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## Variable angle of incidence spectroscopic ellipsometric characterization of TiO<sub>2</sub>/Ag/TiO<sub>2</sub> optical coatings

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### **Abstract**

Optical constants (3000–8000 Å) and layer thicknesses of TiO<sub>2</sub>/Ag/TiO<sub>2</sub> optical coatings are determined using variable angle of incidence spectroscopic ellipsometry. Ellipsometrically determined silver layer thicknesses agree well with those obtained by cross-sectional transmission electron microscopy. Also, spectral characteristics, absent in bulk silver data, are observed in  $n$  and  $k$  spectra for the thin silver layers. It is suggested that these structures may be caused by plasmon effects from the silver layers.

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# Variable angle of incidence spectroscopic ellipsometric characterization of TiO<sub>2</sub>/Ag/TiO<sub>2</sub> optical coatings

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Optical constants (3000–8000 Å) and layer thicknesses of TiO<sub>2</sub>/Ag/TiO<sub>2</sub> optical coatings are determined using variable angle of incidence spectroscopic ellipsometry. Ellipsometrically determined silver layer thicknesses agree well with those obtained by cross-sectional transmission electron microscopy. Also, spectral characteristics, absent in bulk silver data, are observed in  $n$  and  $k$  spectra for the thin silver layers. It is suggested that these structures may be caused by plasmon effects from the silver layers.

## I. INTRODUCTION

Optical filters, transparent to visible light and reflective to infrared, are used on energy efficient windows to reduce excessive heating inside automobiles and buildings. Dielectric-metal-dielectric (DMD) coatings consisting of a high index dielectric material, like ZnO or TiO<sub>2</sub>, and a metal such as silver, are usually used to obtain such coatings. As with almost any thin-film coating design, one main problem is that the optical properties of thin-film materials often deviate from those of the same material in bulk form. In general, optical properties of thin films depend on such factors as void (empty region) fraction, grain size, and the associated induced local electric fields, surface roughness, and other microstructural inhomogeneities. These factors are in turn determined by the method of deposition, and the deposition parameters.<sup>1</sup> Thus, bulk data cannot always be used in thin-film coating designs.

Spectroscopic ellipsometry has been increasingly used in thin-film studies to determine layer thicknesses,<sup>2</sup> optical constants,<sup>3</sup> surface roughness,<sup>4</sup> structural composition,<sup>5</sup> and other microstructurally related factors. Such factors are incorporated as parameters into the model representing the sample during data analysis. The model parameters are then modified iteratively until a best fit is obtained between the experimental and calculated data. In some applications, the effective optical constants of films can be determined from the known bulk data and void fraction, using an effective medium theory.<sup>6</sup> However, this approach has its limitations and cannot always be used successfully. First, one must know the exact optical constants of the bulk material from previously established measurements. Second, various effective medium theories are based on ideal models which assume spherical or cylindrical geometries for the grains present in the actual film. Hence, one effective medium model may work adequately for one sample and result in poor results for another. The choice of the effective medium model is therefore critical, and may require a knowledge of the shape and size of the grains forming the film. Because of the structural complexity of our samples and our prime interest in the simultaneous determination of the silver layer thick-

ness and effective optical constants, as well as the TiO<sub>2</sub> layer thicknesses, we did not attempt to use effective medium models for the layers. Only the pseudo (effective) optical constants (hereafter called optical constants) of the layers resulting in the best fit between the experimental and calculated data were determined.

Here we report on measurements of the optical constants and thicknesses of the layers for two glass/TiO<sub>2</sub>/Ag/TiO<sub>2</sub> samples, using variable angle of incidence spectroscopic ellipsometry (VASE).<sup>7</sup> In addition, a separate glass/TiO<sub>2</sub> sample is studied to independently determine the optical constants for the TiO<sub>2</sub> layer. A similar study was conducted earlier on ZnO/Ag/ZnO DMD coatings.<sup>8</sup>

## II. EXPERIMENT

In ellipsometry, a linearly polarized incident light beam becomes, in general, elliptically polarized after reflection from the sample surface.<sup>8</sup> The new polarization state of the reflected light is a function of the optical constants and parameters of the sample. From ellipsometric measurements of the changes in polarization state one can then determine the optical and structural parameters of the sample. Ellipsometric measurements are expressed in terms of two parameters,  $\psi$  and  $\Delta$ , which are related to Fresnel reflection coefficients by  $R_p/R_s = \tan \psi \exp(i\Delta)$ , where  $R_p$  and  $R_s$  are, respectively, the reflected to incident (complex) ratios of the electric field of light polarized parallel and perpendicular to the plane of incidence.<sup>9</sup>

