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Anisotropy in periodic mesoporous silica and organosilica films studied by generalized ellipsometry

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The dielectric functions of a series of periodic mesoporous silica as well as periodic mesoporous organosilica thin films were measured using generalized variable angle spectroscopic ellipsometry over the spectral range 300-1400 nm. Ellipsometry results indicate that following template removal, both types of films possess uniaxial anisotropy, with the optic axis perpendicular to the plane of the film. This anisotropy is apparently caused by the structural distortion of the channels, oriented primarily parallel to the substrate plane. We also find that the birefringence increases as a function of porosity. © 2005 American Institute of Physics. [DOI: 10.1063/1.2140472]

In order to sustain the ultralarge scale integration (ULSI) of semiconductor circuits, intense research is dedicated to exploring low dielectric constant materials that can provide low resistance-capacitance time delays in various interconnect structures.^{1–3} Silica (SiO₂) has been a longtime industry standard, but with a static dielectric constant of roughly 4.4 is probably twice too large to maintain the ULSI. Periodic mesoporous films are an exciting class of materials with potential to be used in microelectronics, catalysis, and chemical sensing applications. Especially, due to their low dielectric constants, robust mechanical properties, and thermal stability, they are attractive candidates to replace SiO_2 in interconnect structures. Periodic mesoporous silica (PMS), first reported in 1992, are synthesized using surfactant as a selfassembled template, to produce monodispersed, hexagonally ordered channels with diameters tunable with Angstrom dimensional control.⁴ The surfactant template is subsequently removed from the as-synthesized material to obtain ordered mesopores within a silica matrix framework. Extending on this work, in 1999, we⁵ and two other groups^{6,7} independently reported the synthesis of periodic mesoporous organosilica (PMO) in which a variety of bridging organic groups are incorporated into the silica framework without blocking or occupying the pore volume. The motivation to introduce different organic groups is based on the ability to tune the optical, electronic, catalytic, hydrophobicity, hardness, and density properties of the structure.

In the past few years, there have been many studies reported on periodic mesoporous films, especially in terms of synthesis and their structural properties.^{8,9} Very few of these studies have investigated the dispersion of the optical properties as a function of the porosity, and none of these have pursued the question of the degree of anisotropy with respect to the optical constants of these films. If these structures are to be used in optoelectronic applications, it is important

to understand both their dispersion and anisotropy more comprehensively.

Spectroscopic ellipsometry is an efficient method to determine the dielectric functions as well as the thicknesses of thin films without involving Kramers-Kronig transformation.¹⁰ Furthermore, this method can determine the optical anisotropy, and shed light on issues such as molecular orientation in thin films.^{11,12} In the present study we have therefore used ellipsometry to investigate the dielectric functions for a series of PMS and PMO films spin coated on silicon substrates in order to better understand their optical properties.

PMS and PMO films were synthesized using an evaporation-induced self-assembly technique,¹³ and details can be found in Refs. 14 and 9. The PMS films were synthesized from tetramethoxysilane (TMOS), and the PMO films were synthesized using a cyclic three-ring precursor ([(EtO)₂SiCH₂]₃).⁸ Synthesis of the films first involved mixing HCl (10⁻³ M) with CTACl surfactant (25 wt %) and anhydrous EtOH. Once mixed homogeneously, the TMOS or three-ring precursor was added. The CTACl/precursor molar ratios (R) were varied to produce two-dimensional hexagonal mesostructures with increasing volume fraction of surfactant template, which is used to control the final porosity. After the addition of the precursor, the solutions were stirred for 30-40 min before spin coating onto Si wafer at 2000-3000 rpm, to deposit films of thickness 500-800 nm. Finally, in order to remove the surfactant, the films were treated by solvent extraction (EtOH/HCl), plasma oxidation, and calcination (400 °C in air for the PMS films, and 300 °C in nitrogen for the PMO films) for 5 h, using a 1 °C/min ramp.

The lattice parameters of all of the samples were obtained by x-ray diffraction (XRD) experiments using a double crystal diffractometer with Cu $K\alpha_1$ radiation (Bruker D5000). Ellipsometric spectra were obtained using a J.A. Woollam rotating analyzer ellipsometer between 300 and 1400 nm spectral range. For each sample, ellipsometry spectra were obtained at the incidence angles of 70 and 75 deg.

