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Fundamental Properties of Porous Structures and the Dynamics of Adsorbent-Pore Interactions

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In our original proposal, we planned to investigate the physics and the chemistry of porous structures in order to understand the fundamental connection between their macro-micro properties. We set out to explore how the architecture, composition, diameter, distribution and anisotropy of porous structures will influence the optical properties of these fascinating structures. The work performed in the past three years have shed light on this important question. Two important publications in reputed journals (Advanced Materials and The Journal of Physical Chemistry) have details our findings. We reported that the ellipsometric porosometry can be utilized to determine the diameter and the distribution of pores very effectively. Additionally, the microscopic feature of having non-spherical pores manifests optical anisotropy, which is a macroscopic property of the porous structure. We also found that x-ray reflectivity can provide the porosity of these structures quite reliably. We used several systems to pursue our studies; porous films produced with zirconia nanoparticles (~4 nm diameter) separated with either trioctylphosphine oxide or oleic acid, periodic mesoporous film made of silica and titania, hafnia (HfO_2) porous films made of HfO_2 nanorods.

In the past year, we focused on two projects; the completion of our work on the porous films made of hafnia (HfO_2) and the investigation of the origin of anisotropy in silica and titania periodic mesoporous films. The hafnia porous films were fabricated by spin-coating a solution of HfO_2 nanorods of different aspect ratios; 6 nm and 17 nm nanorods with an average diameter of ~2.5 nm. These porous films were deposited on silicon substrates with nominal thicknesses of around 120 nm. After spin coating the films, the ligands were removed by exposing the films to oxygen plasma. We employed ellipsometry and X-ray reflectivity to explore the pore-characteristics of this system. In the previous reporting cycle, we stated our preliminary results on the porosity of these films. In the past year, we focused our attention on the investigation of appropriate effective medium approximation (EMA) models that could best describe this system. Various inhomogeneities, including the shape and the size of pores, as well as their spatial distribution, can impact the EMA model because these inhomogeneties scatter and interfere with the electromagnetic waves. While traditional ellipsometry determines the polarization change due to specular reflection, the scattering due to inhomogeneties produce polarization changes that are not specular. Hence a more sophisticated form of ellipsometry is needed to account for such depolarization effects. We used a technique called Mueller-matrix ellipsometry to investigate these hafnia films, where the depolarization was measured spectroscopically. Subsequently, the scattering due to these inhomogeneities was accounted through the models we developed for these systems. We examined several EMA techniques including, Bruggeman, Maxwell-Garnett and a Volume Averaging Theory (VAT) to describe the hafnia films. We find that the VAT model is appropriate for the hafnia system as the nanoparticles are non-spherical. Using this EMA model, we are able to recover the porosity of this system, which was later confirmed by x-ray reflectivity measurements. We have published these results in an article in Journal of Physical Chemistry.

In our second project, we investigated silica and titania periodic mesoporous films in order to explore the manifestation of their pore-architecture in the optical properties. Periodic mesoporous films are an exciting class of materials with promising applications in microelectronics and photonics, catalysis, and chemical sensing. Specifically, the silica-based films are especially interesting due to their low dielectric constants, robust mechanical properties, and thermal stability, and are potential candidates to replace SiO_2 in interconnect structures, while the titania-based films are recognized as suitable candidates for an array of interesting applications including photo catalysis and chemical sensing, solar cells and electrochromics. The optical properties of periodic mesoporous films were determined using spectroscopic ellipsometry. Spectra were obtained at two angles of incidence (70° and 75°) using an ellipsometer which had a spectral range between 200 nm and 1600 nm. The experimental spectra were fitted using a three-layer model, consisting of Si-substrate, native oxide and mesoporous film. Initially, the mesoporous film was fitted as a Cauchy layer in which the index of refraction was represented as polynomial function. In Figure 1, we show the ellipsometry spectra (Ψ and Δ) obtained for a representative sample of a mesoporous film (denoted by symbols), along with results from our model (solid line). The oscillation-like structure, in both Ψ and Δ spectra, is due to the reflected light undergoing interference originating from the film thickness. The agreement between the experimental and the model spectra gives credence to the model. From our model, the optical properties of the sample (index of refraction and the extinction coefficient) and the thickness of the sample are recovered.