After  $\psi$  and  $\Delta$  values are experimentally determined over the desired spectrum, corresponding theoretical  $\psi'$  and  $\Delta'$  values are calculated from standard ellipsometric equations for a stratified medium, using an assumed model representing the sample. Digital computers are then employed in a regression analysis to fit the calculated data to the experimental data. We used a nonlinear Marquardt algorithm in our data analysis.<sup>10,11</sup>

All samples were magnetron sputtered under similar conditions and the dielectric layers had nearly the same thicknesses (Table I). Thus, the same optical data were used for all TiO<sub>2</sub> layers. Samples were kept in closed containers

TABLE I. Summary of the thicknesses (in angstroms) determined for the three samples studied.

Sample	Structure	Thickness (Å)		
		Nominal	XTEM	Ellipsometry
1	TiO <sub>2</sub> Glass	300	...	288 ± 3 <sup>a</sup>
2	TiO <sub>2</sub> (top)	300	309 ± 17	334 ± 18
	Ag	100	120 ± 6	113 ± 7
	TiO <sub>2</sub> Glass	300	339 ± 17	268 ± 20
3	TiO <sub>2</sub> (top)	300	...	331 ± 3
	Ag	200	209 ± 11	211 ± 4
	TiO <sub>2</sub>	300	339 ± 17	289 ± 11
	Glass			

<sup>a</sup>Obtained for 90% confidence interval.

prior to measurements in order to reduce moisture penetration and accumulation onto the surface. The backsides of the samples were roughened to minimize back surface reflections. All measurements on the samples were made at room atmosphere using an automated rotating analyzer spectroscopic ellipsometer (similar to the type described by Aspnes and Studna,<sup>12</sup> with the added capability of variable angle of incidence<sup>5,7</sup>).

For the glass/TiO<sub>2</sub> sample, data were taken at 60°, 70°, and 75° angles of incidence, in the 3000–8000 Å spectral range at 100-Å intervals. These data were analyzed to independently determine the *n* and *k* spectra for the TiO<sub>2</sub> layers. The optical constants of the silver layers and the layer thicknesses were determined from similar spectral measurements made on the two glass/TiO<sub>2</sub>/Ag/TiO<sub>2</sub> samples which had the same structure but different silver layer thicknesses.

### III. RESULTS

#### A. Glass/TiO<sub>2</sub>

A simple three-phase glass/TiO<sub>2</sub>/air model was used in our data analysis assuming parallel, planar, isotropically homogeneous layers. Micrographs obtained from the samples by cross-sectional transmission electron microscopy (XTEM) later showed sharp parallel boundaries between the layers. Reasonably good fits were obtained using the above simple model. The known parameters of the model were the optical constants of air and the glass substrate (determined by independent measurements on bare glass). The thickness and optical constants *n* and *k* of the TiO<sub>2</sub> layer were determined, and the computed *n* and *k* spectra are illustrated in Fig. 1. As mentioned earlier, no attempt was made to obtain a quantitative measure of the film density (void fraction) by means of effective medium models. The TiO<sub>2</sub> optical data were then used as fixed parameters in the analysis of the glass/TiO<sub>2</sub>/Ag/TiO<sub>2</sub> samples. The underlying assumption was that the TiO<sub>2</sub> films deposited under similar conditions, with nearly the same thicknesses (see Table I), possessed similar optical constants.

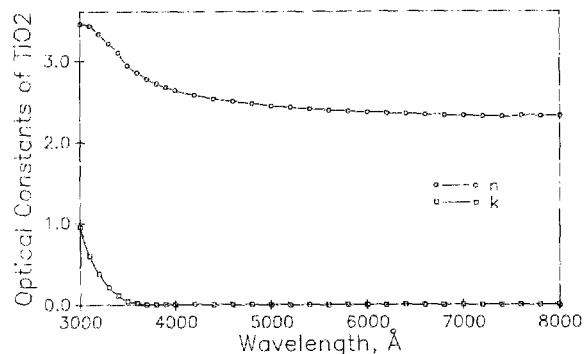


FIG. 1. Optical constants, *n* and *k*, of TiO<sub>2</sub> determined by ellipsometry from a glass/TiO<sub>2</sub> sample.

