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Composition profiling of graded dielectric function materials by spectroscopic ellipsometry

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Abstract

In this work, the characterization of graded composition layers in transparent materials by spectroscopic ellipsometry (SE) is described. The sensitivity limits were modeled by comparing calculated spectra for samples with and without diffusion profiles at the sample surface for several glass compositions. It was found that for known index profile shapes, the depth sensitivity can be quite high. The sensitivity of the technique increases as the diffusion depth and refractive index contrast increases. The accuracy of the thickness determination depends on the total thickness of the graded layer; for a given system, the accuracy of the composition measurements did not depend on the surface concentration. Leached alkali-aluminosilicate and modified lead silicate glasses were examined by SE to experimentally confirm the modeling predictions on the composition depth profiling. Extremely good correlation between the SE-determined depth profile and SIMS measurements on similar samples was obtained for the case of the modified lead silicate glass. For the aluminosilicate glass, simultaneous roughening of the glass surface during etching makes composition profiling more difficult. © 1998 Elsevier Science S.A.

Keywords: Spectroscopic ellipsometry; Composition profiling; Dielectrics

1. Introduction

There are a wide variety of optical and electrical devices, including waveguides and anti-reflection coatings, in which the composition of a dielectric layer is not constant throughout the sample thickness. Similarly, glass surface compositions are frequently modified to affect either the mechanical properties or the nucleation of a surface film. In each of these cases, it would be useful to be able to depth profile the surface composition non-destructively, as an alternative to Auger or SIMS. Several reports on the use of SE to characterize graded index systems are available in the literature. When strong features are present in the dielectric function over the spectral range of interest, as is the case for a number of semiconductor heterostructures, those features can be used to depth profile the composition during growth or etching processes [1,2]. Similarly, Fried et al. have used SE to depth profile composition changes associated with ion implantation in semiconductors [3]. However, in dielectric materials there are few characteristic features in the visible frequency dielectric function which can be used to assign composition unambiguously. Consequently, this study was directed towards determining the sensitivity of spectroscopic ellipsometry to the presence of a continuously varying refractive index with a known shape (due, for example, to a diffusion

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profile) at the surface of a transparent material. To complement the modeling, experimental measurements were also made for leached glass surfaces.

2. Experimental procedure

The modeling procedures used have been described elsewhere [4]. To represent a technologically important continuously varying dielectric function, a diffusion profile into a semi-infinite material was treated using a standard complementary error function. To calculate the complex reflectivity for the sample, the graded region was modeled by subdividing the smoothly varying composition profile into a staircase function. In order to place the layers more closely where the index was changing the most rapidly, the concentration difference between the surface and the bulk was broken into equal-sized steps, and the depth value, d_i, corresponding to each of those points was calculated. The layer nearest the surface was assigned to the surface composition, and its thickness was taken to be half the distance to the next calculated depth. All other layers were assigned layer thicknesses calculated as the midpoints between d_i and d_{i+1}. This approach helped minimize the number of layers required to eliminate the appearance of artifacts such as false interference fringes, and so increased the calculation speed. The diffusion depth in each case was defined as the depth at which the dopant concentration fell to 0.3% of the surface concentration. Δ and Ψ were then calculated for the multilayer stack. In all cases, the calculations were checked to ensure that enough subdivisions were used within the graded layer to ensure that false interference fringes were small in amplitude relative to the experimental accuracy with which Δ and Ψ could be measured.

A series of calculations was then performed to investigate the sensitivity limits of SE to graded composition layers. This was done by calculating the ellipsometric spectra with and without the graded index layer as a function of the depth of the layer and the refractive index contrast between the surface and the bulk glass. SiO_2 modified near the surface with Na_2O was chosen for most of the modeling studies. Reference optical properties were taken from Refs. [5–7]. The optical properties of intermediate compositions were calculated using Bruggeman effective medium averaging.

To determine whether SE can be used to depth profile composition in graded index samples, two types of glasses were leached to remove surface modifier ions. A lead silicate glass with the composition 65.5 SiO_2–28.2 PbO, with low levels of Cs_2O, Al_2O_3, BaO, and Rb_2O, was cleaned in 1 N NaOH solution at 80°C, and then etched in 1 N HCl without stirring for periods between 30 min and 1 day. This was identical to the procedure followed by D'Souza and Pantano [8], for SIMS analysis of the leaching profiles. A similar procedure was used for an alkali-aluminosilicate glass, with the exceptions that there was no pre-clean in NaOH, and concentrated HCl acid was used. In all cases, the back surface of the sample was roughened to minimize error associated with reflection of light from the back face of the glass slide.

