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

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Mesoporous films manifest remarkable properties that are useful in myriad of applications, including catalysis, sensors, solar cells and supercapacitors. In mesoporous films, the pore diameter can be changed between 2-50 nm and its porosity can be changed to over 50%.[1,2] Once these interesting structures are synthesized using various chemical systems, it becomes imperative to characterize the properties of these mesoporous films, such as porosity, pore diameter and crystallinity. In this study, we have explored a porous system consisting hafnia nanoparticles via ellipsometry and X-ray reflectivity. Ellipsometry results detail the dielectric functions, porosity and quality of the films while the X-ray reflectivity measurements reveal the density of the films, complementing the ellipsometry results.

The hafnia (HfO_2) porous films were fabricated by spin-coating a solution consisting of HfO_2 nanorods, which were synthesized using TOPO, hafnium (IV) isopropoxide propanol complex and hafnium (IV) chloride.[3] Changing the heating procedure, the synthesis yielded nanorods of different aspect ratios; 6 nm and 17 nm nanorods with an average diameter of ~2.5 nm). The HfO_2 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 an oxygen plasma. X-ray diffraction experiments revealed that the HfO_2 had a monoclinic phase.

The optical properties of nanoporous hafnia films were determined using spectroscopic ellipsometry. Spectra were obtained at three angles of incidence (65°, 70° and 75°) using a Woollam 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 nanocrystal film. In order to obtain the porosity of the nanocrystal film, an effective medium approximation was used. based on volume averaging theory was used to represent the film as a composite material with two constituents (i.e., hafnia and air). For this particular system, an effective medium approximation based on Volume Averaging Theory (VAT) was used to model the porosity. Porosities from EMA models can be significantly affected by the inhomogeneities (*e.g.,* pore shape, size, and spatial distribution) that scatter and interfere with the electromagnetic waves for nanoporous films when the film thickness is below a critical value.[4] After extensive exploration, the VAT model seemed most appropriate for the hafnia porous films. In order to optimize the fits, a thickness non-uniformity of around 5% was included for the nanocrystal films, which is generally associated with the spin-coating method of fabricating thin films. In the following figure, the ellipsometry spectra, along with the model-fit are shown for a film composed of 6 nm hafnia nanorods.

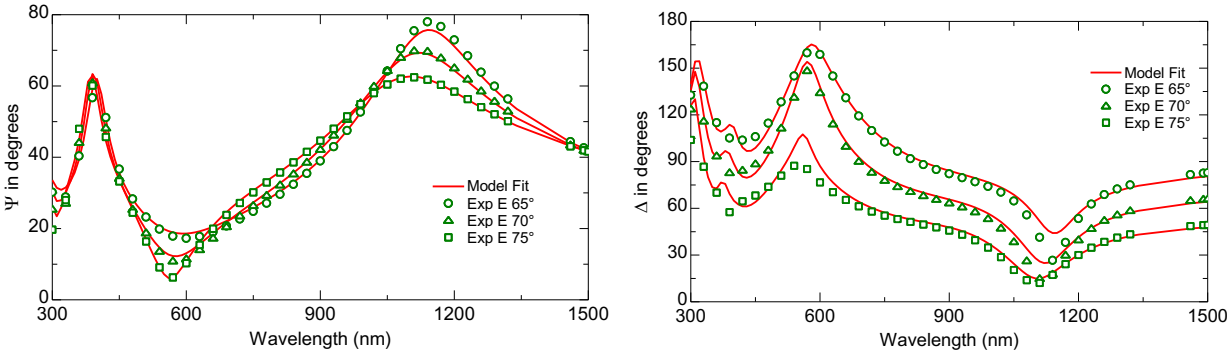

Figure 1. Psi and delta-spectra obtained at three different angles of incidence for a porous film composed of 6 nm hafnia nanorods. While the symbols show the experimental data, the solid lines sow the fitting results when the samples were modelled using a three-layer model, consisting of Si-substrate, native oxide and porous film.

