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THE SENSITIVITY LIMITS OF SPECTROSCOPIC ELLIPSOMETRY FOR THE CHARACTERIZATION OF OPTICAL COATINGS

A Thesis in

Materials

by

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ABSTRACT

Because spectroscopic ellipsometry (SE) involves measurements of both the phase and the amplitude change of light on reflection from a sample at many wavelengths, it can be utilized to determine the depth profile of the sample's refractive index with a resolution as high as the Angstrom level. Due to recent advances in the technique of incorporating an achromatic compensator into a rotating-analyzer ellipsometer, it is now possible to make such measurements on transparent materials such as glasses and dielectrics. In this work, the sensitivity of SE data to the characterization of diffusion profiles in transparent materials for optical applications is shown to be a function of parameters such as the thickness of the altered layer and the refractive index contrast. To determine the sensitivity, a model of the sample with a known compositional depth profile was constructed and the resulting ellipsometric spectra were calculated. These calculated spectra were then compared to that of the unmodified sample surface to determine the relationship between the magnitude of the changes in the optical data and the parameters describing the diffusion. The sensitivity of SE to the depth, refractive index contrast and surface concentration of the graded index layer was reported.

In addition, ellipsometric data on selected samples which have graded index layer structures were quantitatively modeled. The depth profiling results measured by SE were compared with those measured by Secondary Ion Mass Spectroscopy (SIMS). Good quantitative agreement between these completely independent measurements was found.

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Chapter 1

INTRODUCTION

Graded refractive index optical thin films are being increasingly recognized as an attractive alternative to traditional multilayer dielectric stack devices for spectral filters and antireflection coatings. Such coatings are used in many different types of optical systems, and are expected to become progressively more important as systems necessitating optical interconnections between components of different compositions are developed. A waveguide material has the property that the refractive index is varied with depth in the sample. Waveguiding thin films can be achieved by diffusing a dopant into the near surface region or by the ion exchange method. In order to reproducibly produce devices with a given index profile, a technique which is capable of accurately measuring the film index is required. In general, in characterizing such films, it is assumed either that each film is homogeneous throughout its thickness or that the refractive index depth profile is known, largely because measurements of the actual depth profile of the properties has been difficult.

There is a need for a non-destructive analysis tool capable of determining the refractive index (and so the composition) depth-profile of a sample with good resolution. Spectroscopic ellipsometry (SE) is an optical technique sensitive to the depth profile of the dielectric function with Angstrom scale depth resolution. A combination of optimum angle of incidence and variable wavelength (spectroscopic) capability can achieve the highest possible accuracy in measurements of graded index thin films. However, the sensitivity of SE to graded changes in the optical properties is unknown. Consequently, this study was directed towards determining not only the sensitivity of SE to sample composition, and refractive index contrast but also the depth resolution when there is no abrupt interface.

This problem was approached through a series of modeling studies on the sensitivity limits of SE. The modeling studies were cross-checked with experimental data on two kinds of samples. Finally, the SE results were compared with SIMS (Secondary Ion Mass spectroscopy) analyses on the compositional depth profile of the sample surface.

Chapter 2 is the background and literature review which is relevant to this study. It describes the basic theory of SE and the optical modeling used. Chapter 3 describes the experimental procedure and instrumentation used in this study, including the modeling program, the spectroscopic ellipsometer used, and the sample preparation. Chapter 4 contains the results and discussion section of this study. The calculated sensitivity of SE to the depth, composition and refractive index contrast of a graded index layer is presented. Also a comparison of compositional depth profiles on selected samples measured by SE and SIMS is described. Finally, chapter 5 lists the conclusions the proposed and future work.

Chapter 2

LITERATURE REVIEW AND BACKGROUND

Graded refractive index transparent materials are being increasingly considered as an attractive alternative to single or multiple layer dielectric coatings for optical systems (Chartier et al. 1980, Snyder et al. 1992). An effective and nondestructive method to determine the refractive index contrast is needed to facilitate device fabrication. Background material that is relevant to not only the characterization techniques for graded index materials but also to several optical models is discussed in this chapter.

2.1 Spectroscopic Ellipsometry (SE)

Ellipsometry has been widely used to study the optical and microstructural properties of thin films. Ellipsometry is an optical technique that measures the change in the polarization state of a polarized light wave after interaction with the sample. Spectroscopic Ellipsometry (SE) measurements made with the optimum angle of incidence (Zeidler et al. 1974) have been shown to be a powerful technique for nondestructive, quantitative and indirect evaluation of thin films.

Although the theoretical principles of SE were developed more than three decades ago, the introduction of inexpensive computers allowed the ellipsometric technique to develop to its present mature status. Spectroscopic means that the measurement is performed at different wavelengths. The wavelength range frequently spans from the near IR to the near UV. The number of wavelengths measured generally exceeds the number of unknown parameters even for complex multilayer structures. The important advantage of SE over other optical characterization methods is that it can measure independently two parameters, which are the relative phase and amplitude change of polarized light brought about by reflection from a sample. Since the phase change is more sensitive to a small change in the sample surface condition or the thickness of a layer than the amplitude change (Aspnes 1981), the phase data makes ellipsometry very sensitive to compositional non-uniformity. In general, ellipsometry has monolayer sensitivity to surface change through the detection of the relative phase change of the electric field component. Many studies have been conducted to verify the capability of SE to perform multilayer optical analysis as compared with other techniques (Woollam et al. 1987, McMarr et al. 1986). Furthermore, a real-time spectroscopic ellipsometer (RTSE) with an optical multichannel analyzer has been developed to investigate dynamic changes in the microstructure and optical properties of thin films with a time resolution as short as 5ms (Collins 1990). With this technique, the growth mechanism, including phenomena such as nucleation, monolayer formation, coalescence, bulk film growth and the evolution of surface roughness, can be identified *in-situ*.

The SE employed in this study is of the rotating analyzer ellipsometry (RAE) configuration similar in design to that of Aspnes and Studna (Aspnes et al. 1975). This instrument was used at an angle of incidence of 70° over the wavelength range 300-800 nm. For these measurements, at each value of wavelength data from 50 mechanical rotations of the analyzer were used to yield an estimated accuracy for calculated relative phase change of $\pm 0.03^{\circ}$ and an average accuracy for relative amplitude change of $\pm 0.01^{\circ}$ (Chindaudom 1991).

Typically, such an instrument is insensitive in the measurement of transparent samples where Δ is near 0° or 180° (De Nijs and Van Silfhout 1988, Jellison and Modine 1990). However, this difficulty was overcome by utilizing an achromatic compensator to shift artificially the near 0° or 180° Δ to near 90° to satisfy the optimum condition for RAE

(Chindaudom 1991). Since the samples characterized in this study are transparent materials, the compensator-equipped RAE was utilized.

2.2 Other Techniques

Many techniques have been employed to analyze the depth profile of thin films. Among them, Secondary Ion Mass Spectrometry (SIMS), Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS) and Auger electron spectrometry (AES) are commonly used. As shown in Fig. 2.1, several of these methods erode the surface of the sample by energetic particle bombardment, called sputtering. Sputtering provides information on the composition depth profile either by analysis of the remaining surface with electron spectroscopy (XPS, AES) or analysis of the sputtered materials (SIMS). The depth resolutions of these attractive techniques, including SIMS, RBS and AES are generally approximately ~5nm, ~20nm and ~3nm, respectively. However, damage to the sample surface cannot be avoided with techniques employing sputtering. Also, some of the changes in the composition profiles near the surface due to variations in sample charging and 'knock-in' during the initial stages of sputtering would limit these techniques. Rutherford backscattering does not require sputtering and so provides a non-destructive depth profile of the sample. In addition, many researchers have reported that ellipsometry is very powerful tool for the depth profiling of thin films.

Aspnes and Theeten (Aspnes and Theeten 1979) pioneered the study of the optical properties and microstructure of the interface between Si and its thermally grown oxide system by SE. The width of the interface (less than 10Å) is below the depth resolution of ion milling, so that SIMS, AES, XPS and other electron- and ion- spectroscopic techniques (Feldman and Mayer 1986) cannot be used effectively to study it. However, not only the microstructure but also the optical properties were obtained by SE with good depth resolution. Moreover, SE can be applied successfully to the characterization of



Fig. 2.1 : Schematic diagram of several methods to obtain depth profiles in thin films
 (a) Backscattering method, (b) AES, (c) SIMS
 (From Feldman and Mayer 1986)

semiconductors, such as SiGe alloys which show the occurrence of segregation of Ge from SiGe (Hulse et al. 1994). Therefore, it is obvious that SE, which is rapid, relatively cheap, non-destructive and applicable *in situ*, can detect in a straightforward manner the quality (optical and microstructural properties) of thin films.

2.3 Sensitivity of SE

Several studies dealing with the sensitivity of ellipsometric measurement have been reported. Snyder and co-workers (Snyder et al. 1986) reported that the maximum sensitivity of the phase change for AlGaAs grown by MBE can be found at an optimum angle of incidence and wavelength containing direct band gap energy. Cuypers et al. (Cuypers et al. 1978) used ellipsometry as a tool to study protein films at liquid-solid interfaces. They suggested that an automatic ellipsometer for biochemical work should have an accuracy and reproducibility of about 0.005°, corresponding to a layer thickness sensitivity of 5Å.

One major limitation to the accuracy of ellipsometric characterization of some semiconductors is the decrease in sensitivity as one investigates greater depths below the surface (Snyder et al. 1986). Another limitation is caused by correlation between model parameters in the data fitting stage. In general, correlation between parameters become stronger as the number of parameters increases and as the parameter sensitivity decreases. Also since the optical properties (i.e. refractive index, absorption coefficient etc.) depend on the wavelength, understanding the optical wavelength range for high sensitivity in determining the optical profile is important. As yet, the limits of the technique sensitivity for many situations are not known. In particular, the sensitivity of SE to the depth, composition and refractive index contrast in samples with graded index profiles, and the sensitivity of the data to small changes of surface roughness are not known. During the course of this study, the sensitivity limits of SE in detecting graded refractive index layers will be determined. This permits the accurate establishment of optimum sensitivity conditions for planned work.

