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Multilayer model for determining the thickness and refractive index of sol–gel coatings via laser ellipsometry

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ABSTRACT

The optical properties of sol–gel silica coatings on silicon wafers are investigated. During the sol–gel process the samples are subjected to heat treatment with a range of different temperatures on which the resultant film thicknesses and refractive indices are dependent. The morphology of the coating is also dependent on the heat treatment, particularly at higher temperatures where precipitates can form and delamination can occur. We used a model of the coating that not only accounts for the sol–gel film but includes a thin crust on the surface and a layer of oxide in between the coating and substrate. The multilayer model is then used to determine the refractive index of the film by least-squares fitting the measured change in polarization versus the incident angle.

1. Introduction

The advent of sol–gel technology occurred in the 19th century [1–3], although it had been almost unheard of until recent decades where it has seen a surge in interest, i.e., in industry and scientific research. Sol–gel silica films are used for many technical applications, such as optical [4] and electrical applications [5], for corrosion protection [6] and also for manufacturing of micro-structured optical molds, as demonstrated by [7,8]. The sol–gel coating process [9,10] is characterized by the conversion of a liquid sol film, deposited by means of dip or spin coating, into a solid gel film via evaporation of the organic solvent of the sol film. The gel point is achieved if the elastic shear modulus of the sol exceeds the viscosity. For Newtonian liquids, the shear modulus is 0. The sol–gel transition is due to 3-dimensional cross-linking of the metal organic polymers in the sol. After the transition, heat treatment at temperatures up to 800 °C, in ambient air, is carried out in order to convert the gel into a glass-like or ceramic material. During the heat treatment, pyrolysis of organic residues in the gel and sintering processes occur. Therefore, the heat treatment parameters have significant impact on the chemical and mechanical film properties such as the density [11].

Various methods have been used to characterize the thickness and the refractive index of a sol–gel layer. Knowing one parameter, white light reflectometry [12] can be used to find either the thickness or the refractive index. In principle, we can infer the refractive index based on the thickness measurements. However, this assumes the refractive index is a real number, where, in reality, it can be complex. The imaginary component is also called the absorption coefficient, i.e., it determines how optically absorbing the medium is. The presence of amorphous carbon precipitates detected via Raman spectroscopy suggests that the coating can indeed be absorbing. We also expect a thin layer of oxide on the silicon wafer.

Both, spectroscopic ellipsometry [13–15] and laser ellipsometry [16], have been used to characterize sol–gel coatings and to accommodate all the factors mentioned above, via a multilayer model that allows for complex refractive indices. However, in this paper, we discuss the characterization of the optical properties of common silica-based sol–gel coatings set on silicon wafers, each undergoing different heat treatment temperatures, using different measurement methods to verify a particular multilayer model with a crust. Therefore, a description of the multilayer model for fitting the ellipsometric measurements is given first. Second, the experimental methods are presented together with the results in a single section to maintain a contiguous structure for the ellipsometry, refractive index and thickness measurement methodology. The sol–gel coating thickness measurements obtained via ellipsometry are validated against those determined via calotte grinding. The experimental determination of thickness and refractive index using ellipsometry is given. The Abbe refractometer is used to measure the refractive index at the surface of the coating. White light spectroscopic reflectometry is used to further verify the refractive indexes obtained via ellipsometry, whereby they are used as inputs to determine if the measured thicknesses are consistent with those obtained via other means. Finally, the findings are evaluated and discussed.

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2. Multilayer model

The fundamental equation of ellipsometry [17] relates the change in polarization ρ between the incident and reflected beams which is expressed as

$$\rho = \frac{R_p}{R_s} = \tan(\Psi) e^{i\Delta}, \tag{1}$$

where Δ is the phase difference between E_p and E_s, $\tan(\Psi) = E_p/E_s$ is the amplitude ratio between the two components of the reflected field and R_p/R_s is the complex ratio between the corresponding reflection coefficients. Ellipsometric measurements delivers Ψ and Δ, leaving R_p and R_s as the unknowns in Eq. (1).

Although the silicon wafer is coated with a single sol–gel coating, we account for more than a single layer on the substrate. Firstly, silicon wafers usually have a thin (~2 nm) SiO_2 layer [18]. Second, measurements with an Abbe refractometer revealed that the surface of sol–gel coatings have very high refractive indexes. The existence of a crust has been reported in other types of sol–gel films, for instance, those based on indium tin oxide [19,20] and zirconium dioxide [15]. Thus, we included a crust and a SiO_2 layer in our model as depicted in Fig. 1.

The layer which models a surface roughness of the silicon substrate is not included because it is extremely thin ($\approx$2 nm measured by AFM; see [21]). The thickness of the sol–gel coating layer, determined via calotte grinding measurements (see Table 1), varies over a much wider area than the ellipsometer laser beam profile; therefore, the sol–gel surface undulations is not included in the model.

