Simulation of FTIR reflection spectra in non normal incidence

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Abstract. Reflection spectra in non normal incidence of SiO$_2$ films consist of an extra band attributed to the Longitudinal Optical (LO) mode of vibration of the Si – O – Si bridge. In order to simulate spectra taken in non normal incidence we developed analytical expressions describing reflection in non normal incidence of an absorbent film placed on a non absorbent medium. Similar expressions found in the literature are not precise leading to unreliable results for the case of SiO$_2$ films. The optical model is based on the matrix method considering the existence of four Lorentz oscillators same as for the case of the normal incidence. We found that the LO band is anticipated by the optical model without the need of adding extra oscillators for the description of this band. It was also found that the refractive index of the film is depending from the angle of incidence. Increase of the angle of incidence causes a small decrease of the real part of the refractive index in the range 1100 – 1300 cm$^{-1}$ while the imaginary part of the refractive index slightly increases in the same range of wavenumbers.

1. Introduction

SiO$_2$ is a key material for micro and nano-technology. In particular, amorphous silica films ($\alpha$ – SiO$_2$) are used in Metal Oxide Semiconductor (MOS) devices as gate dielectrics and passivation layers, in the core and cladding of optical fibers, as antireflective coatings for solar cells and it is one of the most common components of the multilayer coatings used to produce lenses for optoelectronic devices [1, 2].

There are several methods of growing SiO$_2$ films like the thermal oxidation of Si, Low Pressure Chemical Vapor Deposition (LPCVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD). Depending on the method, the chemistry and the growth conditions, SiO$_2$ films present different macroscopic features like stresses with the substrate, density and dielectric strength [1, 2]. All these features are directly related with the way in which Si and O atoms are arranged in the films. Infrared (IR) spectroscopy has been extensively used due to its known sensitivity to detect even small changes of the Si – O bond and the surrounding chemical environment [3 – 11]. In addition the method has been used to study the first steps of oxidation and the properties of the Si / SiO$_2$ interface [12 – 15].

The need to understand the properties of SiO$_2$ films of ever decreasing thickness increases as the gate dimensions of the MOS devices continue downward. However, changes in the thickness may result differences in the IR spectra like the position and the width of the absorption bands, which do not necessary represent differences on the material. The safer way to extract useful information about the material properties is to study the optical constants of the films namely the real n and the
imaginary part k of the refractive index n. In this work we use dispersion analysis to fit calculated IR reflection spectra to the corresponding experimental taken on LPCVD SiO₂ films in non normal incidence. For the simulation of the reflection in non normal incidence we developed an optical model from which analytical expressions of the reflectivity in non normal incidence are extracted. The calculation of the complex refractive index n was performed after the application of the optical model to the dispersion formulas [10, 11].

2. Experiment
Depositions were carried out in a Tempress model Omega Junior hot wall reactor on 4''<100> Si wafers 5 – 10 Ohm cm from SiH₄+O₂ mixtures. The temperature of deposition was 425 °C and the pressure during deposition was 250 mTorr. The SiH₄ flow ratio was 50 sccm (standard cubic centimeters per minute) and the O₂ flow ratio was 150 sccm. 

Before deposition all wafers were cleaned following the RCA procedure [16], dried in nitrogen and inserted directly in the reactor. After deposition the SiO₂ film was removed from the back (rough) side of the wafer in a reactive ion etcher using SF₆ chemistry.

FTIR reflection spectra were recorded with a Magna single beam IR 550 Nicolet spectrometer connected to a personal computer running the OMNIC software version 1.2a. All spectra were each the average of 512 passes in order to obtain the best possible signal to noise ratio. Before recording a spectrum the background was taken using a piece of silicon cut from the same as for the SiO₂ film wafer. This was made to eliminate absorption caused from the interstitial oxygen of the substrate at 1109 cm⁻¹ [17] and from the Si – Si vibration at 611 cm⁻¹ [18] and also fix the base line at 100%.