2.4 Basic Principle and Theory of Ellipsometry

2.4.1 Propagation of Light in Matter

In general, most optical behavior is governed by the refractive index (n) and extinction coefficient (k), both of which are related to the complex dielectric function ($\bar{\epsilon}$). The dielectric function is also directly related to the electronic structure of the solids. Maxwell's equations (Wooten 1972) deal with the nature of the interaction between electromagnetic fields and matter. Thus, understanding Maxwell's equation is important.

Starting from Maxwell's equations and assuming no external currents and an isotropic and homogeneous medium, the electric field E of a wave is given by (Wooten 1972) (in SI Units),

$$\nabla^{2}\mathbf{E} = \left(\frac{\varepsilon}{c^{2}}\right) \left(\frac{\partial^{2}\mathbf{E}}{\partial t^{2}}\right) + \left(\frac{4\pi\sigma}{c^{2}}\right) \left(\frac{\partial\mathbf{E}}{\partial t}\right)$$
(2.1)

Where, ɛ : relative dielectric function

- c : speed of light in vacuum
- σ : optical conductivity

The solution of this equation is given by

$$\mathbf{E}(\mathbf{r}, \mathbf{t}) = \mathbf{E}_{o} \exp\left[i\left(\mathbf{\tilde{q}} \cdot \mathbf{r} - \omega t\right)\right]$$

=
$$\mathbf{E}_{o} \exp\left[-\left(\frac{\omega k}{c}\right)\mathbf{\tilde{q}} \cdot \mathbf{r}\right] \exp\left\{i\omega\left[\left(\frac{n}{c}\right)\mathbf{\tilde{q}} \cdot \mathbf{r} - t\right]\right\}$$
(2.2)

Where, $\tilde{\mathbf{q}}$: complex wavevector = $\left[\frac{\omega}{c/\tilde{N}}\right]$

 ω : angular frequency

Ñ : the frequency dependent complex refractive index = n+ik

Consequently, the optical properties of solids can be described in terms of complex dielectric function $\tilde{\epsilon}$, where

$$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2 = \tilde{N}^2 \tag{2.3}$$

where, ε_1 and ε_2 are the real and imaginary part of the dielectric function. These descriptions are related by

$$\epsilon_1 = n^2 - k^2$$
, (2.4 a)

$$\varepsilon_2 = 2nk$$
 (2.4 b)

Thus,

$$\begin{split} \mathbf{n} &= \left\{ \frac{1}{2} \left[\left(\epsilon_1^2 + \epsilon_2^2 \right)^{\frac{1}{2}} + \epsilon_1 \right] \right\}^{\frac{1}{2}} \end{split} \tag{2.5 a} \\ \mathbf{k} &= \left\{ \frac{1}{2} \left[\left(\epsilon_1^2 + \epsilon_2^2 \right)^{\frac{1}{2}} - \epsilon_1 \right] \right\}^{\frac{1}{2}} \end{aligned} \tag{2.5 b}$$

2.4.2 Polarized Light

Light may be treated as a transverse electromagnetic wave. Polarization is a property that is common to all types of electromagnetic waves. The polarization state is determined by the shape the electric field vector traces in time. For elliptically polarized light, the resultant electric field vector \mathbf{E} will rotate and change its magnitude. In this case, the endpoint of \mathbf{E} will trace out an ellipse, in a fixed space perpendicular to \mathbf{q} (the wavevector).

The following is one of the representations of the electric field E of a light wave traveling along the z-axis from Eq. (2.2).

$$E_x = E_{ox} \cos(qz - \omega t + \gamma_x)$$
 (2.6 a)

and

$$E_{y} = E_{oy} \cos(qz - \omega t + \gamma_{y})$$
(2.6 b)

where γ_x and γ_y are the phase of E_x and E_y respectively at z = 0 and t = 0.

The ellipse characteristic can be described by two mode parameters, Q and a (Fig. 2.2) where, Q is the angle between the major axis of the ellipse and the x-axis and a is the ratio of the minor to major axis of the ellipse. These two parameters are given by the following equations, (Hecht 1987, Azzam and Bashara 1977)

$$\tan 2Q = \frac{2E_{ox}E_{oy}\cos(\gamma_y - \gamma_x)}{E_{ox}^2 - E_{oy}^2}$$
(2.7)

$$\frac{2a}{1+a^2} = \frac{2E_{ox}E_{oy}\sin(\gamma_y - \gamma_x)}{E_{ox}^2 + E_{oy}^2}$$
(2.8)



Fig. 2.2 : Elliptically Polarized Light

Furthermore, linearly and circularly polarized light are special cases of elliptically polarized light and are generated when the value of 'a' assumes the special values of 0 and ±1 respectively. In other words, linearly polarized light occurs when $\gamma_y - \gamma_x = 0$ ($\mathbf{E} = \mathbf{E}_x + \mathbf{E}_y$) and circularly polarized light occurs when $\gamma_y - \gamma_x = \pm \frac{\pi}{2}$ and $\mathbf{E}_{ax} = \mathbf{E}_{ay}$.

2.4.3 Equations of Ellipsometry

In ellipsometry, light of a known polarization state strikes the sample at an oblique angle. The reflected light from the sample surface is generally elliptically polarized. This polarization state of the reflected light contains information about the sample's properties. The result of this measurement is two angles, Δ and Ψ .

The reflection coefficients for the p and s components of the light wave are defined as the ratio of the reflected and incident field amplitudes,

$$r_{p} = \frac{\left|\mathbf{E}_{p}^{\text{ref}}\right|}{\left|\mathbf{E}_{p}^{\text{inc}}\right|} e^{i(\gamma_{p}^{\text{ref}} - \gamma_{p}^{\text{inc}})}$$
(2.9 a)

$$r_{s} = \frac{\left|E_{s}^{\text{ref}}\right|}{\left|E_{s}^{\text{inc}}\right|} e^{i(\gamma_{s}^{\text{ref}} - \gamma_{s}^{\text{inc}})}$$
(2.9 b)

- rp : reflectivity of p component
- r : reflectivity of s component
- γ : phase component of electric field
- E : amplitude component of electric field

p and s denote electric field // and 1 plane of incidence

ref and inc denote reflected and incident waves.

The complex reflectivity ratio p can be defined by (Muller 1969)

$$\rho \equiv \frac{r_p}{r_s} = \frac{\left| E_p^{\text{ref}} \right| / \left| E_s^{\text{ref}} \right|}{\left| E_p^{\text{inc}} \right| / \left| E_s^{\text{inc}} \right|} e^{i[(\gamma_p^{\text{ref}} - \gamma_s^{\text{ref}}) - (\gamma_p^{\text{inc}} - \gamma_s^{\text{inc}})]}$$
(2.10)

The ellipsometric parameters, Δ and Ψ can be expressed in terms of the phase and amplitude of the p and s component of electric field as follows:

$$\Delta = \gamma_p - \gamma_s \tag{2.11 a}$$

$$\tan \Psi = \frac{\left|\mathbf{E}_{p}\right|}{\left|\mathbf{E}_{s}\right|} \tag{2.11 b}$$

By making use of Eqs.(2.11 a) and (2.11 b), Eq.(2.10) becomes

$$\rho = \frac{\tan \Psi^{\text{ref}}}{\tan \Psi^{\text{inc}}} e^{i(\Delta^{\text{ref}} - \Delta^{\text{inc})}}$$
(2.12)

Which is often written in the simple form as,

$$\rho = \tan \Psi e^{i\Delta} \tag{2.13}$$

From the Fresnel equations for single interface case, we can get (Fig. 2.3),

$$\varepsilon_{a} = \varepsilon_{a} \sin^{2} \theta_{i} \left[1 + \tan^{2} \theta_{i} \left\{ \frac{(1-\rho)}{(1+\rho)} \right\}^{2} \right]$$
(2.14)



Fig. 2.3 : Representation of reflection and refraction at an interface

(Chindaudom 1991)

Where, ε_s and ε_s are the dielectric functions of the substrate and the ambient, θ_1 is the angle of incidence of the beam and n_0 and n_1 are the refractive indices shown in Fig. 2.3. Therefore, for an ideal interface between two media (ambient/substrate), the dielectric function is obtained directly from the two ellipsometry angles Δ and Ψ . On the other hand, consider a multilayer structure consisting of m parallel layers between an ambient (0) and the substrate (m+1) (Fig. 2.4). The scattering matrix **S** represents the overall reflection and transmission properties of a multilayer structure and is given by (Azzam and Bashara 1977),

$$\mathbf{S} = \mathbf{I}_{01}\mathbf{L}_1\mathbf{I}_{12}\mathbf{L}_2 \cdots \cdots \mathbf{I}_{(j-1)}\mathbf{L}_j \cdots \mathbf{L}_m\mathbf{I}_{(m+1)}$$
(2.15)

with I and L the interface and the layer matrices respectively.