To account for the reflections due to multiple interfaces in our model, we adapt the recursive calculations for multilayer reflections presented by Fujiwara [22]; the resultant parallel and perpendicular reflection coefficients are:

$$R_{01234,p,s} = \frac{R_{01,p,s} + R_{1234,p,s} e^{-i2\beta_1}}{1 + R_{01,p,s} R_{1234,p,s} e^{-i2\beta_1}}, \tag{2}$$

where

$$R_{1234,p,s} = \frac{R_{12,p,s} + R_{234,p,s} e^{-i2\beta_2}}{1 + R_{12,p,s} R_{234,p,s} e^{-i2\beta_2}}, \tag{3}$$

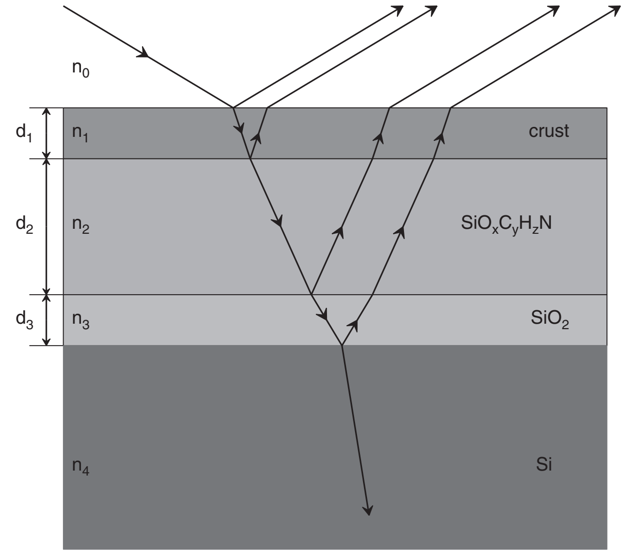

Fig. 1. The model for the sol–gel coating comprises a thin hard crust, the main body of the sol–gel film, a thin SiO_2 layer and the Si substrate.

Table 1
Temperature of heat treatment and the film thickness from calotte grinding measurements.

T (°C)	d (nm)
300	1030 ± 40
400	860 ± 55
500	680 ± 47
600	560 ± 61
700	480 ± 24
800	470 ± 32

$$R_{234,p,s} = \frac{R_{23,p,s} + R_{34,p,s} e^{-i2\beta_3}}{1 + R_{23,p,s} R_{34,p,s} e^{-i2\beta_3}}, \tag{4}$$

where $\beta_j = \frac{2\pi d_j}{\lambda} n_j \cos\theta_j$, and θ_j is the beam angle in medium j with thickness d_j, and $R_{jk,p} = \frac{n_k \cos\theta_j - n_j \cos\theta_k}{n_k \cos\theta_j + n_j \cos\theta_k}$ and $R_{jk,s} = \frac{n_j \cos\theta_j - n_k \cos\theta_k}{n_j \cos\theta_j + n_k \cos\theta_k}$. The angle of the beam θ_j in a given layer is determined by Snell's law.

The unknowns in the $R_{01234,p}$ and $R_{01234,s}$ equations are the refractive indices n_1 for the crust and n_2 for the main sol–gel layer and their respective thicknesses d_1 and d_2. The range for unknown n_1, however, can be narrowed down using the Abbe refractometer [23].

3. Experiments

3.1. Coating process

Sol–gel silica hybrid coatings can be produced from either acid or base-catalyzed sols [11], and are applied using either spin or dip coating. For this study, we use two commonly-used sol–gel precursors, i.e., tetraethyllorthosilicate (TEOS, $Si(OC_2H_5)_4$) and methyltriethoxysilane (MTES, $Si(CH_3)(OC_2H_5)_3$, Sigma-Aldrich) mixed with ethanol (C_2H_5OH, Carl Roth) and water (H_2O) [24], catalyzed with sodium hydroxide (NaOH, Carl Roth). Six samples were prepared by spin-coating the base-catalyzed sol onto polished Si wafers (from Siegert Consulting, Germany) and heat treated at 300 °C for 30 min in a Nabertherm oven (model L 9/11 with temperature controller P 320). Five of the samples were further heat treated at temperatures ranging from 400 °C to 800 °C for 30 min. A photograph of the samples (Fig. 2) shows the change of the optical properties, i.e. colors, due to different refractive indices and thicknesses of the layers. The heat treatment of the silica films was carried out in ambient air (approx. 80 vol.% N_2). Due to the low maximum heat treatment temperature of 800 °C there is no significant dissociation of molecular into atomic nitrogen which could chemically interact with the films. Therefore,

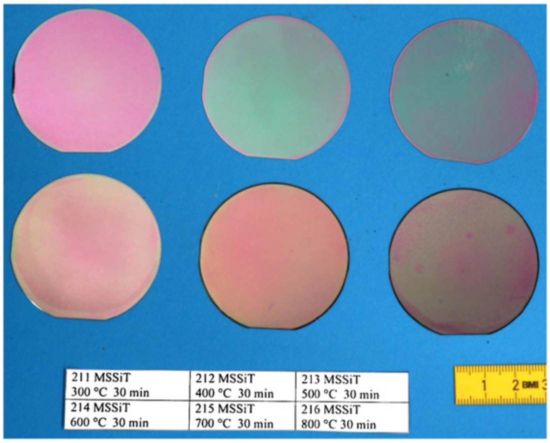

Fig. 2. Coated silicon wafers after heat treatment used for the experiments. The layer thickness decreases from left to right and top–down.