Characterisation of Sol-gel Thin Films by Spectroscopic Ellipsometry

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Abstract: The refractive index and porosity of silicate based sol-gel thin films prepared from tetraethoxysilane and methyltriethoxysilane were characterised using spectroscopic ellipsometry. With the hypothesis of considering the thin films as one mixture of matrix materials with pores for ellipsometric data analysis, linear calculation and effective medium approximation (EMA) models were employed in ellipsometric data analysis. The analysis ambiguity with EMA model was effectively reduced by incorporating the intensity of reflectance of thin films in the data analysis. Results show that data analysis using EMA model with Cauchy equation can significantly improve the accuracy in the determination of the film porosity and refractive index. This approach greatly enhances the applicability of ellipsometry in analysis of porous thin films.

1. Introduction
Sol-gel thin films have been finding more and more applications in various areas such as optics, microelectronics, membranes and sensors. The sol-gel process, which is primarily based on the hydrolysis and condensation reaction of organometallic compounds in alcoholic solutions, offers many advantages for the fabrication of silicate-based porous thin films including ease of compositional modifications, customizable microstructures at the chemical solution stage [1].

To optimize the so-gel thin film process to meet the increasingly stringent requirements in performance and reliability, it is critical to explore advanced analytical tools and techniques to characterise and monitor the thin film structures and properties. Spectroscopic ellipsometry (SE), a non-invasive optical technique, can provide significant insight into thin film structures and properties such as refractive index, percentage of porosity, transparency and dielectric properties. Moreover, SE can be employed for the real-time and in-situ characterization and non-perturbing process monitoring. However, ellipsometry is an indirect technique that relies on fitting of the data to a model and extract the unknown parameters such as film refractive index and thickness. For porous thin films, the number of unknown parameters increases due to the complexity of film structures, the chance of fit parameter correlation increases, which may cause the ambiguity in data analysis. The objective of this work is to apply and compare linear calculation model and effective medium approximation (EMA) model in ellipsometric data analysis, to explore the methodology to improve accuracy and reduce the ambiguity of the analysis in the determination of the film porosity and optical properties of porous thin films.

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2. Methodology

In the analysis with spectroscopic ellipsometry, firstly, it is measured the changes in the polarization state of an incidence light beam when it is reflected off a sample. Then it is followed by extracting physical information about the sample such as film refractive index and thickness from the measure polarization state by fitting the spectra to a physical model. The model is built up based on the available information and knowledge of the layer structure and components of the sample to predict the optical response of the sample to the incident polarized light. For porous thin films, multiple unknowns including refractive index, film thickness, porosity and other fit parameters are to be determined. Normally, models for porous thin films can be reasonably defined to treat the porous film as a mixture of matrix material and pore phases. However, the ambiguity in analysis may arise as the agreement between the modeled and measured optical response may occur because there are more unknowns being varied to force the fit. In this case, it could be helpful by adding more independent experimental data to the fitting to reduce this ambiguity.

For sol-gel porous films under study, the optical model used in the fitting of ellipsometric data consists of 2 layers on substrate. These two layers are native SiO2 layer on Si substrate and porous film layer on top. The refractive index of the SiO2 can directly quoted from the database. Some often-used models in ellipsometric data analysis for porous thin film optical constants are:

2.1. Linear calculation with known material optical properties.

Porosity can be calculated from refractive index using a first-order rule of mixtures, according to the following equation [2]

\[
(1 - X) n_{TD} + X n_{air} = n_{meas}
\]

where \(X\) is porosity, \(n_{TD}\) is the refractive index of the film material (that is SiO2 for silicate sol-gel thin films) at theoretical density and \(n_{meas}\) is the measured film refractive index. The refractive index of air is assumed to be one, \(n_{air}=1\). \(n_{TD}\) was quoted from the database provided by the ellipsometer manufacturer J.A. Woollam for our investigation. The method can give a good estimation of the film porosity but this linear interpolation is not highly accurate.

2.2. Effective medium approximation (EMA)

EMA is the most frequently used approach to model the optical properties of thin films with two or more than two constituents. Three EMA types including linear, Maxwell-Garnett and Bruggemann are most often used. The Maxwell-Garnett EMA[3] is used for our investigations as it is developed for highly diluted spherical inclusions in a host matrix[4]. For porous thin films, it is derived as

\[
\frac{\varepsilon - \varepsilon_{pore}}{\varepsilon + 2\varepsilon_{pore}} = f_{pore} \frac{\varepsilon_{pore} - \varepsilon_{matrix}}{\varepsilon_{pore} + 2\varepsilon_{matrix}}
\]

where \(\varepsilon\) is the effective complex dielectric function of a porous film which consists of matrix material and pores. \(\varepsilon_{matrix}\) and \(\varepsilon_{pore}\) are the complex dielectric functions, and \(f_{pore}\) is the volume fraction (range from zero to one) of pores. The film porosity \(X\) can be calculated by

\[
X(\%) = f_{pore} \times 100
\]

Optical constant and dielectric functions are just different ways of defining the same information. It is possible to convert the complex dielectric function of a material to its refractive index \(n\) by using the equation below,

\[
n = \sqrt{\frac{\varepsilon_{i} + \sqrt{\varepsilon_{i}^{2} + \varepsilon_{r}^{2}}}{2}}
\]
$\varepsilon_1$ is the volume polarization term for induced dipoles and $\varepsilon_2$ is the volume absorption related to carrier generation.

2.2.1. **EMA model with known material optical properties.** To simplify the data analysis, the optical constants of SiO$_2$ in database are used for the matrix materials in sol-gel thin films under investigation, the layer structure built up for ellipsometric data analysis is shown in Figure 1(a). The volume fractions of the pores (or porosity) and thickness of the sol-gel film layer were taken as fitting parameters.