The interface matrix between layers a and b is obtained from:

$$\mathbf{I}_{ab} = \frac{1}{\mathbf{t}_{ab}} \begin{bmatrix} 1 & \mathbf{r}_{ab} \\ \mathbf{r}_{ab} & 1 \end{bmatrix}$$
(2.16)

Where, r and t are Fresnel coefficient for reflection and transmission. The layer matrix can be written as

$$\mathbf{L} = \begin{bmatrix} e^{i\beta} & 0\\ 0 & e^{i\beta} \end{bmatrix}$$
(2.17)

β (the phase shift) is defined as,

$$\beta = \frac{2\pi dn}{\lambda} \cos \phi \tag{2.18}$$



Fig. 2.4 : Schematic representation of a multilayer film

and depends on the refractive index of the layer (n) and on its thickness (d). ϕ is the angle between the incident light and the normal on the surface of the layer and λ is the wavelength. Hence, the complex reflectivity ratio (Eq. 2.10 and Eq. 2.13) can be calculated from the overall scattering matrix **S** for both p and s polarization.

$$\rho = \frac{r_p}{r_r} = \left(\frac{\mathbf{S}_{21p}}{\mathbf{S}_{11p}}\right) \times \left(\frac{\mathbf{S}_{11s}}{\mathbf{S}_{21s}}\right)$$
(2.19)

2.4.4 Dispersion Relationships

To describe the optical properties of a transparent material, a dispersion equation is fitted to experimental data for the refractive index. Various semi-empirical dispersion formulae have been proposed e.g. the Helmholtz-Ketteler formula (Rawson 1980),

$$n^{2} - 1 = A + \sum_{i} \frac{C_{i} \lambda^{2}}{\lambda_{oi} - \lambda^{2}}$$
(2.20)

Where, λ_{oi} is the centers of the strong absorption bands and the constants C_i are weighting factors related to their strengths.

Carniglia and co-workers (Carniglia et al. 1989) proposed an orthogonal form of a general three-term dispersion equation to determine the refractive index of transparent optical materials. This dispersion curve for the refractive index has the form:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$
(2.21)

Where A, B and C are constants to be determined. This form of the dispersion curve is referred to as the Cauchy equation.

Since the samples in this study are optically transparent in the near UV-visible-near IR region, the dispersion of the refractive index can be described by the well-known single term Sellmeier dispersion equation.

$$n^{2}(\lambda) = A + \frac{B\lambda^{2}}{\lambda^{2} - \lambda_{o}^{2}}$$
(2.22)

Where A, B and λ_0 are constants. If the refractive index of the film material and its dispersion with wavelength are to be known, then the three parameters A, B and λ_0 can be determined. For the sake of fitting a wider wavelength range, additional terms or damping terms can be added to this equation.

2.4.5 Effective Medium Approximations

The dielectric response of a layer consisting of a physical mixture of two or more components can be calculated using an appropriate effective medium approximation (EMA). The general form of the EMA of the two-component can be expressed as,

$$\frac{\varepsilon - \varepsilon_{h}}{\varepsilon + 2\varepsilon_{h}} = (1 - \upsilon) \frac{\varepsilon_{1} - \varepsilon_{h}}{\varepsilon_{1} + 2\varepsilon_{h}} + \upsilon \frac{\varepsilon_{2} - \varepsilon_{h}}{\varepsilon_{2} + 2\varepsilon_{h}}$$
(2.23)

Where ε and ε_{h} are the effective dielectric functions of the mixture and host medium respectively. ε_{1} , ε_{2} and υ are the dielectric functions of component 1 and 2, and the volume fraction of phase 2, respectively. Three important cases have been considered (Aspnes et al. 1979, Niklasson et al. 1981).

- a) $\varepsilon_{\rm h} = 1$, the Lorentz-Lorentz approximation
- b) $\varepsilon_{h} = \varepsilon_{1}$, the Maxwell-Garnett approximation
- c) $\varepsilon = \varepsilon_h$, the Bruggeman approximation

The Bruggeman effective approximation has been successfully employed for semiconducting and dielectric materials (Aspnes 1986). The Bruggeman approximation leads to

$$0 = v_1 \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} + v_2 \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon}$$
(2.24)

$$\varepsilon = \frac{1}{4} \left\{ \alpha + \sqrt{\alpha^2 + 8\varepsilon_1 \varepsilon_2} \right\}$$
(2.25)

with $\alpha = (3\upsilon_1 - 1)\varepsilon_1 + (3\upsilon_2 - 1)\varepsilon_2$ (2.26)

This is only valid when the particle size is much less than the optical wavelength. However, the lower limit of size is that the particle keeps its dielectric identity (i.e. there is no size effect). In addition, the host and guest components are treated equivalently.

2.4.6 Data Modeling

In general, ellipsometric data are analyzed by comparison with simulated data determined by calculation for an assumed multilayer model of the material (Azzam and Bashara 1977). The ellipsometric parameters (Δ and Ψ) can be calculated for the model in a straightforward manner and the model parameters adjusted by the linear regression method to give the best fit to measured data. Many fitting parameters are involved in the construction of a model, for example, the constants within the dispersion equation, layer thicknesses, second phase composition and void fraction, etc.

The modeling consists of optimizing the parameters of the model for a minimum difference between calculated and measured values of ρ . The difference is defined by the unbiased mean square deviation σ (Aspnes 1981), given by the following equation.

$$\sigma = \frac{1}{m - p - 1} \left[\sum_{i=1}^{m} \left\{ (\Delta_{cal} - \Delta_{exp})^2 - (\Psi_{cal} - \Psi_{exp})^2 \right\} \right]^{\frac{1}{2}}$$
(2.27)

Here 'm' is the number of data points over a spectral range and 'p' is the number of unknown parameters required in the model and 'exp' and 'cal' denote measured and calculated values respectively (Azzam and Bashara 1977). The (Δ and Ψ) can be replaced by (cos Δ , tan Ψ) (Aspnes and Theeten 1979) or (α , β) (Kim and Vedam 1986), where α and β are Fourier coefficients of the light intensity. The σ values described in chapter 4 were calculated using Δ and Ψ fitting.

The goodness of a fit can be seen from the value of σ and the correlation value between the parameters. In some cases, high correlation values show that the number of parameters should be reduced. Before conducting linear regression analysis (LRA), a grid search is applied over the fitting parameter space to find the local minima. It is essential to choose a proper value for each model parameter during the fitting procedure, otherwise the final linear regression analysis program can find a false minimum.

The selection of particular model is based on the simultaneous completion of all the following criteria:

- a) lowest value of σ
- b) physically realistic model
- c) good agreement between calculated and experimental data
- d) relatively low 90% confidence limits
- e) acceptably low values of the cross correlation coefficient.

If a model cannot fulfill these criteria, the LRA procedure should be repeated.

2.5 Graded-Index Optical Thin Films

Graded refractive index optical thin films have appeared rather recently and are being increasingly considered as an alternative to traditional multilayer dielectric stack devices for spectral filters and optical waveguide materials (Rancourt 1987). One type of optical component in which the optical properties (i.e. the refractive index) are varied with the depth in the sample is waveguide materials. A *waveguide* is a structure capable of guiding the flow of electromagnetic energy in a direction parallel to its axis, while substantially confining it to a region either within or adjacent to its surface (Kapany and Burke 1978). The well-known fiber optic light guide clearly fits this definition.

Planar lightguiding can be achieved by diffusing a dopant into the near surface region of a transparent solid to raise the refractive index. This results in a smoothly changing refractive index profile. Similarly, for ion-implanted and ion exchanged glasses, the refractive index profile is graded smoothly between the surface layer and the bulk value for the unperturbed substrate. Glass is one of the most promising substrate materials for designing optical devices. Ag⁺, Ti⁺, K⁺, Na⁺ and Li⁺ are widely used as dopants (Glebov et al. 1991). Both ion diffusion (Li and Johnson 1992) and ion exchange (Findakly 1985) have been used to fabricate planar optical waveguides. Examples of these techniques are shown in Fig. 2.5 and Fig. 2.6. For such devices, the amount of refractive index change, the composition profile, and the diffusion depth should be known exactly.

Up to the present, many methods have been developed to estimate the refractive index change in waveguides (Kaminow et al. 1973, Tien et al. 1969). For instance, in Tidiffused LiNbO₃ optical waveguide materials, the Ti concentrations in the sample are converted into refractive index change using calibration curves (Minakata et al. 1978). However this technique is limited in resolution for the measurement of refractive index contrast, $<1.05\times10^{-2}$. In SE measurements, the accuracy of modeled values for the refractive index are within 0.001 for bulk vitreous silica (Chindaudom 1991). Better



Fig. 2.5 : Configuration of an optical waveguide made by diffusion (Minakata et al. 1978)



Fig. 2.6 : Schematic diagam of the fabrication of a planar glass waveguide by ion exchange (Okuda et al. 1984)

resolution is expected for higher index materials. Therefore, SE is a promising candidate tool for the characterization of planar optical waveguides due to its good resolution for the depth profile of the refractive index.

2.6 Diffusion in Films on Planar Substrates

Buried glass optical waveguides can be fabricated by diffusion techniques using metallic coating films as finite diffusion sources (Li et al. 1992). Diffusion profiles can be predicted from theoretically calculated results if one can ensure surface concentrations decay to zero in proper boundary conditions (Shewmon 1989). Ramaswamy and co-workers reported optimization of the processing conditions for fabricating ion-exchanged waveguides in a soda-lime silicate glass (Ramaswamy et al. 1988). They used numerical methods for solving the diffusion equation to calculate the buried index profiles. The concentration profile of silver in glass waveguides was measured by atomic absorption spectroscopy (AAS). It was found that the concentration profile showed excellent agreement between an AAS measurement and a numerical calculation. This was possible because changes in glass composition induce changes in the refractive index. The index change, Δn , vs. depth, x, in the substrate follows a law: $\Delta n(x) = \Delta n_o \times f(x)$, where n and n are the original and modified refractive index and f(x) is a decreasing function (Chartier et al. 1980).

The linear differential equation for the dopant concentration distribution due to a diffusional process is given by

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$
(2.28)
where c is the concentration of the dopant, x is the distance from the surface, t is the diffusion time and D is the diffusion coefficient. The solution of Eq. (2.28) for a half infinite plane with boundary conditions, c(x,0)=0 for x>0, $c(\infty,t)=0$ and $c(0,t)=c_0$, is given by the complementary error function;

$$c(x,t) = c_o \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right] = c_o \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$
(2.29)

where c(x,t): concentration at a position x from the surface at time t

- c_ : concentration at x=0 boundary
- erf : error function
- erfc : complementary error function

The composition profile of buried Ag*-Na* ion-exchanged waveguides measured by Atomic Absorption Spectrophotometer (AAS) and Electron Microprobe have the complementary error function profile given by Eq. (2.29) (Ramaswamy et al. 1988).