3. Results and Discussion
3.1. Optical model
Our analysis uses the classical dispersion theory of solids [19] modified so as to account for the amorphous nature of the SiO₂ films. Following this approach the real (ε₁) and the imaginary (ε₂) parts of the dielectric constant vary with frequency ν as

\[ ε_1 = n_1^2 - k_1^2 = ε_\infty + \sum_i \frac{4\sqrt{\pi}}{1.201\delta_i} \rho_i v_0^i \int \frac{\exp \left[ -\left( \frac{v_j - v_0}{1.201\delta_i} \right)^2 \right]}{(v_j^2 - v^2)^2 + \gamma_i v_j^2} dv_j \]

\[ ε_2 = 2n_1 k_1 = \sum_i \frac{4\sqrt{\pi}}{1.201\delta_i} \rho_i v_0^2 \int \frac{\exp \left[ -\left( \frac{v_j - v_0}{1.201\delta_i} \right)^2 \gamma_i v_j v \right]}{(v_j^2 - v^2)^2 + \gamma_i v_j^2} dv_j \]

where ν₀ is the central frequency of the i-th oscillator, γᵢ is damping and ρᵢν₀² is the oscillator strength. To account for the amorphous nature of the films under study, the central frequency, ν₀ was considered to distribute following a Gaussian with FWHM δᵢ.

The refractive index n₁ of an absorbent medium is complex (n₁ = n₁ + ik₁) where n₁ is the real part of the refractive index and k₁ is the imaginary part also known as the extinction coefficient. Inserting a complex refractive index to Snells law we find that the sine of the angle of diffraction \( \theta_i \) equals to [20, 21]

\[ \sin \theta_i = \frac{n_0 n_1}{n_1^2 + k_1^2} \sin \theta_0 + i \frac{n_0 k_1}{n_1^2 + k_1^2} \sin \theta_0 \]
where \(n_0\) is the refractive index of the air and \(\theta_0\) is the angle of incidence. In order to calculate the reflectivity using the Fresnel equations we need to find an expression of the complex cosine \((\cos \tilde{\theta}_1)\). Starting from the fact that \((\sin \tilde{\theta}_1)^2 + (\cos \tilde{\theta}_1)^2 = 1\) we find that

\[
\cos \tilde{\theta}_1 = \left( A_1 + \sqrt{A_1^2 + B_1^2} \right)^{1/2} - i \left( -A_1 + \sqrt{A_1^2 + B_1^2} \right)^{1/2}
\]

where \(A_1 = 1 - a^2 + b^2, B_1 = -2ab\) and \(a, b\) are the real and imaginary parts of \(\sin \tilde{\theta}_1\) given by equation (2).

### 3.2. Application of the optical model

![Figure 1.](image1.png) **Figure 1.** Reflection spectrum (broken lines) and the simulation (continuous lines) of a SiO\(_2\) film with thickness equal to 95.0 nm deposited from SiH\(_4+\)O\(_2\) at 425 \(^\circ\)C. The angle of incidence is between 08 \(^\circ\) and 50 \(^\circ\).

In figure 1 we see the reflection spectrum (broken lines) and the simulation (continuous lines) of a SiO\(_2\) film grown from SiH\(_4+\)O\(_2\) at 425 \(^\circ\)C. The absorption band located at about 1240 cm\(^{-1}\) corresponds to the LO mode of vibration of the Si – O – Si bridge and it appears when the angle of incidence is greater than 08 \(^\circ\). From figure 1 we see that the simulation spectra are in good agreement with the corresponding experimental ones within the studied range of angles of incidence.

