence of the real part of the refractive index, n, of films, with compositions: (a) 100 mol%TiO_2, (b) 25 mol%SiO_2· 75 mol%TiO_2, (c) 50 mol%SiO_2· 50 mol%TiO_2, and (d) 100 mol%SiO_2.

The real part, n, of the (complex) refractive index, calculated by using the FB parameters presented in Table I and Equation 1, is plotted in Fig. 3, for each sample composition, as a function of the wavelength. As expected, the n of the composite films, varies between the values corresponding to pure SiO_2 and TiO_2.

The n value of 1.43 for the 100 mol% SiO_2 sample is in rather good agreement with the 1.421 value reported for the sol-gel 100 mol% SiO_2 films sintered at 500°C, on silicon wafers, of ref. [33]. It is a value somewhat lower than that of ref. [32] (1.47) for non-crystalline SiO_2 which may be attributed to incomplete densification of the coatings due to the low temperature and short duration of the thermal treatment.

It is worth noting at this point that, in spite of the failure of the minimization program to obtain a physically acceptable value of B, for the 100 mol% SiO_2 composition, it gives overall good results. This is due to the mathematical similarity of Equation 1 to formulas describing the refractive index dispersion.

Our n values for the 100 mol% TiO_2 (2.18) are, in good agreement with the n values (2.1) for the 100 mol% TiO_2 films on soda-lime-silicate glass substrates of reference [34], sintered at 450°C. They are lower than those reported in ref. [16] for TiO_2 films produced by anodic oxidation of titanium, which can be assumed to be more dense. This fact could be attributed to differences in the preparation method, that induce differences in film structure.

It is also to be noted in Fig. 3 that the increase in the n values with the increase of the TiO_2 molar content is monotonous. Compared to other values obtained for sol-gel films of similar compositions [18, 33], the composite SiO_2-TiO_2 films (Samples 2, 3) exhibit comparable indices of refraction, taking into account the differences in preparation, and nature of substrates. Our refractive index values can also be compared to the corresponding values 1.48–2.39 obtained in ref. [35] for composite films of similar compositions on fused silica substrates, but produced with an ion beam sputtering process. In that study, where the nature of the substrate remains unchanged throughout the samples, there is, as in our study, a smooth increase in the values of n with the increase of the TiO_2 component molar content. Differences between our results and those of ref. [35], apart from discontinuities in the nature of the substrate for $x = 0$, 25, and 50, could also arise from the fact that the ratios of components of composite oxides we quote represent the ratio of the alkoxides in the preparing solutions and not necessarily the actual ratios of the components in the films.

Fig. 4 shows $(\alpha \cdot E)^{1/2}$ as a function of the photon energy for the various film compositions, where $\alpha\ [=(4\pi k/\lambda)]$ is the absorption coefficient. For Sample 4 ($x = 100$) there is no curve in Fig. 4 because, as mentioned above, the FB model has been modified, in that k has been set to zero for energies smaller than E_g. It is observed that for all of the samples, the absorption edge presents a linear part at higher energies. For the Samples 1, 2, and 3, the slope of this linear part decreases with the increase of the SiO_2 content while, the Tauc energy gap [29] (defined as the point of interception of the linear part of the absorption edge with the energy axis) is blue shifted with it. It is worth noting at this point the significance of the different definitions of the energy gaps within the FB and Tauc's model. While the first indicates the onset of absorption, the second is a means of describing higher values of absorption. In view of the above, the small variations of E_g, as defined by the FB model, reported in Table I, are justified.

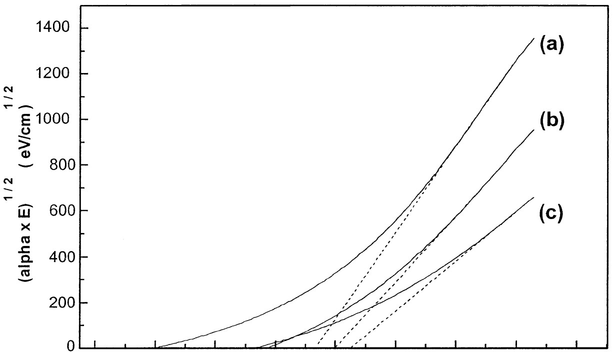

Figure 4 Optical absorption spectra of films with compositions: (a) 100 mol%TiO_2, (b) 25 mol%SiO_2·75 mol%TiO_2, and (c) 50 mol%SiO_2·50 mol%TiO_2. Extrapolating the linear part of each graph the Tauc energy gap value is estimated.

5. Conclusions

We have measured the refractive index dispersion for very thin SiO_2-TiO_2 sol-gel composite films, from their transmittance/or reflectance spectra using a straightforward method. The n, k and film thickness have been determined by one and only measurement with the use of a physical and an exact optical model. The film optical properties were described satisfactorily by the physical method in the range 200–2500 nm and the index of refraction values were observed to increase monotonically with the increase of the TiO_2 molar content, ranging between 1.43 for pure SiO_2 to 2.18 for pure TiO_2. The energy gap values, as defined by the model did not vary appreciably with the TiO_2 molar content, while the Tauc energy gap increases with the SiO_2 molar content.

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