

Ex situ ellipsometric investigation of nanocolumns inclination angle of obliquely evaporated silicon thin films

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We propose an application of spectroscopic ellipsometry pertinent to the characterization of nanostructure inclination of oblique thin films. This technique is employed *ex situ* in the measurement of silicon thin films fabricated at oblique incidence and modeled as aggregate microstructures formed from amorphous silicon, silicon oxide, and void in the effective medium model. The technique may also be utilized *in situ* as a powerful probe for the characterization of oblique thin films during their fabrication and processing. © 2005 American Institute of Physics. [DOI: 10.1063/1.2084329]

In the last ten years the use of spectroscopic ellipsometry (SE) has expanded from the research laboratory to industrial applications due to its numerous advantages, including flexibility to measure most material types, reproducibility, and nondestructiveness. SE applications evolved as well from the well-known techniques of measuring optical constants,¹ and thicknesses,² toward more sophisticated characterization of electronic structure,³ evolution of bonding during nucleation and growth,⁴ doping concentration,⁵ and interface roughness,⁶ by normal or real-time spectroscopic ellipsometry.⁷

In this letter we report the application of spectroscopic ellipsometry for column angle determination of nanostructured oblique thin films (OTFs). Using *ex situ* SE we obtained optical spectra of silicon OTFs, modeled as a biaxial effective medium approximation of amorphous silicon, silicon oxide, and void in the effective medium approximation.⁸

This technique may be used for *in situ* or *ex situ* characterization of OTFs with immediate application in the technologies employing oblique incidence deposition, among which are high density magnetic recording,⁹ growth of biological tissue,¹⁰ optical filters,¹¹ solar cells,¹² as well as characterization of the large number of materials fabricated as OTFs, such as metals, oxides, fluorides, carbides, sulfides, nitrides, etc.

OTFs are fabricated by tilting the substrate with respect to the direction of the incoming vapor, Fig. 1(a)–1(c). These films possess a specific nanostructure composed of columns tilted toward the incoming atomic or molecular flux. The column inclination angle depends on the deposition conditions—a relationship which has been clearly documented in the literature,¹³—and on substrate and deposited material type due to material dependent nucleation and growth effects.

The formation of oblique columns is believed to occur due to geometric shadowing of the initial nuclei (and subsequently of the forming columns), together with limited adatom mobility,¹³ as shown schematically in Fig. 1(d). Both vapor incidence angle or substrate tilt, α , and column inclination angle, θ , are measured from the substrate normal, and are defined in Fig. 1(d). The plane containing both the substrate normal and the vapor incidence vector is referred to as the deposition plane. Fig. 1(d) is a schematic cross-section in the deposition plane.

Employing electron-beam evaporation, silicon thin films were deposited in an ultrahigh vacuum system, described elsewhere.¹⁴ The depositions were performed at room temperature (30 °C) and at base pressures of 10^{-9} Torr, with a deposition rate of 0.5 nm/s, as measured by a quartz crystal deposition rate monitor. Si(100) polished substrates were cleaned in an ultrasonic bath of isopropanol for 10–20 minutes, followed by a rinse in deionized water, and then dried with pressurized dry nitrogen gas. Silicon wafers used throughout this work had an overlayer of oxide measured by SE to be approximately 3 nm. The films were deposited on the wafers with the oxide layer intact.

The inclination of nanocolumns was determined by ellipsometric analysis and scanning electron microscopy (SEM). Ellipsometric spectra were taken with a J. A. Woolam M-2000VI, a rotating compensator ellipsometer covering a wavelength range of 370 to 1670 nm (0.74–3.35 eV). The software used for data acquisition and fitting was

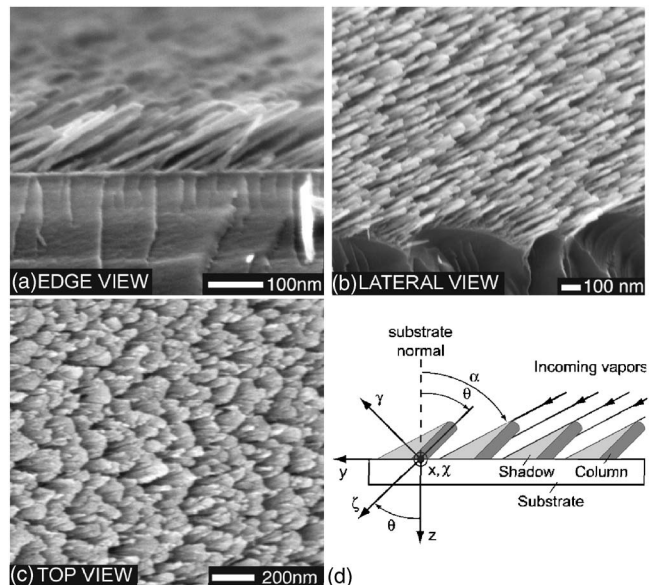


FIG. 1. (a) SEM images of silicon OTF showing edge view, (b) lateral view, (c) top view of films deposited at 85° incidence; (d) Schematics of oblique film microstructure showing the shadowing and conservation of parallel momentum mechanisms together with the propagation axes frame (xyz) versus material axes frame ($x'z'$). Here it was assumed x' is along x , otherwise an additional rotation is needed. xz is the incidence plane.