Because it is advantageous to use a functional relation for the index profile, as it will reduce the number of unknown parameters which have to be calculated through the regression program, the complementary error function was chosen to fit diffusion depth profiles in this thesis.

2.7 Optical Models

Several modeling techniques have been tried to calculate SE data. There are mainly two numerical methods for modeling multilayer structures. The first one (Nguyen et al. 1990, Erman and Theeten 1982) is to use a number of layers with constant composition. The thickness and composition of each layer are unknown parameters which must be determined from the SE data. The second method uses a given function to describe the variation of properties with depth as mentioned in section 2.6. In this case, a functional form is used to describe the variation of composition with depth for graded index samples; the composition profile shape is fixed. During the fitting procedure only a few parameters (from the functional formula) are varied. This permits a smoothly varying composition change to be modeled with a minimum number of fitting parameters.

Erman and Theeten (Erman and Theeten 1982) used a linear profile with many layers of identical thickness to calculate the complex reflectance ratio p corresponding to the idealized multilayer structure shown in Fig. 2.7. Fried and co-workers (Fried et al. 1992) describe the damage depth profiles for the Ge-implanted Si samples by either rectangular, trapezoid-type, or coupled half-Gaussian optical model (realistic model) with 2, 4 and 5 parameters each as shown in Fig. 2.8.

In this work, a stair-case model was employed to calculate the ellipsometric data. The material under study was subdivided into many layers parallel to the surface. As the refractive index changes quickly near the surface, the layers were spaced closely near the film-air surface, and more widely further into the bulk of the material. A schematic representation of this approach is given in Fig. 2.9. This model combined with the diffusion equation (Eq. 2.29) was chosen to analyze the ellipsometric data. It was necessary to adopt this approach, rather than a large number of equally spaced layers, to avoid time -consuming calculations.



Fig. 2.7 : The simulated linear profile used by Erman et al. (20-layer model) (From Erman and Theeten 1982)



Fig. 2.8 : (a) Rectangular model, (b) trapezoid-type model, (c) realistic model for Ge-implanted Si samples (From Fried et al. 1992)



Fig. 2.9 : Stair- case optical model for a Na2O-modified SiO2 glass surface

Chapter 3

INSTRUMENTATION AND EXPERIMENTAL PROCEDURE

The spectroscopic rotating-analyzer ellipsometer (RAE) employed in this study was constructed (Mariner 1981) and revised (McMarr 1985, Chindaudom 1991, Gibbons, unpublished) at the Intercollege Materials Research Laboratory (IMRL) of the Pennsylvania State University. Fig. 3.1 shows the RAE instrument used in this study, which may be grouped into two parts, the optical components and the electronic components (section 3.2 and 3.3).

The modeling program which converts the data for Δ and Ψ to dielectric functions for the sample was also developed by the ellipsometry group at the IMRL. Modifying this program to fit graded index layer profiles is the key work for this study. Hence, considerable emphasis is given to the modeling procedure in this chapter.

This chapter also describes briefly each component of an RAE, as well as the alignment, calibration procedure and the experimental errors caused by the low intensity of light reflected from transparent samples. This error can be reduced by dark cycle correction, PMT non-linearity correction and through use of a compensator (Chindaudom 1991).

The final part of this chapter describes the use of the modeling procedure to characterize graded index profiles associated with leaching of glass plates as well as SIMS measurements.



Fig. 3.1 : Schematic diagram of the Rotating Analyzer Ellipsometer (RAE) system

3.1 Modeling Procedure

For thin film/substrate systems involving a large contrast in the refractive index such as SiO₂/Si, direct inversion of ellipsometric data can be used to get the optical properties and thickness of the film (Charlot and Marauni 1985). However, in the case of a thin transparent film (i.e. $n_{25\%Na2O+75\%SiO2} \approx 1.4977$ at $\lambda \approx 589$ nm) on a silica substrate ($n_{SiO2} \approx$ 1.458 at $\lambda \approx 589$ nm), the small refractive index difference leads to large uncertainty in the resulting values for the refractive index and thickness when a direct inversion of the data is used (Gustin 1987). Hence, in this study a modeling procedure was developed to fit experimental data on graded index systems. A flow chart for the modeling procedure employed is shown in Fig. 3.2. This section deals with reference optical properties and the modeling program utilized in this study.

3.1.1 Reference Optical Property Data

Using accurate optical data is essential to obtain accurate ellipsometric models. Thus, before entering the linear regression analysis, it is necessary to determine as accurately as possible the dielectric functions of the reference materials. The dielectric function of a mixture can then be estimated via the Bruggeman effective medium approximation as mentioned in section 2.4.5.

A hypothetical system was constructed to examine the sensitivity limits of SE to graded index layers. This model consists of a graded layer induced by diffusion of a modifier (Na₂O) into bulk SiO₂. A model of this type requires knowledge of the refractive index of the glass as a function of composition. SiO₂ and 25%Na₂O + 75%SiO₂ (called Na₂O:25) were chosen as end member compositions. While the dispersion of the refractive index is well-known for fused SiO₂ (Malitson 1965), a complete dispersion relation for



Fig. 3.2 : Flow chart for the modeling procedure used in this study

Na2O:25 was not available and had to be estimated from available data. This was done as follows:

A simple empirical formula that fits the refractive index data of many commercial silicate glasses between about 300nm and 1000nm can be expressed as (Doremus and Bansal 1986) (λ in nm),

$$n = A + \frac{B}{\lambda}$$
(3.1)

Using reported values of refractive index for the Na₂O:25 at three different wavelengths $(n_{\lambda=589,3nm}=1.4977, n_{\lambda=632.8nm}=1.4953, n_{\lambda=486nm}-n_{\lambda=656nm}=0.0086)$ (Doremus and Bansal 1986, Mazurin et al. 1985), the dispersion of Na₂O:25 was fitted to Eq. (3.1). The resulting fitted dispersion is (λ in nm)

$$n = 1.456 + \frac{24.94}{\lambda}$$
(3.2)

The three-term Sellmeier equation of fused silica (SiO2) is (Malitson 1965):

$$\varepsilon = 1 + \frac{0.6961663\lambda^2}{\lambda^2 - (68.4043)^2} + \frac{0.4079426\lambda^2}{\lambda^2 - (116.2414)^2} + \frac{0.8974794\lambda^2}{\lambda^2 - (9896.161)^2}$$
(3.3)

Where ε is the dielectric constant and λ is wavelength expressed in nm.

The optical behavior of sodium silicate glasses of intermediate compositions was described by modeling it as a simple mixture of SiO_2 and $Na_2O:25$ using the EMA. The result is shown in Fig. 3.3. The fitted refractive indices at 589.3nm (n_D) for several intermediate compositions are identical to the literature data up to third decimal place (Doremus and Bansal 1986).



Fig. 3.3 : Refractive index dispersion for several compositions of

sodium silicate glasses

Fig. 3.4 shows the composition variation of the refractive index for the Na₂O-SiO₂ mixture at 589nm. The refractive index varies almost linearly with composition. The reason for this change of refractive index is that the molar refractivity (R_1) of the Na ion (0.50) is greater than that of the Si ion (0.10) (Rawson 1980). The value of R_1 is strongly related to the polarizability of the materials. A 3-dimensional plot for the dispersion of $(SiO_2)_x(Na_2O)_y$ is represented in Fig. 3.5. The composition dependence of refractive index can be seen in Fig. 3.4 and Fig. 3.5.

3.1.2 Modeling Program

The computer program utilized in this work is an extension of the existing program developed by the ellipsometry group of MRL. All of the computer code, including the program to calculate the dielectric function for each layer, was written and compiled using Microsoft FORTRAN Powerstation for an IBM-compatible personal computer. IMSL (International Mathematical and Statistical Library) subroutines were used to calculate the error function and the inverse error function.

Numerous fitting parameters are incorporated into the program. The program tries to determine the values which lead to the best fit of the experimental Δ and Ψ data by utilizing a combination of a grid search and linear regression analysis. For the system of Na₂O:25 diffused into bulk SiO₂, the function describing the composition depth profile is a type of complementary error function (Eq. 2.29).

$$c(x, t) = c_o \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right] = c_o \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$
(3.4)

Two parameters, Dt (diffusion coefficient×time), and c_o (surface concentration), are chosen in this system. These two parameters completely describe the depth profile.



Fig. 3.4 : Effect of composition on the refractive index of $(SiO_2)_x(Na_2O)_y$ at a wavelength of 589.3nm (Doremus and Bansal 1986)



Fig. 3.5 : Dispersion phenomena of sodium silicate glasses

Fig. 3.6 shows a calculated depth profile of a typical Na₂O concentration vs. depth into SiO₂ at different times for a diffusion coefficient of $1.70 \times 10^{-17} \text{cm}^2/\text{s}$ (Doremus and Bansal 1986). In order to calculate Δ and Ψ for this profile, the material was subdivided into many layers which have different thicknesses. However, the composition is uniform within each sub-layer. Eq. (3.5) is a numerical equation for setting the concentration of Na₂O for each layer.

$$\mathbf{c}(\mathbf{x}_{i}) = \left[1 - \sum_{i=1}^{m} \left(\frac{i-1}{j}\right)\right] \mathbf{c}_{0}$$
(3.5)

Where, m and j are the layer number and the total number of subdivided layers, respectively, c_0 is the surface concentration and x_i is the position of the ith layer from the surface. This arrangement ensures that there are closely-spaced layers in regions where the refractive index changes rapidly. Where the refractive index changes more slowly, the layers are more widely spaced. The corresponding depths into the surface x(i) at these concentrations, are then calculated from Eq.(3.6) using the inverse complementary error function.

$$\mathbf{x}(\mathbf{i}) = 2\sqrt{(\mathbf{Dt})} \operatorname{erfc}^{-1} \left(\frac{\mathbf{c}}{\mathbf{c}_{o}} \right)$$
(3.6)

Using the values from Eq.(3.6), the thickness of the individual layers are defined as,

$$t(i) = \left(\frac{x(i) + x(i-1)}{2}\right) - (summed thickness of the previous layers) \quad (3.7)$$

Where, t(i) is the thickness of the ith layer.