#### B. Glass/TiO<sub>2</sub>/Ag/TiO<sub>2</sub>

The thickness of the thin silver layer in the three-layer samples was critical to the proper overall performance of the final optical coating. It was therefore useful, as a measure of the accuracy of the results, to know the sensitivity of the experimental data to the silver layer thickness. This aspect was investigated as follows. The model shown in Fig. 2 was used to obtain simulated plots of the effect of a small change in silver layer thickness on the  $\psi$  and  $\Delta$  spectra. First,  $\psi$  and  $\Delta$  spectra were calculated for the assumed model ( $t_1 = 300$  Å,  $t_2 = 100$  Å, and  $t_3 = 300$  Å) using optical data available in the literature for bulk silver<sup>13</sup> and the computed TiO<sub>2</sub> data from the single layer sample. Then, the silver thickness was increased by 10 Å and the  $\psi$  and  $\Delta$  spectra were again calculated. Finally, the difference between the second and the first  $\psi$  and  $\Delta$  spectral curves was plotted, as shown in Fig. 3. The angle of incidence,  $\phi$ , used in the calculations was 70°. It is apparent that both  $\psi$  and  $\Delta$  are moderately affected by a small change in the silver layer thickness. Since this is a reasonably good representation of the  $\psi$  and  $\Delta$  sensitivity to the silver layer thickness at the selected angle of incidence, one can conclude that the silver layer thickness can be determined very accurately from the experimental  $\psi$  and  $\Delta$  spectra. The main requirement is an accurate determination of  $\psi$  and  $\Delta$ , which is easily met using the new automated rotating analyzer spectroscopic ellipsometers. Typical uncertainties in  $\psi$  and  $\Delta$  measurements are about  $\pm 0.02^\circ$  and  $\pm 0.05^\circ$ , respectively. The angle of incidence is accurate to within  $\pm 0.02^\circ$  in our system.

Assuming again parallel, planar, and isotropically homogeneous layers a five-phase glass/TiO<sub>2</sub>/Ag/TiO<sub>2</sub>/air model (Fig. 2) was used to fit the calculated data to the experimental data. As an example of the quality of the fits, results for the experimental and calculated  $\psi$  and  $\Delta$  curves for one sample are shown in Figs. 4 and 5, respectively.

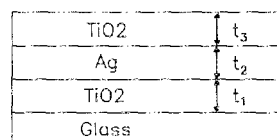


FIG. 2. Assumed structural model in the ellipsometric analysis of the three layer samples.

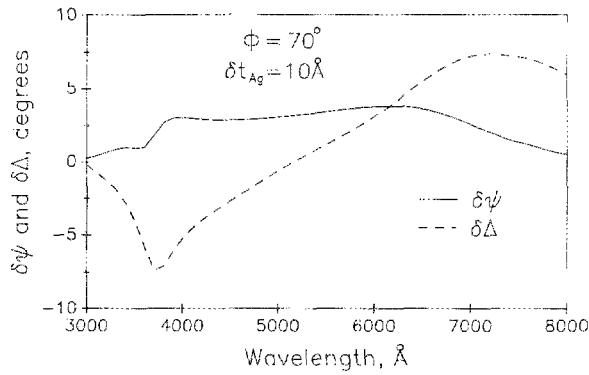


FIG. 3. Spectral sensitivity of the ellipsometric parameters,  $\psi$  and  $\Delta$ , to a 10-Å change in silver layer thickness. These data were generated by subtracting the  $\psi$  and  $\Delta$  calculated for a glass/TiO<sub>2</sub>(300 Å)/Ag(110 Å)/TiO<sub>2</sub>(300 Å) structure from the  $\psi$  and  $\Delta$  calculated for a glass/TiO<sub>2</sub>(300 Å)/Ag(100 Å)/TiO<sub>2</sub>(300 Å) structure.

Silver layer thicknesses determined by ellipsometry were in good agreement with the XTEM measurements as summarized in Table I. Not quite as good but reasonable agreement was found for the TiO<sub>2</sub> layer thicknesses. Computed refractive indices and extinction coefficients of the silver layers for the two samples are depicted in Figs. 6 and 7. Relatively large peaks are present in the  $n$  spectra. Similar peaks were observed in the optical spectra of silver layers in our previous study of glass/ZnO/Ag/ZnO samples.<sup>8</sup> In the latter study, the amplitudes of the peaks decreased and occurred at lower energies for thicker silver layers. In the present study, the spectral locations of the peaks show the same dependence on the film thickness as found in the previous study, but amplitudes of the peaks appear to be approximately the same for both silver film thicknesses. Also the silver layers exhibit higher index of refraction in the 4500–8000 Å region.