![Figure 2.](image2.png) **Figure 2.** Calculated refractive index of the film shown in figure 1. a: Real part (\(n_1\)) b: Extinction coefficient (\(k_1\)).
Figure 2(a) shows the calculated real part of the refractive index ($n_1$) and figure 2(b) shows the calculated extinction coefficient ($k_1$). The real part of the refractive index presents a local maximum at about 1000 cm$^{-1}$. The minimum value of this local maximum appears for the smaller angle of incidence. As the angle of incidence increases $n_1$ becomes higher at this region. In the range between 1100 and 1300 cm$^{-1}$ $n_1$ presents two local minima. In this range the refractive index appear to have the strongest dependence with the angle of incidence because of the activation of the LO modes. As the angle of incidence becomes higher, within the studied range of angles, $n_1$ is getting lower. The extinction coefficient $k_1$ shown in figure 2(b) presents one local maximum at about 1075 cm$^{-1}$ and a second one at about 1225 cm$^{-1}$. Increase of the angle of incidence causes an increase of $k_1$. Similar dependence of the real and imaginary part of the refractive index with the angle of incidence was also found for MgO films [22].

4. Conclusions
The real and imaginary part of the refractive index of SiO$_2$ films were calculated in the range of the asymmetrical stretching motion of the Si – O – Si bridge from the simulation of reflectance spectra taken between 08$^\circ$ and 50$^\circ$. It was found that the optical constants of the studied films present a small dependence with the angle of incidence due to the activation of the LO modes of vibration. Increase of the angle of incidence causes a small decrease of the real part of the refractive index in the range 1100 – 1300 cm$^{-1}$ where the LO modes appear, while the imaginary part of the refractive index slightly increases in the same range of wavenumbers.

5. References
[1] Katz L E VLSI Technology 2nd Edition 1988, Sze S M Editor (Mc Graw – Hill International Editions)
[2] Fair R B ULSI Technology 1996, Chang C Y and Sze S M Editors (Mc Graw – Hill International Editions)
[3] Pliskin W A and Lehman H S 1965, J. Electrochem. Soc. 112(10) 1013
[4] Boyd I W and Wilson J I B 1982 J. Appl. Phys. 53(6) 4166
[5] Pai P G, Chao S S, Takagi Y and Lucovsky G 1986 J. Vac. Sci. Technol. A 4(3) 689
[6] Lucovsky G, Fitch J T, Tsu D V and Kim S S 1989 J. Vac. Sci. Technol. A 7(3) 1136
[7] Calleja W, Falcony C, Torres A, Aceves M and Osorio R 1995 Thin Solid Films 270 114
[8] Falcony C, Calleja W, Aceves M, Siqueiros J M, Machorro R, Cotta – Araiza L, Soto G and Farias M H 1997 J. Electrochem. Soc. 144(1) 379 (1997)
[9] Tsu D V 2000 J. Vac. Sci. Technol. B 18(3) 1796
[10] Davazoglou D and Vamvakas V Em 2003 J. Electrochem. Soc. 150(5) F90
[11] Vamvakas V Em and Davazoglou D 2004 J. Electrochem. Soc. 151(5) F93
[12] Weldon M K, Queeney K T, Chabal Y J, Stefanov B B and K. Raghavachari K 1999 J. Vac. Sci. Technol. B 17(4) 1795
[13] Queeney K T, Weldon M K, Chang J P, Chabal Y J, Gurevich A B, Sapjeta J and Opila R L 2000 J. Appl. Phys. 87(3) 1322
[14] Chabal Y J, Raghavachari K, Zhang X and Garfunkel E 2002 Phys. Rev. B 66 161315(R)
[15] Queeney K T, Herbots N, Shaw J M, Athuri V and Chabal Y J 2004 Appl. Phys. Lett. 84(4) 493
[16] Kern W and Puotinen D A 1970 RCA Rev. 31 187
[17] Herman I P Optical diagnostics for thin film processing 1996 (Academic Press Inc.)
[18] Philipp H R Properties of Silicon 1987 INSPEC The Institution of Electrical Engineers, EMIS Dataview RN=16133 1019
[19] Seitz F Modern Theory of Solids 1940 (New York: McGraw-Hill)
[20] Born M and Wolf E Principles of Optics 1959 (Pergammon Press)
[21] Heavens O S Optical Properties of Thin Solid Films 1991 (New York: Dover Publications Inc.)
[22] Roessler D M 1965 Brit. J. Appl. Phys. 16 1359