Fig. 3.6 : (a) Typical calculated Na2O diffuison profile and

(b) Schematic of layer thickness subdivision used in modeling of SE data

In summary, for compositionally graded layers, the dielectric function is a continuously varying function of depth. This smoothly changing function was treated as a step function as shown in Fig. 3.7. This permits calculation of the ellipsometric data using the values of thickness of each layer from Eq.(3.7).

3.2 Optical Components of PSU Spectroscopic Ellipsometer

A 75 W high pressure Xe short-arc lamp is used to supply a broad spectrum from the near Infrared (IR), through the visible to the near Ultraviolet (UV). Since the output intensity of the Xe arc is approximately proportional to the current flowing in the lamp, it is essential that the lamp power supply should be stable during measurements.

The light beam from the lamp is focused and directed to the monochromator. The monochromator does not vary the position of the output beam over the wavelength of interest. Rochon prisms of crystal quartz are used for the polarizer and analyzer. These components induce polarized light by spatially separating the two polarization components. An aperture is needed to filter the unwanted beam. In this study, an achromatic compensator was also used. Because the experimental error in Δ for an ellipsometric measurement is proportional to $1/\sin\Delta$ (De Nijs and Van Silfhout 1988), the errors are unacceptably large near $\Delta=0^{\circ}$ or 180° . This difficulty can be overcome by inducing a phase change deliberately from 0° or 180° to near 90° with a compensator (King and Downs 1969, Kizel et al. 1964, Chindaudom 1991).

A Photomultiplier tube (PMT) is used as the detector. The intensity can be detected as a function of analyzer position using the PMT. All of the components except the lamp and monochromator are mounted on a Rudolph ellipsometer table (model # 436).



Fig. 3.7 : Refractive index (n) profile at 589.3nm wavelength for a Na₂O-modified SiO₂ glass. (a) Actual diffusion profile, (b) Approximation of the diffusion profile used in this study (step function)

3.3 Electronic Components of PSU Spectroscopic Ellipsometer

In outline, the electronic part of the RAE instrument consists of a signal processing unit, a digital conversion unit and a control computer.

The photomultiplier output current is converted to a voltage by means of a Keithley 427 current amplifier. The PMT control circuit maintains a constant signal level from the PMT output by regulating the high voltage to the PMT. The signal is digitized for data processing by means of analog/digital converter (ADC). The analyzer is mounted in a motor and is continuously rotated during measurement. All of these units are connected to the control computer. Moreover, scanning the monochromator, changing the shutter, and calculating the Fourier coefficients (α and β) and Δ and Ψ are performed by the control computer.

3.4 Calibration of PSU Spectroscopic Ellipsometer

The calibration procedure is essential to accurate measurements. The system constants, A_s , P_s , δ_A and δ_p are determined by calibration, where A_s is the angle between the azimuth of the analyzer and the reference frame at A(analyzer angle) = 0, P_s is the angle of the polarizer with respect to the reference frame at P(polarizer angle) = 0, and δ_A and δ_p are the optical activity coefficients for the analyzer and polarizer.

Residual and phase calibration are widely used in ellipsometric measurements. Residual calibration gives accurate results when Δ is near 90°. On the other hand, phase calibration is superior to the residual calibration when $|\Delta| < 30^{\circ}$ or $|\Delta| > 150^{\circ}$ (De Nijs and Van Silfhout 1988).

In this work, a highly absorbing sample (i.e. gold) is used for residual calibration because gold can reflect linearly polarized light when the incident light is also linearly polarized if the beam is either parallel or perpendicular to the plane of incidence (Aspnes 1974). However, the polarization rotation shifts the maximum modulation from P_s to a nearby angle P_1 (the minima in the residual $R(P)=1-(\alpha^2+\beta^2)$) due to the optical activity of the polarizer. P_s is given by (Aspnes 1974),

$$P_{s} = P_{1} - \frac{\delta_{A} \tan \Psi + \delta_{P} \cos \Delta}{\sin \Delta} \Big|_{P \equiv P_{s}}$$
(3.8)

If the "P" are chosen in the vicinity of the 90° (P \cong P_s + $\pi/2$), then

$$P_{s} = P_{2} + \frac{\delta_{A} \cot \Psi + \delta_{P} \cos \Delta}{\sin \Delta} \bigg|_{P \equiv P_{s} + \frac{\pi}{2}}$$
(3.9)

where P_2 is the minima in the residual R(P) near $\pi/2$. Therefore, the polarizer is moved from -5° to $+5^{\circ}$ around 0° and 90° of P. Finally, these two values (Eq. 3.8 and 3.9) are averaged to get a value of P_s .

$$P_s = \frac{P_1 + P_2}{2} + \frac{\delta_A \cot 2\Psi}{\sin \Delta}$$
(3.10)

To obtain the calibration parameters for the analyzer, A₁ should be first calculated from (Aspnes and Studna 1975):

$$A_1 = \frac{1}{2} \tan^{-1} \left(\frac{\beta}{\alpha} \right)_{p=p_1}$$
(3.11)

Then,

$$A_{s} = A_{1} - \frac{\delta_{p} \cot \Psi + \delta_{A} \cos \Delta}{\sin \Delta} \bigg|_{p \equiv p_{s}}$$
(3.12)

Similarly, in the near local minima $P \equiv P_s + \pi/2$,

$$A_{s} = A_{2} - \frac{\delta_{p} \tan \Psi + \delta_{A} \cos \Delta}{\sin \Delta} \bigg|_{p \equiv p_{s} + \frac{\pi}{2}}$$
(3.13)

Therefore, the average value of As is given by,

$$A_{s} = \frac{A_{1} + A_{2}}{2} - \frac{\delta_{p} \cot 2\Psi}{\sin \Delta}$$
(3.14)

3.5 Alignment and Signal Correction

Alignment is a process in which the optical components are centered in the beam. A reference laser beam (HeNe laser) is used for centering the optical components by means of backward tracing of the laser light to the source.

The alignment condition can be checked by measuring the symmetry of the two optical cycles, which differ by a 180° rotation of the analyzer. The ideal case is that the intensity difference between the two cycles is equal to zero. However, a difference of 0.1% is enough for a well aligned system (Aspnes and Studna 1975).

The dark correction (background noise correction) is performed before taking data by measuring the average intensity signal with a deliberately blocked beam, while manually increasing the PMT voltage. This noise is subtracted from the measured intensity before the data reduction process. This correction is important for transparent samples, because the measured intensity of the samples with low reflectivity is significantly affected by dark current.

The intensity of light (I) incident on the PMT is given by (Aspnes and Studna 1975),

$$I = I_{\alpha} (1 + \eta \alpha \cos 2A + \eta \beta \sin 2A)$$
(3.15)

Where, I_0 is the average light intensity and η describes the difference in amplification of the ac and dc components of the incident light as the voltage of the PMT is increased. The value of η can be calculated at different PMT voltage as (Chindaudom 1991):

$$\eta = \frac{1}{\sqrt{\alpha^2 + \beta^2}} \tag{3.16}$$

When transparent samples are measured, the reflected intensity is particularly low at both ends of the spectral range. Hence, the wavelength dependence of η should be resolved (Chindaudom 1991). In this work, η was measured as a function of the PMT voltage in the straight-through configuration of the system and the results were used to correct all subsequent data.

3.6 Sample Preparation

To study materials with graded composition depth profile, two materials, leached soda-lime-silicate glass and lead-silicate glass, were chosen. Because these samples contain distinct compositional profiles with depth, it is possible to evaluate the sensitivity of SE. This section discusses the preparation of the samples used in this study.

3.6.1 Soda-Lime Silicate Glass

Chemically leached Fisher Brand glass slides were used to examine the effect of a depth profile on SE data. The original composition and density of these samples are given in Table 3.1. The samples were prepared in the following manner:

Oxide	Weight %
SiO ₂	72.1
Na ₂ O	14.0
CaO	7.3
MgO	3.8
Al ₂ O ₃	1.8
SO3	0.3
K ₂ O	0.15
Fe ₂ O ₃	0.045

Table 3.1 : Composition and Density of Fisher Brand Glass Slide

Density : 2.4667 g/cm3

Since glass slides are transparent over the visible spectrum, the incident light beam can pass through the sample. If the front and back sides of this sample are parallel, the light reflected from the back side is detected by the photomultiplier tube along with the reflection from the front side. This complicates analysis of the data. In order to eliminate the effect of the reflection from the back surface, the back side of all transparent samples were roughened.

Thereafter samples were leached in hydrochloric acid (37.0%) for different times (48-hour, 7-days, 10-days) at room temperature (Fig. 3.8). The solution was stirred throughout the leaching time. As mentioned in Table 3.1, the glass slide consists of eight components. Since all the cations except Si and Al are soluble in a hydrochloric acid, the aluminosilicate network should remain, where the other cations are leached from the sample surface (Rawson 1980). In other words, the longer samples are leached, the more modifier ions diffuse out. The relative amount of SiO₂ is higher in the top region compared to the unchanged bulk of the glass slide. Therefore, the compositional depth profile of SiO₂ which is left over in the glass slide should be as shown by Fig. 3.9. Finally, the back side of the sample was given a coat of black paint to minimize scattered light from the back surface.