The overall deviation of the thin silver layer optical data from the bulk silver data may be due to factors such as grain size and shape, scattering at the rough surfaces, and microstructural defects not being included in our simple model

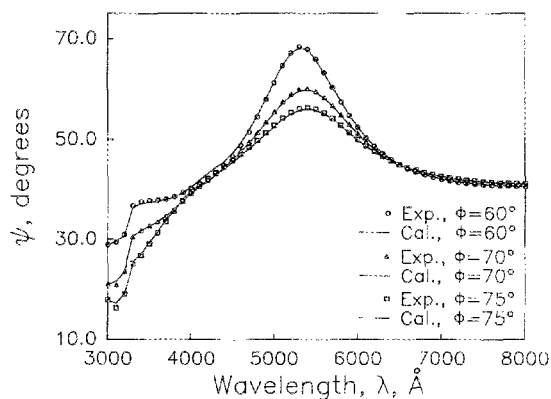


FIG. 4. Measured and calculated (best fit)  $\psi$  spectra for glass/TiO<sub>2</sub>(289 Å)/Ag(211 Å)/TiO<sub>2</sub>(331 Å) at three angles of incidence.

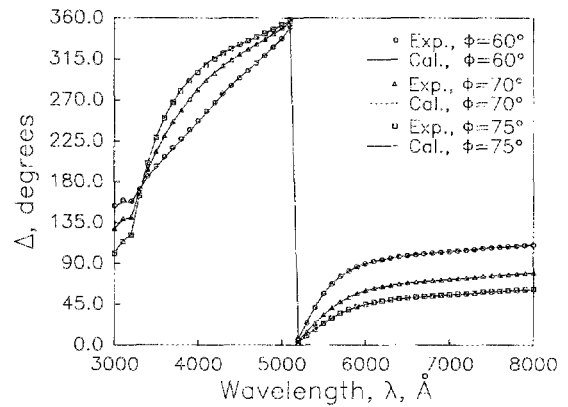


FIG. 5. Measured and calculated (best fit)  $\Delta$  spectra for glass/TiO<sub>2</sub>(289 Å)/Ag(211 Å)/TiO<sub>2</sub>(331 Å) at three angles of incidence.

used to represent the samples. We believe that the large peaks observed in the  $n$  spectra of the silver layers may be due to plasmon effects in the thin silver films, caused by perturbation of the surface and/or volume charges by the external electric field intensity of the light. A definitive conclusion requires a more detailed investigation of the thin silver layers.

#### IV. CONCLUSION

It has been demonstrated that VASE is a nondestructive and powerful technique for DMD thin-film analysis. Layer thicknesses and effective optical constants of constituent layers in glass/TiO<sub>2</sub>/Ag/TiO<sub>2</sub> were determined using measurements at three angles of incidence. Thicknesses of silver layers determined by ellipsometry agreed well with those determined by XTEM, within the accuracy of the two techniques. Also large peaks, absent in bulk silver data, were observed in the  $n$  spectra of the thin silver layers which may be due to bulk and/or surface plasmon effects.

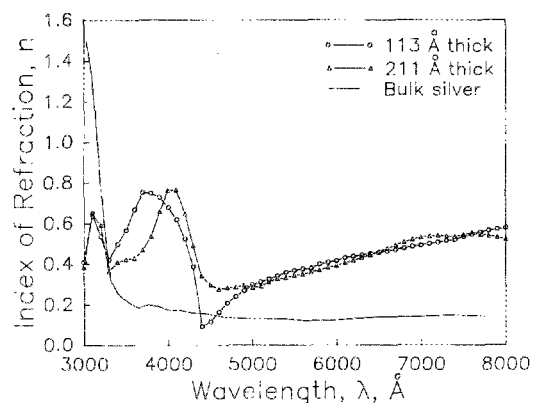


FIG. 6. Index of refraction of the silver layers computed from the measurements on two samples with the structures shown in Fig. 2. The bulk data are from Ref. 13.

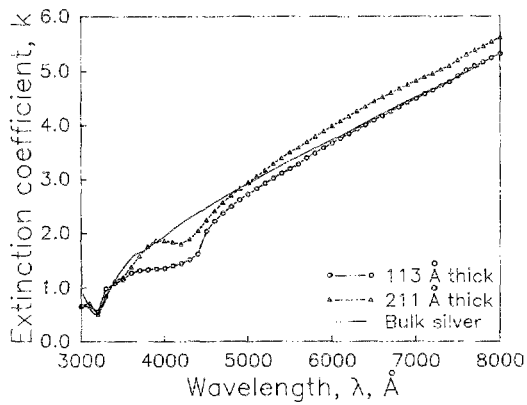


FIG. 7. Extinction coefficient of the silver layers computed from the measurements on two samples with the structures shown in Fig. 2. The bulk data are from Ref. 13.

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