The oscillation-like structure, in both Ψ and Δ spectra, is due to the reflected light undergoing interference originating from the film thickness. This structure can be exploited to determine the thickness of the the HfO_2 films. More importantly, the fitting result produces the porosity of the films. This is because the model allows one to calculate the dielectric function of the specific film, and since the dielectrc function of bulk-HfO_2 are known, the porosity can be recovered through the effective medium approximation that was discussed previously. In figure 2 (left-side), the dispersion of the index of refraction is shown for two HfO_2 porous films with different porosities. For reference, we also show the dispersion of the index of refraction for a bulk HfO_2 sample, which can be used to deduce the porosities.

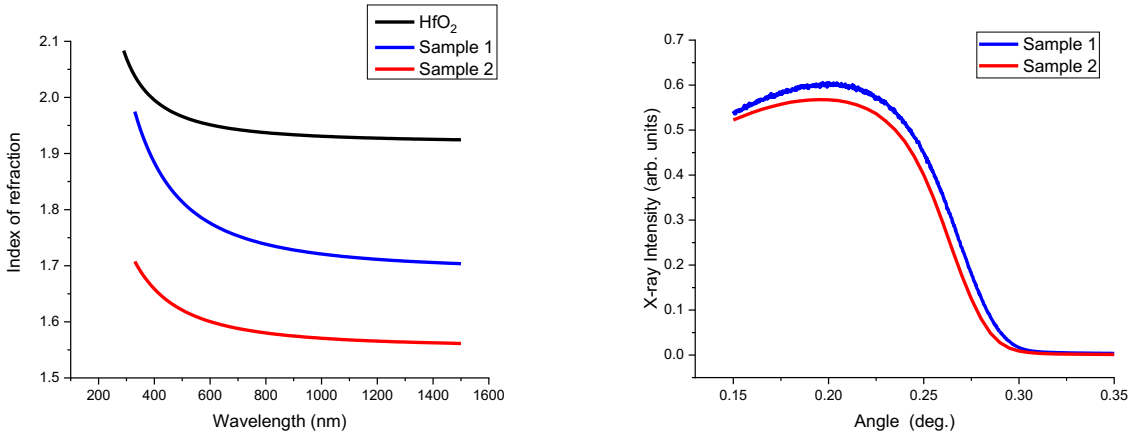

Figure 2. Dispersion of the index of refraction for two HfO_2 porous films along with the values for a bulf HfO_2 sample (left). X-ray refelectivity spectra for the two samples which is used to calculate the critical angle (right).

In order to further characterize the HfO_2 films, X-ray reflectivity (XRR) measurements were performed using a high-resolution Rigaku Smartlab X-ray diffractometer with a Cu-Kα source. The incident and reflected beams were collimated with slits of 0.05 mm. Before obtaining the specular scans, a fairly rigorous alignment process was employed which was controlled by a computer algorithm. In figure 2 (right-side), we show the XRR spectra obtained for two HfO_2 porous films. Moving from high to low angles, one observes the onset of total reflection. The intensity profiles of the XRR spectra were subsequently analyzed using a simulation software provided by the vendor. XRR measures the overall electron density of the film via the critical angle. In addition, if the films are sufficiently thin, the XRR spectra manifest interference oscillations which can be used to determine the thicknesses of films. In our case, since the thicknesses of the films were around 120 nm, we did not observe any interference oscillations. From the XRR data we can get bounds on the critical angle. Using these bounds, we can get bounds on the density and finally, deduce the porosity. Both ellipsometry and X-ray reflectivity results indicate that the HfO_2 films had porosities in the rage of 40%. In the next year, we plan to investigate the absorption/desorption properties of this system via ellipsometric porosimetry, and also to explore a few other porous systems. Ideally, we want to understand how the microscopic properties of these systems are registered via their optical properties.

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