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Optical constants of RF sputtered amorphous TiO_2 Films

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ABSTRACT
Amorphous TiO_2 films were prepared by RF sputtering of TiO_2 target in pure Argon atmosphere. The films were characterized by SEM, TEM, XRD and EDAX. The optical properties of TiO_2 films depend on the processing conditions, crystallinity and the surface morphology. Various methods of determining the optical constants are available in the literature. In this paper we present and compare four such methods namely the direct inversion of reflectance and transmittance spectra, unconstrained optimization of transmittance spectra, Forouhi-Bloomer dispersion modeling and our modeling of the dielectric function with the OJL model for interband transitions and harmonic oscillators.

1.INTRODUCTION

Titanium dioxide thin films have potential application as surfaces for solar energy conversion devices[1] and as gate dielectric in metal oxide semiconductor field effect transistors[2], because of their well known physical properties such as high refractive index and high transmittance in the visible wavelength region[3]. The refractive index of TiO_2 films strongly depend on the preparation conditions. Most of the TiO_2 films are amorphous and only few have crystalline phases. Determination of optical constants of thin films is an interesting and challenging area of research in thin film studies. Various techniques and options exist for the thin film scientist. Of all, the computer optimization techniques play a crucial role in the determination and the subsequent design of such coatings and films. For the proper optical cherecterisation the film thichness , the refractive index n and the extinction coefficient k should be determined over the spectral range of interest. In this paper we describe how the amorphous TiO_2 films can be optically cherecterised by different methods available. For this study we compare four of the methods available and widely used.

2.EXPERIMENT

TiO_2 films of various thicknesses are deposited in different substrates by RF sputtering of TiO_2 target(Kurt J. Lesker, USA) of 99.90% purity and 100mm diameter. Films were deposited on various substrates for characterization purposes. The depositing system (Edwards Auto 500) consists of a stainless steel chamber evacuated by an oil diffusion pump with liquid nitrogen trap. The chamber was evacuated to a base pressure of $3x10^{-4}$ mbar. The pressure during deposition was $1.2x10^{-2}$ mbar or less. Mass flow-controlled pure argon (99.99%) was delivered to the chamber. The substrate to target distance was13cm. The RF power used for the deposition was kept constant at 200 watts after a careful optimization of various parameters.. The thickness and surface roughness were measured by DEKTAK surface profiler. The transmittance(T) and specular reflectance(R) of the films were recorded with Cary500 UV-VIS-NIR spectrophotometer in the 300-2500nm wavelength range. The EDS and SEM analysis were performed with Philips XL 30 ESEM attached with EDAX EDS system.

2.1 Optical Modelling

The near normal reflectance and transmittance of the samples coated on micro glass slide, obtained from the spectrophotometer is used to extract the optical constants n and k of the coatings by various methods. The fitting of model dielectric functions to the transmission and reflectance was performed by the commercially available software Scout2[5].

3. THEORETICAL BACKGROUND: OPTICAL CONSTANTS DETERMINATION

3.1 Direct inversion of reflectance and Transmittance (RT method)

In this technique both the near normal reflectance and the transmittance T were inverted to find the optical constants n and k of the films. We can write the reflectance and transmittance of an absorbing film on a non-absorbing substrate in the form

$$R=r(n,k,n_0,n_s,d,\lambda) \qquad (3.1)$$

$$T=t(n,k,n_0,n_s,d,\lambda). \qquad (3.2)$$

N and k are the refractive indices of the film, n_0 and n_s are those of the surrounding medium and substrate, d is the thickness and λ is the wavelength. The optical equations 3.1 and 3.2 are inverted by iterative technique [5] to yield n and k. Since the functions R and T are non-linear no analytical solution is possible. Also the solutions

to the equations 3.1 and 3.2 are not single valued which resulted in multiple solutions at a given wavelength..

3.2 Estimating the Thickness and optical constants from transmittance data only

Since the optical transmission of films provide accurate and rapid information the spectral behaviour many times this method is found suitable for weakly absorbing films. For this study we used the method proposed by Birgin et al [6] using unconstrained optimisation for the retrival of the optical constatnts from the transmittance data only.

3.3 Forouhi-Bloomer dispersion relation

Among the various available dispersion relation, the formulation based on completely quantum mechanical approach to interband electronic transistions by Forouhi-Bloomer[7] has attracted widespread attention due to its simplicity with reduced number of fitting parameters for amorphous materials. The Forouhi-Bloomer (F-B) equations are expressed as

$$n(E) = n(\infty) + \sum_{i=1}^{q} \frac{B_{0i}E + C_{0i}}{E^2 + B_iE + C_i} \qquad (3.3)$$

$$k(E) = \sum_{i=1}^{q} \frac{A_i(E - E_g)^2}{E^2 + B_iE + C_i} \qquad (3.4)$$

The integer "q" in eqns.3.3 and 3.4 specify the number of terms and the first term (q=1) describes the spectra for amorphous materials. E_g represents the optical energy band-gap. The parameters A_i,B_i and C_i are fitting parameters related to the electronic configuration of the material. The parameter $n(\infty)$ represents the limit of n(E) as E approaches infinity.