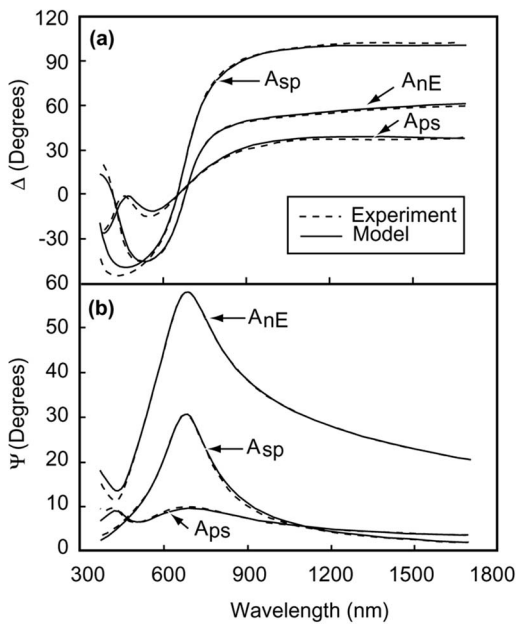


FIG. 2. Analysis of oblique films: (a) and (b) ellipsometric spectra of silicon films on Si(100) substrate deposited at an angle of incidence of 83° .

WVASE32, provided with this instrument. The relative composition of the film constituents, its thickness, column angle θ , angle between deposition and incidence plane $90 \pm \varphi$, depolarization factors L_x , and L_y , were designated as fit parameters.

Silicon oblique films were deposited at substrate tilt angles of 50° , 70° , 75° , 80° , 83° , 85° and 87° . Images showing edge, lateral and top views of silicon OTFs deposited at 85° are given in Fig. 1.

The characteristics of obliquely deposited films are strongly dependent on incident angle and process parameters. The morphology of the films depends on several competing mechanisms, among which the most important are shadowing and conservation of parallel momentum.¹³ Shadowing leads to the column separation and is strongly enhanced by incidence angle. When the vapor is incident at an angle from the normal, previously formed nuclei and columns prevent the ballistic vapor from reaching the space directly behind them, as seen in Fig. 1(d). The conservation of parallel momentum is responsible for the larger separation between columns when added to the effect of shadowing. Hence, OTFs are morphologically composed of inclined columns separated from each other, with the degree of separation dependent on the incidence angle. The larger the separation, the higher the content of oxide layer that has to be taken into account in optical modeling of the system for angles up to 75° . For small incidence angles, α , the columns grow tightly together, the oxidation being active only at the top surface layer unlike the case of high incidence angles, where the large distance between columns allows oxidation throughout the entire thickness of the film.

Figure 2 shows typical measured ellipsometry data from a silicon OTF deposited at 83° tilt angle. The resulting fits follow very close to the data. Figure 1(d) indicates the relation between the ellipsometer coordinates and that of the film. The natural film coordinates are: along column direction, ζ , perpendicular to column direction and in the deposition plane, γ , and normal to the deposition plane, χ . Because two of the optical axes are inclined with respect to the

substrate, generalized (anisotropic) ellipsometry is needed to determine the film coordinates and optical constants. By using the generalized ellipsometry technique, three sets of data are taken $A_nE: \rho \equiv \tilde{R}_{pp}/\tilde{R}_{ss} = \tan \Psi e^{i\Delta}$, $A_{ps}: \rho \equiv \tilde{R}_{ps}/\tilde{R}_{pp} = \tan \Psi_{ps} e^{i\Delta_{ps}}$, $A_{sp}: \rho_{sp} \equiv \tilde{R}_{sp}/\tilde{R}_{pp} = \tan \Psi_{sp} e^{i\Delta_{sp}}$, where the subscript “ps” and “sp” denotes p -wave converted to s -wave, and s -wave converted to p -wave, respectively, whereas “pp” represents p -wave reflected as p -wave. In addition to normal ellipsometry, the last two equations describe the conversion of s - to p -polarization, and vice-versa.¹⁵

Euler angles are used to transform the propagation coordinates into the material coordinates.¹⁶ To align x -axis with χ , a φ rotation of x - y plane about z -axis is required. A consequent tilt of z -axis towards the new y -axis by θ aligns the resulting z -axis with ζ (i.e. with column direction). To ensure the validity of our results spectra were collected with the sample at several azimuthal positions with respect to the plane of incidence. These spectra were distinct from each other. An excellent fit was obtained each time however by only adjusting φ to account for the rotation of film coordinates.