SE data were collected on each of the samples before and after etching. Data were collected at 5 nm increments between 300 and 750 nm at an angle of incidence of 70° using a rotating analyzer instrument with an achromatic compensator. This system has been shown previously to measure Ψ and Δ with an accuracy of 0.01° and 0.03°, respectively on transparent samples [9,10]. To eliminate errors associated with the onset of the absorption edge, the low wavelength data were truncated where necessary for the modeling. To obtain reference data for the unetched glasses, data from 400 to 750 nm were modeled assuming a thin layer of roughness existed at the surface. A Sellmeier oscillator of the form:

$$n^2 = 1 + \frac{B\lambda^2}{\lambda^2 - \lambda_o^2} \quad (1)$$

was used to describe the bulk glass optical properties, where n is the refractive index, λ is the wavelength in nm, and B and λ_o are constants determined in the modeling. To model data with a diffusion profile, the profile was parameterized in terms of two fitted variables, the surface concentration and the product of the diffusion coefficient and time. The lowest value of the unbiased estimator for the error, σ, was used to choose the best fit model. As has been described previously, σ was calculated from Δ and Ψ rather than from $\tan\Psi$ and $\cos\Delta$, so that both sets of data were weighted more evenly [11]. In all cases, the 90% confidence limits and the correlation coefficient matrix for the fitting variables were also examined. Only models which were physically reasonable were considered (i.e. no negative thicknesses). The modeled SE results were then compared to SIMS analyses on glasses etched in the same manner.

3. Results

Na_2O diffused into SiO_2 was chosen as a model system to examine the sensitivity of spectroscopic ellipsometry to diffusion profiles. Na_2O increases the refractive index of the glass composition across the entire wavelength range of interest. Fig. 1 shows calculated ellipsometric spectra as a function of diffusion depth for systems with a surface concentration

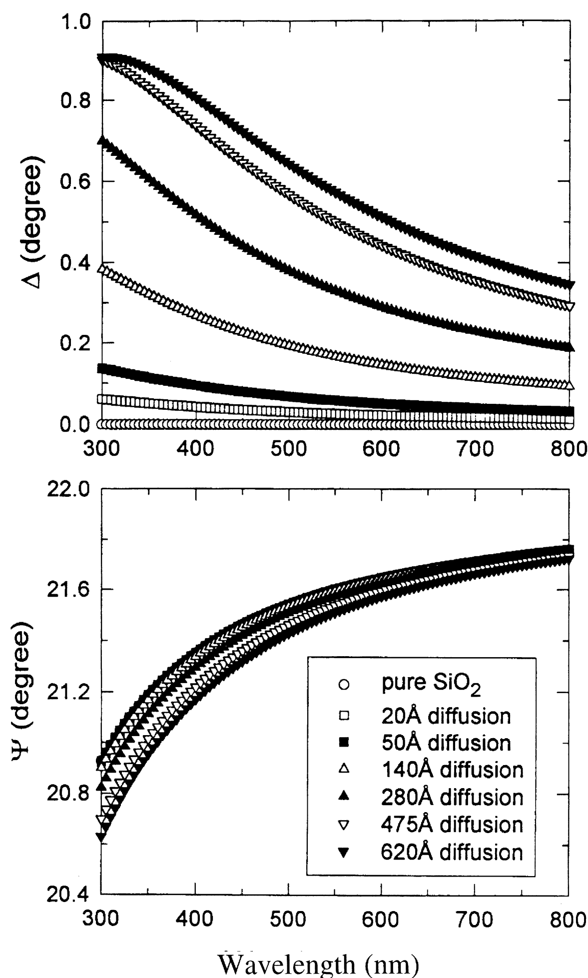

Fig. 1. Calculation of SE spectra for Na_2O diffused into SiO_2. Surface concentration = 10% Na_2O, diffusion depth given in inset. In $\Psi(\lambda)$, the curves shift lower progressively as the diffusion depth is increased over the range calculated.

of 10% Na_2O. As can be seen there, the parameter Δ is more sensitive to the surface composition change than is Ψ. Given an instrumental accuracy of 0.01° in Ψ and 0.03° in Δ, diffusion depths as small as 5 nm can, in principle, be detected. The sensitivity of the parameter Δ goes through a maximum as the diffusion depth is increased so that eventually, as the same composition change is spread out over hundreds of nm, the change in Δ becomes considerably smaller.

The sensitivity of SE to small concentration changes at the surface depends on the refractive index contrast between the surface and the bulk. The larger the difference, the more easily the composition change can be identified. For example, in the case of a fixed diffusion depth of 376 nm, Δ shows a nearly linear increase in sensitivity with increasing surface Na_2O concentration.