3.6.2 Alkali-Lead Silicate Glass

The lead-silicate glass that was studied has the composition 65.5 SiO_2 -28.2 PbO with small amounts of Cs_2O , Al_2O_3 , BaO and Rb_2O . The samples were initially immersed in 1N NaOH solution for 20 min. at 80°C in order to clean the surface. Subsequently, the samples were leached in 1N HCl solution at room temperature for different times (30 min., 1 hr., 5 hr. and 1 day). Unlike the leaching procedure for soda-lime-silica glasses, no stirring was used to this sample. This was done in order to match the leaching conditions







Fig. 3.9 : Compositional depth profile of SiO2 within a leached glass slide

used by Dr. Pantano's group (D'Souza and Pantano, unpublished). Other treatments were the same as in section 3.6.1.

3.7 Secondary Ion Mass Spectrometry (SIMS)

As mentioned in section 2.1, ellipsometry is an indirect technique to characterize the depth profile. One of the direct depth profiling techniques, SIMS, was performed independently in order to compare with the depth profiling results from SE. The soda-lime-silica glass slide were depth-profiled using a Perkin Elmer 6300 SIMS with a 20nA, 6KeV, 60° impact angle and O_2^+ primary ion beam at Evans East Company. The lead-silicate glasses were depth-profiled using a Cameca IMS-3F SIMS with a 125nA, 14.5KeV and O' primary ion beam by Dr. Pantano's group in Pennsylvania State University. The results are presented in section 4.3 and 4.4.

Chapter 4

RESULTS AND DISCUSSION

4.1 Introduction

The sensitivity limits of spectroscopic ellipsometry (SE) for the characterization of optical coatings are not known as yet. The sensitivity of SE data to graded refractive index depth profiles in transparent materials is known to be a function of parameters such as the thickness of the graded layer and the refractive index contrast (McKinstry 1992). In this work, to determine the sensitivity, a hypothetical model with a known compositional depth profile (complementary error function-like) is constructed and the ellipsometric spectra are calculated. At the opening part of this chapter, these calculated spectra are compared with those of an unmodified sample to determine the relationship between the parameters describing the diffusion and magnitude of the changes in the optical data. The sensitivity of SE to the depth, composition and refractive index contrast will also be reported in this chapter. Finally, a comparison between compositional depth profiles measured by SE and those measured with secondary ion mass spectrometry (SIMS) will be presented.

SE allows the phase and amplitude change of the light beam caused by reflection from the sample to be measured independently. In most cases the phase change parameter is more sensitive to a small change of layer thickness and composition than the amplitude change. Consequently, the ellipsometric technique becomes very sensitive to the sample condition due to the phase information (Aspnes 1981). In this work, all SE measurements were performed at room atmosphere and 70° angle of incidence. Fig. 4.1 shows the calculated change of the ellipsometric parameters (Δ and Ψ) for the case of Na₂O diffusing into the surface of pure SiO₂ for an incidence angle of 70°. In the figure, the



Fig. 4.1 : Calculated ellipsometric data for Na₂O diffused into SiO₂ (Surface concentration = 10%)

surface concentration of the Na₂O is 10% and the diffusion depth for this system is about 140Å. Throughout the modeling studies, the diffusion depth is defined as the depth where the concentration drops to 0.3% of the surface concentration. Notice that the amplitude parameter (Ψ) remains almost unchanged, while the difference in the phase change (Δ) is easily distinguished. Hence, most of the data listed in this chapter are represented only by Δ values for convenience.

4.2 Modeled Change of Ellipsometric Parameters

There are many parameters which affect the <u>calculated</u> ellipsometric data for a sample with a diffusion profile, such as the dopant concentration, the modified depth and the number of sub-layers used in the modeling. In this section, the changes in the calculated ellipsometric spectra due to these factors are described and three-dimensional plots of parameter changes describing the sensitivity to the modeled parameter are generated.

4.2.1 Effect of Surface Concentration of a Modified Glass

In this section, the changes in the calculated ellipsometric phase parameter Δ as a function of dopant concentration and wavelength are described.

The altered value of Δ ($\delta\Delta$) is calculated by taking the numerical difference between two simulated data sets (unmodified SiO₂ and SiO₂ with a layer of Na₂O rich material diffused into the surface) at 101 wavelengths. The plot in Fig. 4.2 is the $\delta\Delta$ of the SE data obtained for the cases of 5%, 10% and 20% surface dopant concentration (C_s) of Na₂O. The diffusion depth of this profile was held for all cases to 3760Å. This profile is subdivided into 300 layers parallel to the surface. This plot clearly shows the strong C_s dependence of $\delta\Delta$, as well as the wavelength dependence. As the dopant concentration



Fig. 4.2 : Calculated change of ∆ as a function of wavelength of the SE data for different dopant concentrations

becomes larger, easily distinguishable changes in Δ appear. 300 sub- layers were used to descibe this thick graded layer in order to avoid false interference fringes in the calculated spectra. Fig. 4.3 shows the difference in Δ change for a graded layer and a homogeneous layer with a composition equivalent to the surface concentration of the graded layer. The solid and dotted lines represent $\delta\Delta$ for the graded layer with 5% C_s (from Fig. 4.2) and a 5% homogeneous layer of the same thickness respectively. It is immediately apparent that the graded index layer possesses SE data much closer to the unmodified sample. Fig. 4.4 shows a plot of concentration sensitivity for different surface compositions with the diffusion depth fixed at 3760Å. For this diffusion depth, an increase in the dopant concentration at the surface leads to a nearly linear change in Δ .

4.2.2 Effect of Modified Depth

As stated in section 2.8.6, SE is an effective and accurate technique to investigate the depth profile of samples. In order to determine the depth resolution of SE to graded index layers, the change of the calculated ellipsometric phase parameter Δ as a function of modified depth is described.

Ellipsometric data were first calculated as in Fig. 4.5, assuming $C_s = 10\%$ and allowing the diffusion depth to vary by changing the "diffusion time". As can be seen in Fig. 4.5, the change of Δ and Ψ increases with an increase in diffusion depth. Because the SE used in this study can measure Δ within 0.03-0.05°, samples with modified depth of ~50Å can be detected for a refractive index contrast between the surface and the bulk of 0.02 at 500nm (Fig. 4.5). Fig. 4.6 shows a 3-dimensional plot of Δ with varying diffusion depth and wavelengh. As shown in Fig. 4.6, the maximum change of Δ is approximately 0.89° at the diffusion depth of ~620Å. With increased diffusion depth, the change of Δ decreases rapidly until ~3800Å. At this point, changes in the Ψ spectra should be large enough to detect the graded layer, even though the changes in Δ are relatively small.



Fig. 4.3 : Comparison of the change of ∆ between a homogeneous layer and a graded layer

Diffused Depth : 3760 Å fixed



Fig. 4.4 : Calculated change of Δ as a function of dopant concentration and wavelength



Fig. 4.5 : Effect of the diffusion depth on the ellipsometric spectra



Fig. 4.6 : Change of Δ of SE data with varying diffusion depth at wavelengths between 300 and 800nm (C_s=10%) for Na₂O diffused into SiO₂.
4.2.3 Effect of Number of Layers Used to Model

As stated in section 3.6.3, the material under study was subdivided into many layers parallel to the surface which have different thickness for the sake of calculating Δ and Ψ . The composition and refractive index were fixed at the mean value within each slice.

If too few layers are used to describe the system, then the relatively large changes in the composition and refractive indices between sublayers result in artificial interference fringes, and the calculated ellipsometric data oscillate around the true solution as a function of wavelength. On the other hand, it may take a lot of time to calculate Δ and Ψ if too many layers are utilized. Therefore, the number of sub-layers was chosen as a compromise between resolution and the required computing time.

Fig. 4.7 and Fig. 4.8 show how the calculated ellipsometric parameters converge to the true values as the number of layers used to model the graded layer increases. For a diffusion depth of 5100Å and a refractive index contrast of 0.02 at 500nm, the calculated ellipsometric data have largely converged to a consistent solution when 500 layers are used to describe the graded index region. It is important to note, however, that even for 100 and 150 layer models, the oscillation are small in amplitude (<0.03°). Since this is on the order of the instrumental accuracy, artificial interference fringes of this magnitude would not affect modeling results. Again, the Ψ value is less sensitive to the number of layers used to model the graded layer (see Fig. 4.8). The larger the diffusion depth, the more layers are required to eliminate artificial interference fringes.

4.3 Determination of the Sensitivity of SE

In this section, the sensitivity of the ellipsometric parameters to depth, composition and refractive index gradient for graded index layers as a function of wavelength is presented. The sensitivity is calculated by taking numerical differences between two



Fig. 4.7 : Oscillations of modeled ∆ values due to artifacts associated with the number of sub-layers describing the graded index region (Surface concentration (C_s) = 10%, Diffusion depth = 5100Å fixed, L = number of layers)



Fig. 4.7 continued



Fig. 4.8 : The change of modeled Ψ values associated with the number of sublayers describing the graded index region

simulated data sets, each with 101 wavelengths and 70° angle of incidence. The two data sets came from a model with a known compositional profile and one with a slightly modified composition profile.

4.3.1 Determination of the depth sensitivity of SE for graded index layers

The plots in Fig. 4.9 and Fig. 4.10 show the differences between Δ values for models of SiO₂ with Na₂O or a higher index material (modeled using data for crystalline Al₂O₃) diffused into the top surface with a 10% surface concentration and diffused depth increased by 10Å, 20Å, 30Å, 50Å or 100Å each. The scale is in degrees per 10Å, 20Å, 30Å, 50Å or 100Å depth change. The original modified depth was 140Å and 20 layers were used to describe the graded index region. In Fig. 4.9 and Fig. 4.10, the refractive index contrasts (Δ n) between the top surface and the bulk are 0.0174 and 0.030 at the wavelength of 500nm, respectively. These plots show the depth and refractive index contrast dependence of the Δ sensitivity, as well as the wavelength dependent changes. By comparing these two plots, a significant increase in Δ occurs (from 0.132 to 0.323) at 500nm for the 100Å depth increased model as Δ n is increased from 0.0174 to 0.030. Based on these data, it is clear that a larger relative change in thickness is more readily detected. That is, the accuracy of the thickness measurement is relative to the total modified depth. In addition, the sensitivity to thickness measurement is improved as the rrefractive index contrast between the surface and bulk is increased.