3.4 Spectra simulation by dielectric modelling

In this dielectric modelling the optical properties of the TiO_2 samples were represented by the following procedure. The dielectric function ε which relates the dielectric displacement D and the electric field vector can be written as[8]

$$D = \varepsilon_0 \varepsilon E \qquad (3.5)$$

where $\varepsilon = 1+\chi$ and χ is the susceptibility.

We can write the polarization of the medium as

$$P = \varepsilon_0 \chi E. \qquad (3.6)$$

The complex dielectric function ε is given as

$$\varepsilon = \varepsilon_{re} + \varepsilon_{im} = 1 + \Sigma\chi_i \qquad (3.7)$$

where χ_i is the result of various mechanisms of polarisation.

The complex refractive index is given as

$$N = n+ik = \sqrt{\varepsilon_{re} + \varepsilon_{im}} \qquad (3.8)$$

where n is the refractive index and k is the extinction coefficient.

The following steps were followed in the dielectric modelling of the coatings.

1.Formulation of the susceptibility χ with free parameters is set up.

2.To make the dielectric function consistent with Kramer's-Kroniq relation a KKR susceptibility is implemented.

3.Initial values of the free parameters and the estimated thickness are entered.

4.Tramsmittance and reflectance spectra are computed by assuming single or multilayer structure. The free parameters and thickness were varied to achieve the best fit by minimizing the deviation (mean squared difference) between simulated and measured spectra.

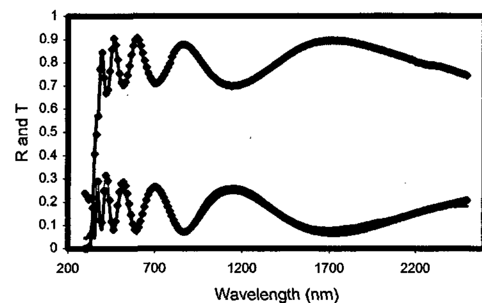

Figure 1. Experimental (solid line) and Simulated (---) R and T spectrum by single layer model

Figure 1 is the best fit we obtained for a typical sample. It was arrived by assuming a single layer on a glass substrate. The dielectric function of the glass substrate (micro slide) which was determined in the wavelength of interest from its near normal reflectance and transmittance is used in the layer model. We assumed incoherent interference and negligible absorption for the thick glass substrate. The dielectric function of the layer in first approximation, modelled with the standard formulations available in the fit program.

The model dielectric function consist of a constant dielectric background contributing to the real part of the dielectric function and for the interband transition we used the OJL [9]model where expression for the joint density of states are given for the optical transition from the valence band to the conduction band. The imaginary part of χ thus calculated is used to obtain the real part by a Kramers-Kronig [8] transformation. This also provides the consistency of the model with KK

relation. A simple harmonic oscillator model was implemented for the interband transitions into the upper half of the conduction band.

The fit suffers from the fact that with a single layer on a transparent substrate the reflectance can never be smaller than that of glass, which is 8% around 500nm. This result also strengthens our view that effective optical modelling of thin films from spectrophotometric data should involve both the Reflectance and Transmittance spectra but not only one of them.Our analysis of the surface of the films by surface profilometry show a considerable level of surface roughness that suggests that the modelling cannot be physically accurate without including a surface roughness layer. So the above spectra were simulated with an additional surface roughness layer whose dielectric function is modelled with the effective medium approximation. The surface roughness layer is generally modelled with the Maxwell-Garnett[10] or Bruggeman[11] effective medium theories. This approach has been found to yield very accurate and reliable results in spectroscopic ellipsometry [12]. For the modelling we constructed a two layer structure on glass substrate with the top surface roughness layer. The surface layer was constructed as a composite of the main layer and voids (air). The effective dielectric function of the surface layer was computed using the dielectric function of the main layer and air by Bruggeman effective medium approximation . The volume fraction of the surface layer, thickness of the surface and main layer are used as fit parameter. Figure 2. shows the improved fit between the experimental and the computed spectra.

4.RESULTS

4.1 Composition

The composition of the films were analysed by EDS spectra and fig.3 show the typical EDS spectrum of TiO_2 films. For this analysis we used the TiO_2 target as the standard for stoichiometry. Table 1 shows the EDS elemental analysis of the sample.

4.2Structural

The X-ray diffraction done on the samples did not give any noticeable peaks and it can be concluded that the depositied films were amorphous.

4.3Optical constants

In figures 4 and 5 we present the real and imaginary part of the optical constants extracted by the four methods we discussed above and with the data obtained for the electron beam evaporated films in the literature[13].