It is also useful to look at the sensitivity of SE to small changes in parameters describing the composition profile. To do this, a set of calculations were

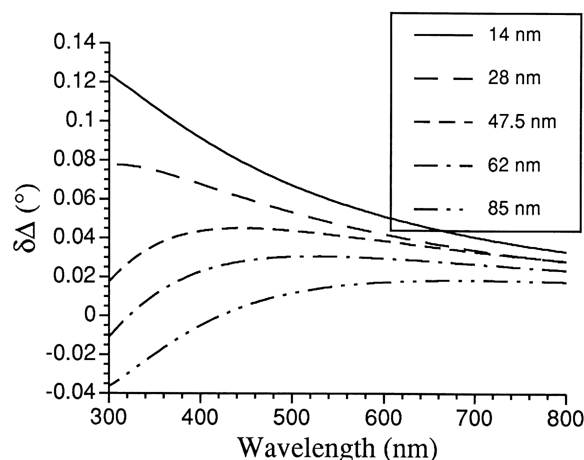

Fig. 2. Sensitivity (δΔ) of the SE parameter Δ to a change in modified depth. The scale is in degrees per 50 Å depth change. The legend shows the original diffusion depth.

made for pairs of diffusion profiles which differed only by 5 nm in diffusion depth. Fig. 2 shows a representative result. It is clear from the figure that SE is sensitive to a relative change in thickness. That is, whereas for a 14 nm diffusion depth, a change of 5 nm is readily detectable, as the total diffusion depth increases, the 5 nm increment in depth results in progressively smaller changes in Δ. Thus, the accuracy of the thickness of the modified layer determination depends on the diffusion depth.

On the other hand, the sensitivity of SE to a small change in surface composition depends on the refractive index contrast between the surface and the bulk. Fig. 3 shows a comparison of the SE spectra calculated as a function of changes in the surface composition. It can be seen there that for a 14 nm diffusion depth, a 2% change in the surface composition can be detected when the refractive index contrast is 0.0174 at $\lambda = 500$ nm, but a 1% change in the surface composition can be detected when the index contrast is 0.030 at the same wavelength.

The calculations above describe the optimal sensitivity of SE to compositional profiles. However, there are several reasons why this sensitivity might not be achieved in real samples. Firstly, particularly in the case where the composition changes are just above the detection threshold, the two parameters describing the profile are generally strongly correlated. Thus, while SE will be sensitive to the surface modification, interpretation of the changes may be difficult. A second source of error is surface roughness. Since the refractive index contrast associated with a rough layer is often quite large, it can swamp out changes in the ellipsometric spectra due to small composition differences, particularly when the index contrast between surface and bulk is also small. Roughness can be minimized as an error source if measurements are

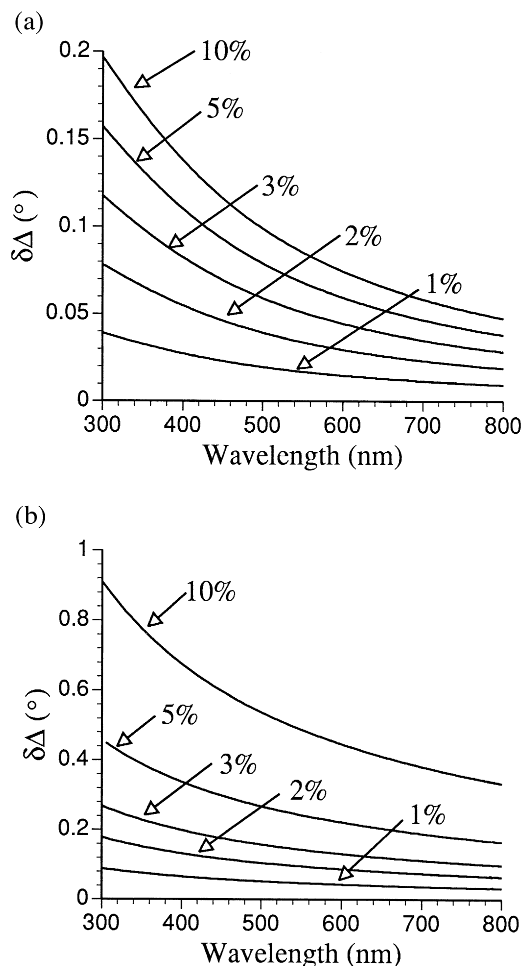

Fig. 3. Sensitivity ($\delta\Delta$) of the SE parameter Δ to a change in surface concentration. The scale is in degrees per 1%, 2%, 3%, 5%, or 10% surface concentration change. The modified depth is 14 nm. (a) $n_{\text{surface}} - n_{\text{bulk}} = 0.0174$, (b) $n_{\text{surface}} - n_{\text{bulk}} = 0.030$ at $\lambda = 500$ nm.

made on the sample prior to surface treatment to characterize the roughness layer. If the roughness is then assumed to be unaltered by the subsequent surface treatment, the composition change following modification would be detectable. This may not be a good assumption, however. Fortunately though, the development of a thicker roughness layer on the surface is often evident on modeling the experimental data, so at least the error can be detected.