The plots in Fig. 4.11 show the difference of ellipsometric parameters (Δ , Ψ) for models of SiO₂ with Na₂O diffused into the top surface and the diffusion depth increased by 50Å each. For instance, the solid line in Fig. 4.11 represents the numerical difference of Δ and Ψ values for models with 140Å and 190Å of modified depth. The scale is in degrees per 50Å depth change. 20, 40, 80, 120 and 150 layers were used to describe the graded



Fig. 4.9 : Sensitivity (δΔ) of the ellipsometric parameter Δ to various modified graded index layer depth changes. The scale is in degrees per 10Å, 20Å, 30Å, 50Å and 100Å depth change. The original modified depth is 140Å. (n_{surface} - n_{bulk} = 0.0174 at λ = 500nm).



Fig. 4.10 : Sensitivity (δΔ) of the ellipsometric parameter Δ to various modified graded index layer depth changes. The scale is in degrees per 10Å, 20Å, 30Å, 50Å and 100Å depth change. The original modified depth is 140Å. (n_{surface} - n_{bulk} = 0.030 at λ = 500nm).



Fig. 4.11 : Sensitivity (δΔ, δΨ) of the ellipsometric parameter (Δ, Ψ) to a change in modified depth. The scale is in degrees per 50Å depth change. The legend shows the original diffusion depth.

index region for 140Å, 280Å, 475Å, 620Å and 850Å of modified depths, respectively. As the graded index layer depth exceeds 500Å, the magnitude of Δ change is negligible.

On the other hand, Ψ is sensitive to a 50Å change of modified layer thickness up to ~850Å as seen in Fig. 4.11. This decrease in sensitivity to a 50Å change in modified layer thickness at larger thickness values is not surprising, given the decreasing percentage of the total depth the change represents. These results reinforce the fact that the larger the relative change in thickness, the better the sensitivity. However, when the original value of modified depth is high, the sensitivity of Δ as well as Ψ to small changes of depth is not good.

4.3.2 Determination of composition sensitivity of SE

As in the case of the sensitivity to the depth for graded index layers, compositional sensitivity is also calculated by taking the numerical difference between two simulated data sets.

Fig. 4.12 shows the sensitivity of the ellipsometric parameter Δ to the compositional change corresponding to 1% surface concentration increase of a Na₂O-doped SiO₂ glass with 5%, 10% and 20% surface concentration. The diffusion depth is held at 140Å and 20 sub- layers were used. For this simulation, the compositional change can be detected only in the limited energy range (300-400nm) and causes the same effect in the SE data for different surface concentration values. Consequently, for this refractive index contrast, there would be a minimum of 1% error in the calculated surface composition. The plot in Fig. 4.13 is the sensitivity of Δ to a change in composition in 10% C₃ Na₂O into SiO₂. The refractive index contrast between the top surface and the bulk of this model is 0.0174 at the wavelength of 500nm and the diffusion depth is held at 140Å (again 20 sub-layers were used to describe the graded index region). The scale is in degrees per 1%, 2%, 3%, 5% and 10% addition of Na₂O. More than a 2% increase of surface concentration can be



Fig. 4.12 : Sensitivity (δΔ) of the ellipsometric parameter Δ to a change in the surface concentration. The scale is in degrees per 1% surface concentration increase. The modified depth of model is held at 140Å.



Fig. 4.13 : Sensitivity (δΔ) of the ellipsometric parameter Δ to a change in the surface concentration. The scale is in degrees per 1%, 2%, 3%, 5% and 10% surface concentration change. The modified depth of model is held at 140Å. (n_{surface} - n_{bulk} = 0.0174 at λ = 500nm)

detected using the SE adopted in this study. However, for a refractive index contrast between the top surface and the bulk of 0.030 at 500nm, a change in the surface concentration characteristic of the diffusion layer can be determined within 1% as can be seen in Fig. 4.14. It is apparent that the sensitivity is higher for larger refractive index contrasts. Fig. 4.15 and Fig. 4.16 show the sensitivity of Δ to models in which the diffusion depth is held at 3760Å and other conditions are identical to Fig. 4.12 and Fig. 4.13, (except 300 sub-layers were used in this modeling). The changing parameter, C_s, can be modeled within 2% over the entire spectral range of 300-800nm.

4.4 Soda-Lime-Silicate Glass

In order to verify the conclusions of the modeling, experimental studies on selected systems were also undertaken. Chemically leached glasses were chosen as a convenient means of preparing graded index materials.

SE data for the soda-lime-silica glasses were taken over the spectral range of 400-750nm. Because the dispersion relation for these samples used in this work was not known, ellipsometric data for the unleached glass was used to determine reference optical properties.

For this sample, the dispersion of the refractive index was expressed by the Sellmeier dispersion equation with one oscillator term as in equation 4.1.

$$n^{2}(\lambda) = A + \frac{B\lambda^{2}}{\lambda^{2} - \lambda_{o}^{2}}$$
(4.1)

Where A, B and λ_0 are unknown parameters and λ is in nm. It was assumed that the glass could be described as an otherwise homogeneous material with a thin layer of surface roughness. Bruggeman effective medium theory and linear regression analysis were used



Fig. 4.14 : Sensitivity (δΔ) of the ellipsometric parameter Δ to a change in the surface concentration. The scale is in degrees per 1%, 2%, 3%, 5% and 10% surface concentration change. The modified depth of model is held at 140Å. (n_{surface} - n_{bulk} = 0.030 at λ = 500nm)



Fig. 4.15 : Sensitivity (δΔ) of the ellipsometric parameter Δ to a change in the surface concentration. The scale is in degrees per 1% surface concentration change. The modified depth of model is held at 3760Å.



Fig. 4.16 : Sensitivity (δΔ) of the ellipsometric parameter Δ to a change in the surface concentration. The scale is in degrees per 1%, 2%, 3%, 5% and 10% surface concentration change. The modified depth of model is held at 3760Å. (n_{surface} - n_{bulk} = 0.0174 at λ = 500nm)

to get the best fit value of Δ and Ψ . Because the correlation between the thickness of the surface roughness layer and the volume fraction of void is very strong for this sample, the volume fraction of air in the roughness layer was kept constant at 0.5. Equation 4.2 is the dispersion relation for the unmodified soda-lime-silica glass determined using these methods (λ in nm).

$$n^{2}(\lambda) = 1 + \frac{1.258\lambda^{2}}{\lambda^{2} - 105.3^{2}}$$
(4.2)

Fig. 4.17 is a schematic diagram showing the model of the unmodified glass. This model enabled us to determine the thickness of rough surface layer. It is seen that σ (the unbiased estimator) was 0.08° and the 90% confidence limit for the roughness layer thickness is good for this model. This σ value is on the order of the accuracy of the experimental data, so it was judged that additional complication of the model was statistically unwarranted.

Soda-lime silica glasses leached with hydrochloric acid (37.0%) for different times were modeled using the optical data of the unmodified glass as reference data. A two layer model was adopted to describe the leached glasses, which consisted of a rough surface layer and a void-free graded layer. The graded layer was described by a mixture of the reference glass and SiO₂. This effectively mimicked the leaching of modifiers from the glass surface. Many sub-layers are superimposed in the second layer. The thickness of the rough surface layer (t), surface concentration of SiO₂ (volume fraction of SiO₂ at surface, C_s) and diffusion coefficient×diffusion time (D×t) are chosen as the model parameters for the leached glasses. The values of C_s and D×t are sufficient to describe the modified depth corresponding to the concentration profile. Fig. 4.18 shows the ellipsometric spectra as a function of leaching time for a soda-lime silica glass. It can be seen that larger changes occur in Δ than in Ψ . The schematic diagrams for the two layer model used are shown in



Fig. 4.17 : One layer model of an unmodified glass with a rough surface layer



Fig. 4.18 : Ellipsometric spectra (Δ,Ψ) as a function of leaching time for a commercial soda-lime silica glass

Fig. 4.19 to Fig. 4.21. The use of similar models when a roughness layer (SiO2+air) and a pure SiO2 layer are substituted for the top layer (base glass+air) leads to poor matching with the experimental data. It has been shown previously by Clark et al. (Clark et al. 1979) that leaching of modified aluminosilicate glasses can lead to a discrete layer of Na2Odepleted material near the surface on top with graded composition (i.e. the composition profile does not follow the error function shape because the sodium diffusion coefficient in the glass is concentration dependent). It was found that it was extremely difficult to model this behavior for the aluminosilicate glasses due to the strong correlation between the roughness layer and SiO2- rich layer. Consequently, the simplified model shown in Fig. 4.19 to Fig. 4.21 were used instead. This leads, as is described in the next section, to some problems in the calculated thickness of the graded layer. It is possible that this problem could be eliminated by fitting multiple data sets simultaneously to find the global minimum in sigma. Fixing the thickness and varying the void volume fraction of the top layer in two layer model was also tried. However, this led to poor fits (e.g. $\sigma = 5.8^{\circ}$). This indicates that fixing the composition of the air at 0.5 and varying the thickness of the rough surface layer is appropriate to model the experimental data. Similarly, models in which it was assumed that there was no roughness at the glass surface led to poor fits. The surface roughness increase during leaching is also shown in Fig. 4.22. It is apparent that increase in surface roughness leads to significant change in SE data. 200 sub- layers were used to describe the graded index layer. Fig. 4.23 shows the depth profile of leached soda-lime silica glass based on the modeling results.