2.2.2. **EMA model with Cauchy equation.** Cauchy equation describes the dispersion of film refractive index as a slowly varying function of wavelength, $\lambda$, with an exponential absorption tail [5].

$$ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^2} $$  \hspace{1cm} (5)

The three parameters in dispersion equation (5) are $A$, $B$, and $C$. In this study, $C$ is ignored for this study as it is close to 0 for most of the transparent films.

The layer structure built up for ellipsometric data analysis is shown in Figure 1(b). The volume fractions of the pores and thickness of the film layer and $A$ and $B$ in Cauchy equation were taken as fitting parameters. Cauchy equation used for the film optical refractive index can reflect the actual film properties which is highly depending on the film deposition process, but unfortunately will increase the number of the fit parameters and lead to the ambiguity of the results. One approach in our investigation is to add in the intensity reflectance data and fit the data with the ellipsometric data simultaneously in order to reduce the ambiguity in analysis.

3. **Experiment**

The sol-gel solution used for coating was prepared by the hydrolysis and condensation reactions of the precursors of solvent ethanol C$_2$H$_5$OH diluted tetraethoxysilane (TEOS) with a TEOS-to-H$_2$O molar ratio of 1:3 in the presence of hydrochloric acid catalyst. Methyltriethoxysilane (MTES) solution was prepared in the same way but using acetate acid as the catalyst. After pre-hydrolysis TEOS and MTES solutions were separately stirred for at least 1 hour, and mixed at molar ratios of 1:0, 1:0.5 and 1:1 and then further stirred at room temperature to get the required sol. Dip coating method was employed for thin film preparation on Si<100> substrate with a 100 nm thick native SiO$_2$ layer. Heat treatment at 350°C for 15 minutes was carried out to dry up the films and complete the condensation.

Sol-gel thin films were characterized for optical constant, porosity and thickness using a J.A. Woollam Co. VASE variable-angle spectroscopic ellipsometer. The ellipsometric spectra recorded ranged from 250 nm to 1100 nm with incident angles of 70° and 75°. Reflectance spectrum at an incident angle of 75° was collected.

4. **Results and discussions**

Determined by the ellipsometric analysis, the thickness of three thin films under study are 95 nm, 191 nm and 219 nm with a TEOS-to-MTES molar ratios of 1:0, 1:0.5 and 1:1 respectively.
The linear calculation results in Figure 2 show that film porosity increases with the molar ratio of TEOS to MTES. All these three films have a lower refractive index than SiO₂. It implies that they are less dense than SiO₂. The porosity calculated varies with wavelength, which is slightly confusing. Therefore, the linear calculation can only give an estimation of the film porosity. The porosity and refractive index at the wavelength of 630 nm are normally quoted as an indication of the film properties.

Figure 2. (a) Refractive index vs. wavelength from ellipsometric analysis, refractive index of SiO₂ is included in the graph as a reference; (b) porosity vs. wavelength from the linear calculation.

Figure 3 demonstrates that there is some difference in refractive index between the matrix of sol-gel film under investigation and SiO₂ from database. This deviation is clearly linked to the coating method and process conditions which will affect the film composition and structure, therefore, the film optical properties. Hence, when the Cauchy equation was used to describe the matrix refractive index, the refractive index and porosity obtained are more representative and accurate.

Figure 3. Refractive index of the matrix of sol-gel film (TEOS:MTES 1:1) applying EMA model with Cauchy equation. Refractive index of SiO₂ from database is included for reference.

Figure 4 plots the film porosity and refractive index results from the linear calculation (the refractive index and porosity data from the values at 630 nm), EMA model using SiO₂ for the matrix, and EMA model using Cauchy model for the matrix, respectively. A higher film refractive index and lower porosity were obtained from the EMA model with Cauchy equation comparing the results from the EMA model using SiO₂ for the matrix.

The approach in our investigation by incorporating the intensity reflectance data into the data processing by EMA model with Cauchy equation can reduce the uncertainty of the ellipsometry analysis effectively and improve the analysis accuracy. Figure 5 shows a good fitting between the experiment data and fitted data from EMA model with Cauchy equation by analyzing ellipsometric and the intensity reflectance data simultaneously in data processing.
2.0
4.0
6.0
8.0
10.0
12.0
Porosity, %

TEOS T/MTES1:0.5 T/MTES1:1
Samples

1.41
1.42
1.43
1.44
1.45
EMA_SiO2

EMA_Cauchy

Figure 4. Results of (a) porosity and (b) refractive index at 630 nm obtained from linear calculation (-- --), EMA model with SiO2 (---•--), EMA model with Cauchy equation (---∆--).

5. Conclusions
The porosity and refractive index of the sol-gel thin films were determined by spectroscopic ellipsometry using a few models in its data analysis, including linear calculation, EMA model using SiO2 for matrix material, and EMA model with Cauchy equation for matrix material. EMA model with Cauchy equation which produces accurate results is recommended for the ellipsometry analysis for porous films. The thickness of sol-gel thin films determined by this model is from 95 nm, 191 nm and 219 nm with a porosity of 3.5%, 5.5% and 7.6% for films with a TEOS-to-MTES ratio of 1:0, 1:0.5 and 1:1. It is found the ambiguity in analysis, which caused by the increased number of fit parameters, with EMA model using Cauchy equation for matrix material was effectively reduced by incorporating the intensity of reflectance of thin films in the analysis. This methodology greatly enhances the applicability of ellipsometry for porous thin film analysis.

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