To confirm the utility of these modeling predictions experimentally, glasses were chemically etched for varying lengths of time, and SE data were collected. Because modifier ions typically leach from the surface of silicate glasses faster than the network cations dissolve, etching can be used to produce a composition profile. For the leached lead silicate glass, two different models were used to fit the resulting data. For short etching times, the surface was described using a thin layer of roughness on top of a graded composition layer. The optical properties of the diffusion layer were calculated using graded mixtures of an unknown oscillator and the reference data for the bulk composition. In the oscillator, λ_o was set to 120 nm to minimize correlation between the fitting variables. For longer times it was assumed that a surface SiO_2 layer with nearly constant composition appeared on top of the graded composition layer. This led to better fits to the experimental data, but it is likely that the surface layer is a mixture of the roughness and SiO_2. The resulting fits all produced σ values of the order of the experimental accuracy of the data. Table 1 shows a comparison of the results from the SE analysis and the SIMS depth profile. The SIMS depth profiles are also shown in Fig. 4. It can be seen that for all of the etching times, the agreement in the leached layer thickness and the surface SiO_2 layer thickness is extremely good.

For the modified aluminosilicate glass, the glass surface roughens appreciably during the leaching process. While it was easy to determine the evolution in the thickness of the roughness layer as a function of etching time, the fitting parameters describing the roughness and those describing the diffusion profile were strongly correlated. For these samples, the change in the glass optical properties on leaching was smaller than was the case for leaching of Pb from the lead silicate glass. This, combined with the roughening during etching led to difficulties in the simultaneous determination of the composition profile.

Table 1
Comparison of SE and SIMS depth profiles of the lead content in a set of leached lead silicate glasses. B is a constant describing the oscillator (Eq. (1))

Etching time	σ(°)	B	SE surface roughness thickness (nm)	SE surface SiO_2 layer thickness (nm)	SE diffusion depth (nm)	SIMS SiO_2 layer thickness (nm)	SIMS diffusion depth (nm)
30 min	0.11	1.60 ± 0.14	2.7 ± 0.6	—	45.0 ± 3.2	—	
1 h	0.09	1.12 ± 0.06	4.0 ± 0.3	—	55.0 ± 3.8	—	~ 71
5 h	0.25	1.64 ± 0.04	8.4 ± 0.6	—	96.0 ± 6.6	—	~ 100
1 day	0.42	1.63 ± 0.27	—	16.4 ± 7.8	129.0 ± 12.4	~ 18	~ 130

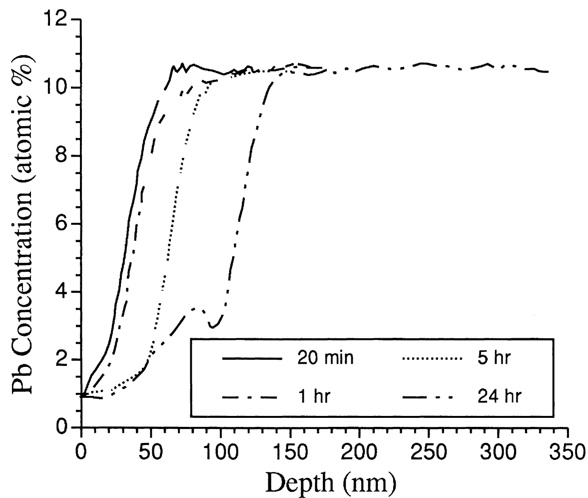

Fig. 4. SIMS data for leached lead silicate glass (adapted from [8]).

4. Conclusions

SE is a useful diagnostic technique for depth profiling the composition of graded refractive index dielectric samples. The sensitivity of the technique to changes in the composition profile depends on the refractive index contrast and the depth of the modified layer. The accuracy of the thickness determination is a function of the total thickness of the graded layer; for a given system, the accuracy of the composition measurements do not depend on the surface concentration. Additional factors such as simultaneous roughening of the sample surface complicate the analysis, particularly in the case of low index contrast samples, and can lead to excessive correlation between fitting variables. When the impact of factors such as roughening can be minimized, however, good agreement between SE and SIMS depth profiles of glass compositions can be obtained.

Acknowledgements

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