The hexagonal mesostructure is shown schematically in Fig. 1(a), where the chemical precursors (i) and (ii) are

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FIG. 1. (a) Schematic illustration of (i) PMO and (ii) PMS chemical precursors and the hexagonal mesostructure, (b) XRD patterns for assynthesized and calcined silica films having R=0.079, (c) SEM (and TEM inset) of film cross section, and (d) *d* spacing and porosity of PMS films with respect to surfactant/Si molar ratio.

shown for the three-ring PMO and PMS materials, respectively. Figure 1(c) shows a cross-sectional view of the film obtained through scanning electron microscopy (SEM), and the orientation of the channels in the *xy* plane [transmission electron microscopy (TEM) insert of the aligned channels]. The high degree of order produces sharp peaks in XRD [Fig. 1(b)], which shift to smaller *d* spacing due to condensation contraction after high temperature calcination. Finally, the change in *d* spacing (and porosity) due to increasing surfactant template volume fraction (surfactant/Si molar ratio) is shown in Fig. 1(d). The surfactant/Si molar ratio increases the final surfactant volume fraction in the film, and so can be used to increase the porosity,¹⁵ and decrease the channel *d* spacing.¹⁶

For isotropic samples, the two parameters, Ψ and Δ measured by ellipsometry at each wavelength are related to the ratio of reflection coefficients by

$$\rho = \frac{r_{pp}}{r_{ss}} = \tan(\Psi)e^{i\Delta},$$

where r_{pp} and r_{ss} are the complex reflection coefficients for light polarized parallel (*p*), and perpendicular (*s*) to the plane of incidence, respectively. For anisotropic samples, all four components in the Jones matrix, which relates the *p* and the *s* states of the incident and reflected waves, must be evaluated using generalized ellipsometry.¹⁷ Unlike conventional ellipsometry, where only a single ρ is measured, in generalized ellipsometry, one measures two additional ρ 's (i.e., r_{ps}/r_{pp} and r_{sp}/r_{ss}) to determine all four matrix elements in the Jones matrix defined as follows:

$$J = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix},$$

where r_{ps} and r_{sp} are the Fresnel coefficients for mixed polarizations, and contains Ψ and Δ values associated with each of them. However, the measurement of zero offdiagonal terms in the Jones matrix does not automatically indicate an isotropic film. This is because an anisotropic sample with its optic axis directed in one of the principle axis of the experiment will also have its off-diagonal terms zero. This was indeed the case we observed for all of the



FIG. 2. Experimental and modeled Ψ and Δ spectra for the PMO sample with surfactant/Si molar ratio (*R*)=0.206. The continuous and dashed lines represent best-fit results obtained by modeling the PMO layer as an isotropic and an anisotropic material, respectively.

samples measured in this study, where both r_{ps} and r_{sp} were zero. However, in order to model the experimental spectra accurately, the periodic mesoporous films had do be considered anisotropic.

The experimental Ψ and Δ , along with the values obtained from our model are shown in Fig. 2 for a representative sample from this study. For clarity, we have shown only the spectra obtained at one incidence angle (i.e., 75 deg). In the figure, the continuous line showing a very low value of the error function [mean squared error (MSE)=1.1], represents a fit based on uniaxial anisotropy. Keeping the same layered-model, but by relaxing the anisotropy, one obtains a fit with a MSE value that is four times higher, represented by the dashed line. Similarly, the rest of the samples also had lower MSE values when the mesoporous layer was represented using an anisotropy model. These results indicate that the anisotropy model is far more suited in representing the films studied in this work. It must be noted that the uniaxial anisotropy model could not be further improved by introducing a biaxial anisotropic model, which is also confirmed by the fact that both Ψ and Δ spectra did not show any notable changes when the experiment was performed for different azimuthal angle.

The n values derived from the earlier scheme are displayed in Figs. 3 and 4 for PMS and PMO films, respectively. Both types of periodic mesoporous films are negatively birefringent; higher n for light propagating with its electric field vector oscillating along the plane of the film, compared to light propagating with its electric field perpendicular to the plane of the film. The birefringence for these films is very small (roughly an order of magnitude) in comparison to polymers that exhibit uniaxial anisotropy.^{1,18} In the case of these polymers, it is well established that the bonding electrons in the chain are mainly localized parallel to the polymer backbone resulting in a situation where $n_{\rm r}$ $=n_{y}>n_{z}$. However, polarized Raman experiments²² performed on both types of mesoporous films studied in this work reveal that there is no preferential bond ordering within the channel walls of the film, eliminating the possibility of bond orientation giving rise to anisotropy. Since we were able to model the ellipsometry spectra of the as-synthesized



FIG. 3. Dispersion of the index of refraction for template-free PMS films with different surfactant/Si molar ratios (*R*). Ordinary $(n_x = n_y)$ and extraordinary (n_z) indices of refraction are represented by solid and dashed lines, respectively.

samples (i.e., before the removal of the surfactant) using only an isotropic model, it was clear that the surfactant removal resulted in the anisotropy. It has been previously found that there is an anisotropic contraction of mesoporous films along z axis [see Fig. 1(c)] due to constraint in the xy plane.²⁰⁻²² We found that all three different methods of surfactant removal (i.e., solvent extraction, plasma oxidation, and calcination) produced an anisotropy although they varied slightly with respect to the degree of anisotropy, with the calcination and the solvent extraction giving the highest and the lowest anisotropy, respectively. There seems to be a direct correlation between the degree of anisotropy and the contraction of the lattice, as indicated by our XRD results; the calcination and the solvent-extraction procedures introduce the highest and the lowest contraction of the (100) lattice spacing, respectively. In addition, as the surfactant/ precurcor (R) is increased, and the resulting porosity increases in these structures, there is a slight enhancement in the birefringence (see Figs. 3 and 4) because the lattice is able to contract more in the z axis.