Fig. 4.24 to Fig. 4.27 show the SIMS depth profile for unleached and leached sodalime-silica glass. The SiO₂ profile is plotted relative to the right side axes whereas the other elements are plotted relative to the left side axes on an extended scale. It can be seen that the sum of the concentrations at a given depth in the SIMS profiles does not total 100%. This is probably because there is some uncompensated sample charging that causes all of the profiles to fall as the charging increases. In order to compare the Na₂O



Fig. 4.19 : Depth profile of the 48 hours leached soda-lime silicate glass using two-layer model



Fig. 4.20 : Depth profile of the 7 days leached soda-lime silicate glass using two-layer model



 $Dt = 5.0E6 \pm 2.1E5 \text{ Å}$

Fig. 4.21 : Depth profile of the 10 days leached soda-lime silicate glass using two-layer model



Fig. 4.22 : Change of surface roughness during leaching of soda-lime silicate glasses



Fig. 4.23 : Depth profiles (error-function-like) of the SiO₂ volume fraction within the graded layer for soda-lime silicate glass determined from the SE models



Fig. 4.24 : SIMS compositional depth profile of an unleached soda-lime silicate glass



Fig. 4.25 : SIMS compositional depth profile of 48 hours leached soda-lime silicate glass





Fig. 4.26 : SIMS compositional depth profile of 7 days leached soda-lime silicate glass



Fig. 4.27 : SIMS compositional depth profile of 10 days leached soda-lime silicate glass

concentration of each glasses at certain depth, the Na₂O depth profile was normalized. Fig. 4.28 is a plot of normalized depth profile for Na₂O. Through the normalized profile, it can be seen that the area under the curve corresponds to the remaining relative Na₂O concentration within the glass. The depth profiles from the SIMS and SE results are not well matched to each other. The thicknesses which the Na₂O concentration becomes constant are ~5200Å and ~1500Å measured by SE and SIMS, respectively. This may be due to two factors. The model used to fit the experimental SE data includes a rough surface layer. As can be seen in Fig. 4.22, the surface roughness increases as leaching time becomes longer. The roughness layer significantly affects the modeled SE data describing the graded layer. Another reason might be the small refractive index contrast between sublayers within graded layer. Therefore, leached lead-silicate glass which has higher refractive index than soda-lime silica glass was also measured by SE as well as SIMS. This is described in section 4.5.

4.5 Alkali-Lead-Silicate Glass

It is known that the leaching of lead-silicate glasses in acidic solutions results in the formation of a SiO₂ rich layer at the top surface of the glass due to the preferential leaching of Pb (Wood and Blachere 1978). A comparison between compositional depth profiles measured by SE and those measured with SIMS was also done using a lead-silicate glass.

The procedure to determine a reference optical properties of lead-silicate glass was the same as that of the soda-lime silica glass. The dispersion relation for the unleached glass is (λ in nm)

$$n^{2}(\lambda) = 1 + \frac{1.775\lambda^{2}}{\lambda^{2} - 141.2^{2}}$$
(4.3)



Fig. 4.28 : Normalized SIMS depth profile of Na₂O in the soda-lime silicate glasses with different leaching times

Lead-silicate glasses chemically leached with 1N HCl solution for varying amount of time, (ranging from 30 min. to 1 day) were modeled using the optical data of an unleached glass as reference data. The proposed model of the leached lead-silicate glasses is similar to that of soda-lime silica glasses. However, the Sellmeier dispersion equation with one effective oscillator (Eq. 4.1) was used to describe the depth profile of graded layer instead of SiO2, because the refractive index of the remaining material following the leaching process will not necessarily be identical to that of pure SiO2. The volume fraction of void in the top roughness layer, A and λ_o in Eq. 4.1 were fixed to 0.5, 1 and 120, respectively. The two layer model describing the leached glasses consists of a rough surface layer and a void-free graded layer (Fig. 4.29). The parameters utilized to fit this model are the thickness of the rough surface layer, the diffusion coefficient × diffusion time (Dt) and constant B in Eq. 4.1. The surface concentration of the low refractive index surface material (osc) was fixed at 100%. Another model was proposed to fit the ellipsometric data for 1 day leached glass. This model (Fig. 4.30) includes a SiO2 layer on the top surface instead of rough surface layer. The unbiased estimator (σ) of 0.42^o is good for this model compared to the model including just a rough surface layer (3.8°). Comparison between model and experimental curves of the leached glasses for different times (30 min., 1 hr., 5 hr. and 1 day) are shown in Fig. 4.31 to Fig. 4.34. The results of the models for leached lead-silicate glass are summarized in Table 4.1. The numerical values of the model parameters and their 90% confidence limits are given except for the parameters which are fixed in the modeling. It is important to note that for samples leached longer, higher values of surface roughness and diffusion depth were obtained. The diffusion depth listed in Table 4.1 corresponds to the thickness which the amount of oscillator reached 0.3% of the surface concentration. Fig. 4.35 shows the calculated depth profile within the graded layer for leached lead-silicate glasses.











Fig. 4.31 : Experimental and calculated ellipsometric spectra (Δ, Ψ) for the 30 min. leached lead-silicate glass



Fig. 4.32 : Experimental and calculated ellipsometric spectra (Δ , Ψ) for the 1 hr. leached lead-silicate glass



Fig. 4.33 : Experimental and calculated ellipsometric spectra (Δ, Ψ) for the 5 hr. leached lead-silicate glass


Fig. 4.34 : Experimental and calculated ellipsometric spectra (Δ , Ψ) for the 1 day leached lead-silicate glass

ه ()	B	λ ₀ (nm)	ິ	Dt (Å)	Thickness of surface roughness(Å)	Thickness of SiO ₂ layer(Å)	Diffusion depth (Å)
0.11	1.60±0.14	120	1.0	22096± 259	27.1±5.9	1	450±32
0.09	1.12±0.06	120	1.0	33533± 185	39.9±2.7	1	550±38
0.25	1.64±0.04	120	1.0	100747± 4760	84.2±5.7	1	960±66
0.42	1.63±0.27	120	1.0	132035± 8743	1	164±78	1290±124

Table 4.1 : Model parameters for the leached lead-silicate glasses

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Fig. 4.35 : Depth profiles (error function-like) of the oscillator describing the graded layer for lead-silicate glass

Fig. 4.36 presents the SIMS depth profile for Pb. This plot indicates that the SiO₂ rich surface layer grows in thickness with increasing leaching time. The fact that a small amount of Pb and other components (Ba, Rb, Cs) remain in the leached layer leads to a poor fit of the SE data when the optical properties of pure SiO₂ are used to describe the surface material for the 30 min. 1 hr. and 5 hr samples. The SIMS depth profile in Fig. 4.36 also shows the depth at which the Pb concentration becomes constant. The thickness of the leached layer of 1 hr, 5 hr, and 1 day samples measured by SIMS corresponds to 710Å, 1000Å and 1300Å, respectively. Also the diffusion depths measured by SE are 550 \pm 38Å, 960 \pm 66Å and 1290 \pm 124Å, respectively. Furthermore, the constant concentration region can be seen in Fig. 4.36 at the initial depth of 24 hr. leaching sample. This should be the SiO₂ layer on the top surface of the 1- day leached sample. The thickness of this layer corresponds to ~180Å and 164Å measured by SIMS and SE, respectively. It is shown that SE results are in good agreement with the independent results obtained using SIMS.





Chapter 5

CONCLUSIONS AND FUTURE WORK

The studies of the correlation between the ellipsometric data (Δ , Ψ) and many parameters (e.g. surface concentration, modified depth and refractive index contrast) and sensitivity of ellipsometric data were described in chapter 4. This chapter discusses the conclusions and future work.

5.1 Conclusions

The phase change information of ellipsometric data (Δ) makes spectroscopic ellipsometry (SE) sensitive to a small change of layer thickness and refractive index contrast. The power of SE, which is a non-destructive analytical technique, to characterize graded composition layers formed by a leaching process was demonstrated and verified by comparison with another analytical technique, SIMS. That is, SE also allows us to obtain compositional depth profiles of layers with varying refractive index. The sensitivity of the ellipsometric parameters to layer thickness, composition and refractive index contrast for graded index layers was calculated. The sensitivity is a strong function of the layer thickness and refractive index contrast. For example, the SE technique has a sensitivity limit to ~20Å and ~30Å change in diffusion depth for a layer thickness of 140Å with refractive index differences of 0.03 and 0.017, respectively, at 500nm. It was apparent that the larger the relative change in modified depth, surface concentration or refractive index contrasts, the better the sensitivity.

It was shown that the SE results are not good agreement with the results of the SIMS measurement when additional factors (i.e. a roughening of the surface for low index contrast samples) complicate the data interpretation. This is due to the fact that SE is sensitive to the large index contrasts in the specimen. As the refractive index contrast was considerably larger between the roughness layer and the bulk of the glass than within the graded layer, some correlation between the fitting variables leads to inaccuracies in the modeled diffusion profile. However, in the case of higher index contrast materials, the SE results are in good quantitative agreement with the results of the direct technique SIMS. This indicates that the optical model and algorithm could be applied successfully in the ellipsometric investigation of materials with graded index layers. Also, the refractive index contrast (Δn) and the modified depth are key parameters to determine the sensitivity of SE.

5.2 Future Work

Although the positive experimental results presented in this thesis are limited to leadsilicate glasses, the data provided give strong evidence of the potential application of the spectroscopic ellipsometry as a characterization tool to study the graded refractive index transparent materials.

Ion-implantation is widely used for processing semiconductors and dielectric coatings. Depth profile of implanted material can usually be described by a Gaussian function. Therefore, by applying an other optical model consisting of a stack of layers with varying thickness and composition levels described by a half Gaussian function, ionimplantation depth profiles can be evaluated. Also, SE can be applied to depth profiling of the refractive index for an optical waveguide material including graded layers with good resolution.

Another modeling method should be developed to decouple the effect of surface roughness from the actual optical properties of a graded index transparent materials. One of the data analysis methods, σ -minimization (Li 1992) can be applied to analyze the spectra of soda-lime silicate glasses leached for different times. This may be a possible means to decouple the effect of surface roughness from the real ellipsometric data.

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