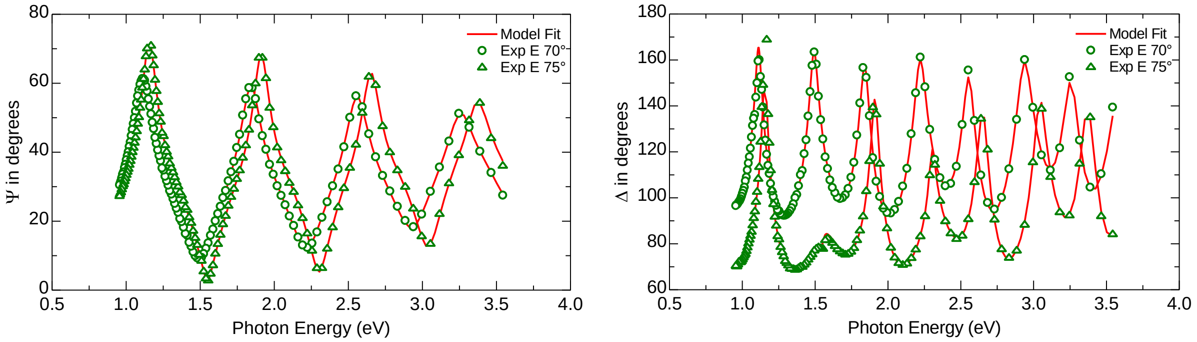

Figure 1. Psi and delta-spectra obtained at two different angles of incidence for a periodic mesoporous sample. This particular sample is a silica mesoporous film with a thickness of 1100 nm. The symbols show the experimental data while the solid lines show the fitting results. The sample was modelled using a three-layer model, consisting of Si-substrate, native oxide and mesoporous film.

In addition, ellipsometry spectra can be used to determine the porosity of the mesoporous films. This is accomplished by an effective medium approximation, where the film was represented as a composite material with two constituents (i.e., silica/titania and air). The silica and titania films that were investigated in this study had porosities in the range of 30%. What is of significance is that we find that the index of refraction of these mesoporous films cannot be represented by an isotropic model. In other words, the models demand that the index of refraction be anisotropic for both silica and titania mesoporous films. Specifically, the films require a uniaxial anisotropic model where the in-plane indices of refraction (n_x and n_y) are equal while the out-of-plane index of refraction (n_z) is different. As shown in Figure 2, both types of mesoporous films require that the in-plane index of refraction be slightly greater than the out-of-plane index of refraction. Interestingly, both mesoporous films require that the extinction coefficient remains isotropic. In order to explain why these porous films have anisotropic optical properties, their pore-structure had to be investigated carefully. Through careful scanning electron microscopy work, we have found that the pores are not spherical. In fact, as the films are calcined and their organic template material is extracted, there seems to be a contraction of the film thickness. This contraction influences the pores to become slightly elliptical. While a comprehensive study is on-going, preliminary results suggest that the there is a correlation between the anisotropy of the optical properties and the calcination temperature. From ellispsometry, we have also found that as the temperature of the calcination process is increased, the films undergo a higher contraction. Possibly, this might result in a higher ellipticity in the pores, which then leads to a larger anisotropy in the optical properties. It is interesting that even if the original material had isotropic optical properties, the inclusion of non-symmetrical pores in such a material will probably lead to an anisotropy, which can be exploited for specific applications.

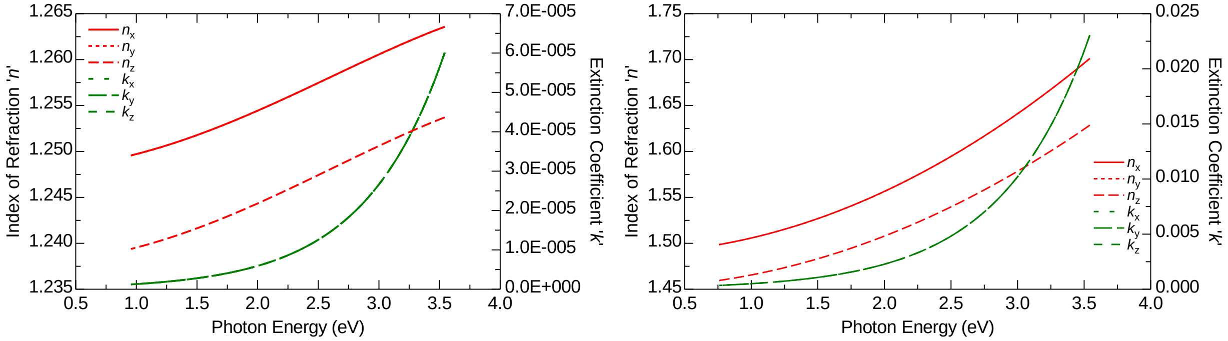

Figure 2. The anisotropic dispersion of the index of refraction for silica (left) and titania (right) mesoporous films obtained from modeling the ellipsometry spectra. The ellipsometry models require that both mesoporous films be uniaxial anisotropic, where the in-plane indices of refraction (n_x and n_y) are equal while the out-of-plane index of refraction (n_z) is different. The extinction coefficient is still isotropic.