These results therefore clearly indicate that the anisotropy is induced because of the contraction of the lattice. While first-principle calculations that would identify the changes to the bonding structure—as a result of the lattice contraction—are beyond the scope of this paper, one could speculate that this distortion probably results in more bonding electrons parallel to the channels [i.e., x and y directions in Fig. 1(a)] compared to perpendicular direction (i.e., z axis), and therefore causes n in the x and y directions to be slightly higher in comparison to the n in the z direction.

We have investigated the optical properties of PMS and PMO thin films using spectroscopic ellipsometry. The experimental ellipsometry spectra were best modeled by representing the mesoporous films as uniaxially anisotropic with its optic axis directed perpendicular to the plane of the film. We find that both types of mesoporous films are negative birefringent, where the index of refraction perpendicular to the film is smaller than the index of refraction parallel to the film. This anisotropy is a direct consequence of the surfactant



FIG. 4. Dispersion of the index of refraction for template-free PMO films with different surfactant/three-ring precursor molar ratios (*R*). Ordinary $(n_x=n_y)$ and extraordinary (n_z) indices of refraction are represented by solid and dashed lines, respectively.

removal procedure, and is caused by the lattice contraction.

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- ¹J. J. Senkevich and S. B. Desu, Appl. Phys. Lett. **72**, 258 (1998).
- ²K. Postava and T. Yamaguchi, J. Appl. Phys. **89**, 2189 (2001).
- ³H. J. Lee, C. L. Soles, D. W. Liu, B. J. Bauer, E. K. Lin, W. Wu, and A. Grill, J. Appl. Phys. **95**, 2355 (2004).
- ⁴C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, Nature (London) **359**, 710 (1992).
- ⁵T. Asefa, M. J. MacLachlan, N. Coombs, and G. A. Ozin, Nature (London) **402**, 867 (1999).
- ⁶S. Inagaki, S. Guan, Y. Fukushima, T. Oshuna, and O. Terasaki, J. Am. Chem. Soc. **121**, 9611 (1999).
- ⁷B. J. Melde, B. T. Holland, C. F. Blanford, and A. Stein, Chem. Mater. **11**, 3302 (1999).
- ⁸K. Landskron, B. D. Hatton, D. D. Perovic, and G. A. Ozin, Science **302**, 266 (2003).
- ⁹B. D. Hatton, K. Landskron, W. Whitnall, D. D. Perovic, and G. A. Ozin, Adv. Funct. Mater. **15**, 823 (2005).
- ¹⁰P. Lautenschlager, S. Logothetiidis, L. Vina, and M. Cardona, Phys. Rev. B **32**, 3811 (1985); M. R. Buckley, F. C. Peiris, O. Maksimov, M. Muñoz, and M. C. Tamargo, Appl. Phys. Lett. **81**, 5156 (2002).
- ¹¹M. Losurdo, M. M. Giangregorio, P. Capezzuto, G. Bruno, F. Babudri, D. Colangiuli, G. M. Farinola, F. Naso, and A. Irene, Macromolecules **36**, 4492 (2003).
- ¹²B. P. Lyons and A. P. Monkman, J. Appl. Phys. **96**, 4735 (2004).
- ¹³Y. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M. H. Huang, and J. I. Zink, Nature (London) **389**, 364 (1997).
- ¹⁴B. D. Hatton, D. D. Perovic, and G. A. Ozin (unpublished).
- ¹⁵A. R. Balkenende, F. K. de Theije, and J. C. K. Kriege, Adv. Mater. (Weinheim, Ger.) **15**, 139 (2003).
- ¹⁶S. Besson, T. Gacoin, C. Ricolleau, C. Jacquiod, and J. P. Boilot, J. Mater. Chem. **13**, 404 (2003).
- ¹⁷M. Schubert, Phys. Rev. B **53**, 4265 (1996).
- ¹⁸M. Losurdo, G. Bruno, and E. A. Irene, J. Appl. Phys. **94**, 4923 (2003).
- ¹⁹O. Dag and G. A. Ozin, Adv. Mater. (Weinheim, Ger.) **13**, 1182 (2001).
- ²⁰H. Yang, N. Coombs, I. Sokolov, and G. A. Ozin, Nature (London) **381**, 589 (1996).
- ²¹M. Klotz, P. A. Albouy, A. Ayral, C. Menager, D. Grosso, A. Van der Lee, V. Cabuil, F. Babonneau, and C. Guizard, Chem. Mater. **12**, 1721 (2000).
- ²²D. Grosso, F. Babonneau, P. A. Albouy, H. Amenitsch, A. R. Balkenende, A. Brunet-Bruneau, and J. Rivory, Chem. Mater. **14**, 931 (2002).

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