The spectra were modeled in the biaxial effective medium approximation, the oblique films consisting of amorphous silicon, silicon dioxide and void in the Bruggeman formalism.⁸ Optical constants of amorphous silicon were modeled as a single Tauc-Lorenz oscillator,¹⁷ the parameters of which were allowed to vary. The depolarization factor of a field along the direction of the columns (i.e. when the electric field vector of the wave is parallel to column boundaries) was taken as zero. The depolarization factors L_x and L_y were selected as fit parameters, with the constraint to add up to unity.¹⁸ Other fit parameters were the percentages of void and oxide, film thickness, and Euler angles θ and φ . The thickness of the substrate and of the native oxide were kept fixed. The main challenge was to devise an appropriate model that has only a few parameters but adequately describes the physical system. In doing so, correlations among parameters can not completely be avoided, leading to many local minima to which the parameter space converges depending on slight variation in initial conditions, as in the case of films deposited at lower incidence angles (with low porosity).

Figure 3(a) shows the experimental data of column angle and normalized film thickness versus incidence angle deduced from ellipsometry analysis and from SEM measurements. The errors in measurements are shown by error bars. The SEM errors are related to misalignment of the cleaved plane compared to the deposition plane, SEM imaging of polar angles different than 90° , and naturally occurring column orientation variation with SEM sampling location. Due to the inherent precision of ellipsometry, the errors associated with the thickness derived from a fit are small. One mentionable characteristic in this figure is the normalized thickness saturation between 75° and 87° . This was associated to nonunitary values of the sticking coefficient.¹⁹ Systematic errors are introduced due to simplification of models compared to the real physical system, for example, ignoring the natural variation in a given parameter. The errors for incidence angles higher than 80° are small, the results of SE being in a perfect agreement with those of SEM. However, the errors for angles between 75° and 80° are higher, and are probably associated with the feature observed in the normal-

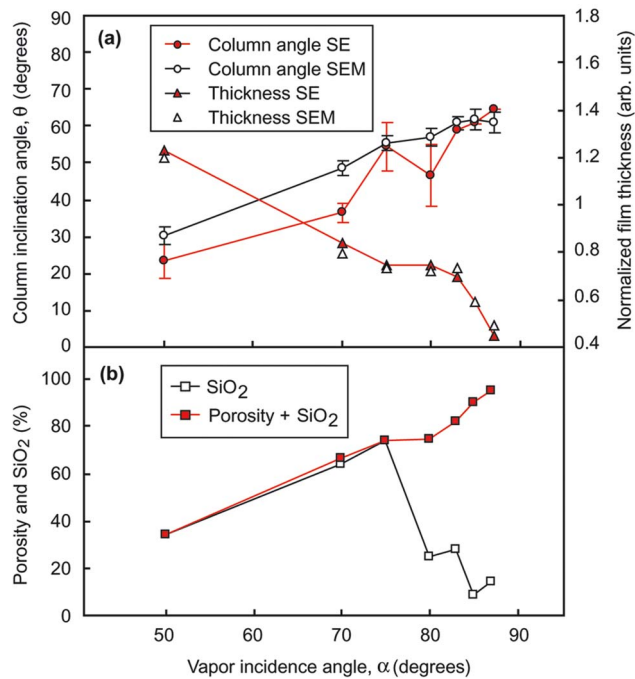


FIG. 3. (Color online) (a) Column angle and normalized film thickness vs the incidence angle comparison of SE and SEM data; (b) Porosity and oxide percentages vs incidence angle.

ized thickness variation with the incidence angle in the same angle region. It seems possible that for aggregate dense structures, the optical axis is not coincident with the direction of the columns.

Figure 3(b) shows the porosity and silicon oxide percentage versus the incidence angle. The results are consistent with the general expected trends of increased porosity with incidence angle. A similar method used at a single incidence angle was shown to produce porosity values consistent with those deduced from scanning electron microscope images.¹⁷ Also, the silicon oxide percentage increases with the incidence angle up to 75°, followed by a decline at higher angles, expected from a column surface-area/volume reduction.²⁰

SEM has been the primary technique for analysis of nanostructures inclination in OTFs. The SE method we propose in this letter has certain advantages over SEM. First, SE is a nondestructible method. Second, SEM is sensitive to misalignment between the deposition plane and the fracture plane, as well as polar misalignment. Usually, when measuring the column angle by SEM one inspects the edge of a film in the deposition plane. In order to measure the actual column inclination one must fracture the sample in the deposition plane, introducing a new source of error. Moreover, as one can see in Fig. 1(b), the columns situated near the frac-

ture site have slightly different inclinations due to edge irregularities as well as physical damage of some nanocolumns. Another advantage of SE over SEM is the potential of applying *in situ* for column angle determination.

In summary, in this letter we propose the use of spectroscopic ellipsometry as a measurement method of nanostructure inclination in silicon oblique thin films. This technique gives good results for column angles of very porous films. For films of lower porosity finding a unique solution is considerably more difficult, although our results indicate that a successful determination of film parameters is possible even in this case. This technique can be utilized *in situ* or *ex situ* as a powerful probe for the characterization of OTFs during their fabrication and processing. The main advantages of SE over microscopic characterization are nondestructiveness and accuracy.

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- ²⁰One most note that the lack of optical absorption in silicon oxide within the spectral range of SE measurements makes it difficult to distinguish between oxidized silicon and void in the effective medium model.