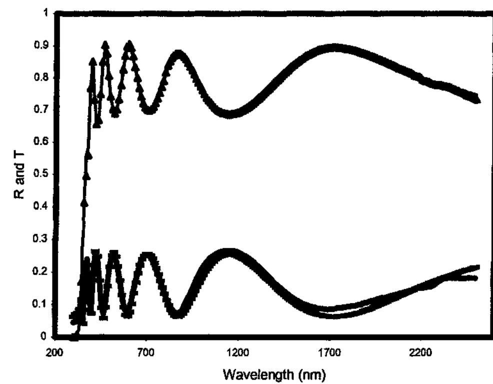

Fig.2. Experimental (solid line) and Simulated (---) R and T spectrum by double layer model

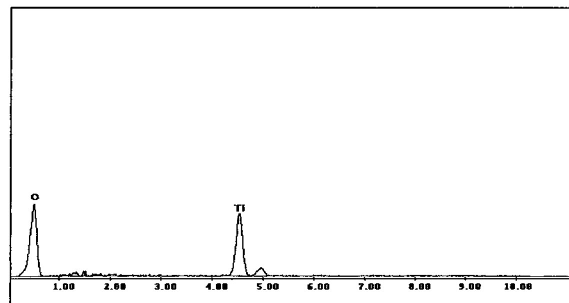

Fig.3. EDS spectrum

Element	Wt %	At %	K-Ratio	Z	A
O K	35.44	62.07	0.092	1.120	0.231
Ti K	64.03	37.45	0.591	0.921	1.002
Total	100	100			

Table 1. EDS Elemental composition

As we see from the figures the RT method gives multiple solutions for n and k when d/λ approaches unity. The real part n obtained by F-B and our dielctric modelling agrees well with the published values though the published values for n are higher than our results in the shorter wavelength region. This can be attributed to the preparation conditions and loss in stochiometry. However the transmittance alone method gives higher n values for the larger portion of the wavelength region studied. Also the thickness of the film extracted by this method (350nm) does not agree with the thickness obtained with the surface profiler and our dielectric modelling.

The imaginary part k of the samples by all the models as in fig.5 shows marked diference especially in the shorter wavelength region. In this

region higher k values reported in the literature agrees with our dielectric modelling but apart from the RT metod others are not capable of obtaining accurate values for the imaginary part.

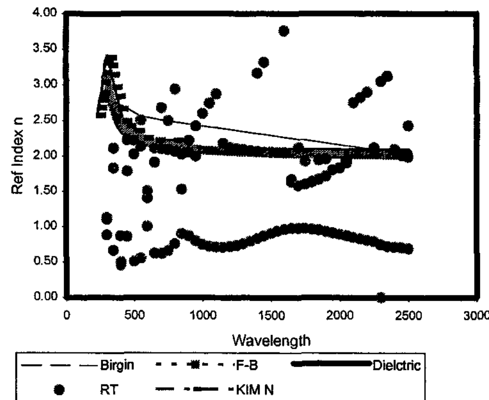

Fig.4. real part n by various methods

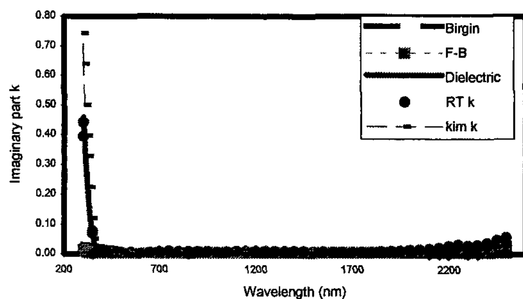

Fig.5. Imaginary part k of the refractive index

With the dielectric modelling and Foruhi-Bloomer dispersion relations we also obtained information regarding the bandgap, thickness and void distribution in the surface layer. These values were used in the fitting procedure. The values obtained are summarised in table

Model	Surface layer vol%	Surface layer thickness	Main layer thickness	Band Gap eV
F-B	0.423	35nm	380 nm	3.12
Dielectric	0.435	30 nm	390 nm	3.33

As we see from these figures that our dielctric model based on OJL and harmonic oscillators give a very accurate results for the optical constants and thickness. They agree well with the published n and k for e-beam evaporated films which were analysed by spectroscopic ellipsometry.

5. Conclusions

The TiO_2 films prepared by RF sputtering TiO_2 target are amorphous and present refractive index compareable to electron beam evaporated TiO_2 films. They exhibit optical behaviour, which can be modelled based on the so-called OJL model for interband transitions by O'Leary et al[9]. The procedure to retrieve the dielectric functions from the experimental spectra is robust and well conditioned. Our model with only 4 free parameters over a wide spectral range is capable of accurately determining the dielectric function of the coatings and the extracted optical constants are Kramers-Kronig consistent. The number of fit parameters can be effectively lowered, as more and more physical details of the coatings are known. This combination of powerful algorithms and readily available spectrophotometric data of transmittance and near normal reflectance provides an accurate and fast way of analysing new and complex type of thin films. One concludes that the optical properties of TiO2 coatings are mainly controlled by the experimental conditions such as the base pressure, the composition and microstructure. Optical constant parameterisation can be done as efficiently and accurately with spectrophotometric data as sophisticated techniques like variable angle spectroscopic ellipsometry.

6.References

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