Ellipsometry and X-Ray Reflectivity Analysis of Nanoporous Hafnia Films

R. Oliver VandenBerg and Frank Peiris
Kenyon College Summer Science 2017

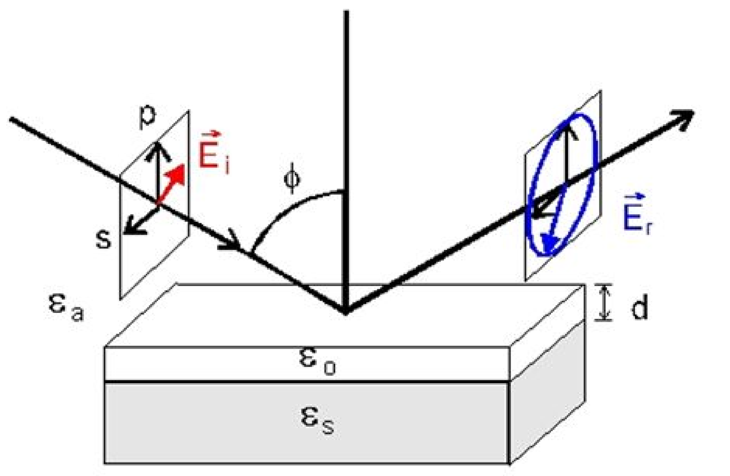
Abstract

Due to unique characteristics, such as having a high dielectric constant and a low electric conductivity, nanoporous hafnia films can be used for interesting optical and electrical applications. In this work, we analyzed a series of nanoporous hafnia films using ellipsometry, ellipsometric porosimetry (EP) and X-ray reflectivity. The hafnia films were produced by spin-coating hafnia nanoparticles on to silicon substrates. All of the samples were examined by ellipsometry, and a volume averaging theory was used to model the experimental spectra. These models produced porosity values around 45%, which was corroborated by other experimental techniques. The films were also analyzed using X-Ray reflectivity, which gave a range of porosity values between 45% and 55%. Finally, we used EP to monitor the optical signal from the samples as a function of the solvent pressure, and to further explore the pore-dynamics of the hafnia films.

Experimental Techniques

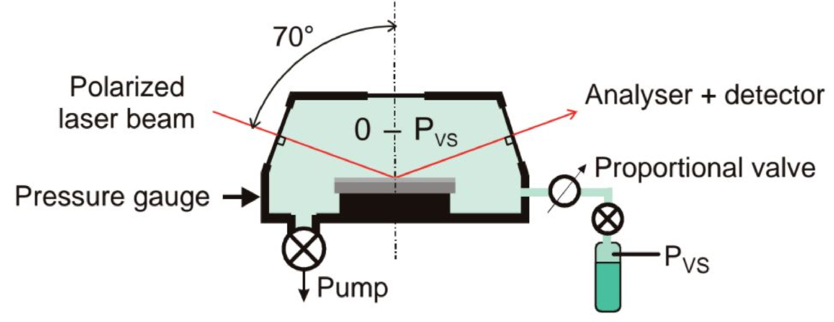
Ellipsometry

- Uses polarization of light to find psi and delta values
- These values can be fit with models based on layers of known materials to find the thickness and optical constants of layers in the system



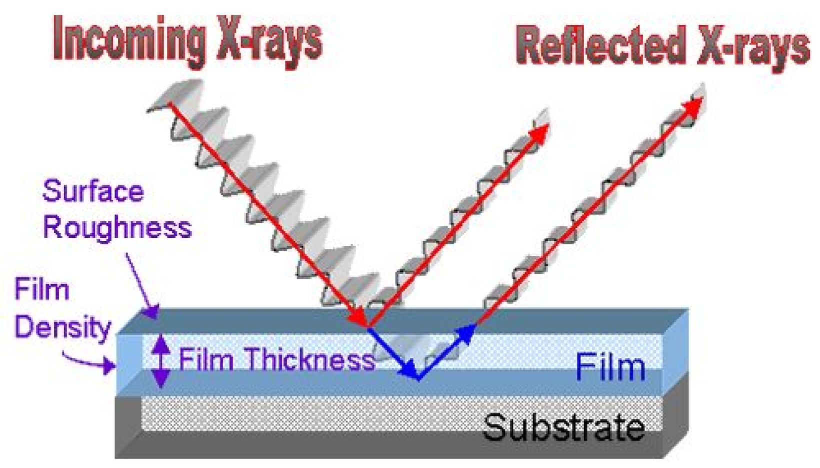
Ellipsometric Porosimetry

- Looks at adsorption and desorption of a solvent
- Use EMA modeling to look at changes in thickness and the filling of the pores
- Can calculate Young's Modulus based on these curves[1]



X-ray Reflectivity

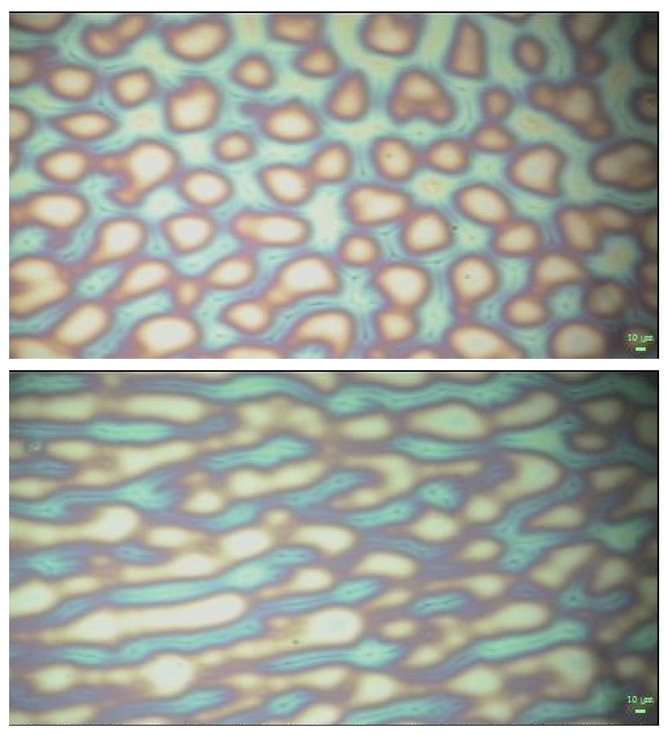
- Reflects an x-ray beam at a low angle off of the material and measures intensity loss.
- This can be modeled knowing the molecular mass of the material for the density.
- The density of a porous material can be used to calculate its porosity, knowing that the density of the crystals themselves will be unchanged.[2]



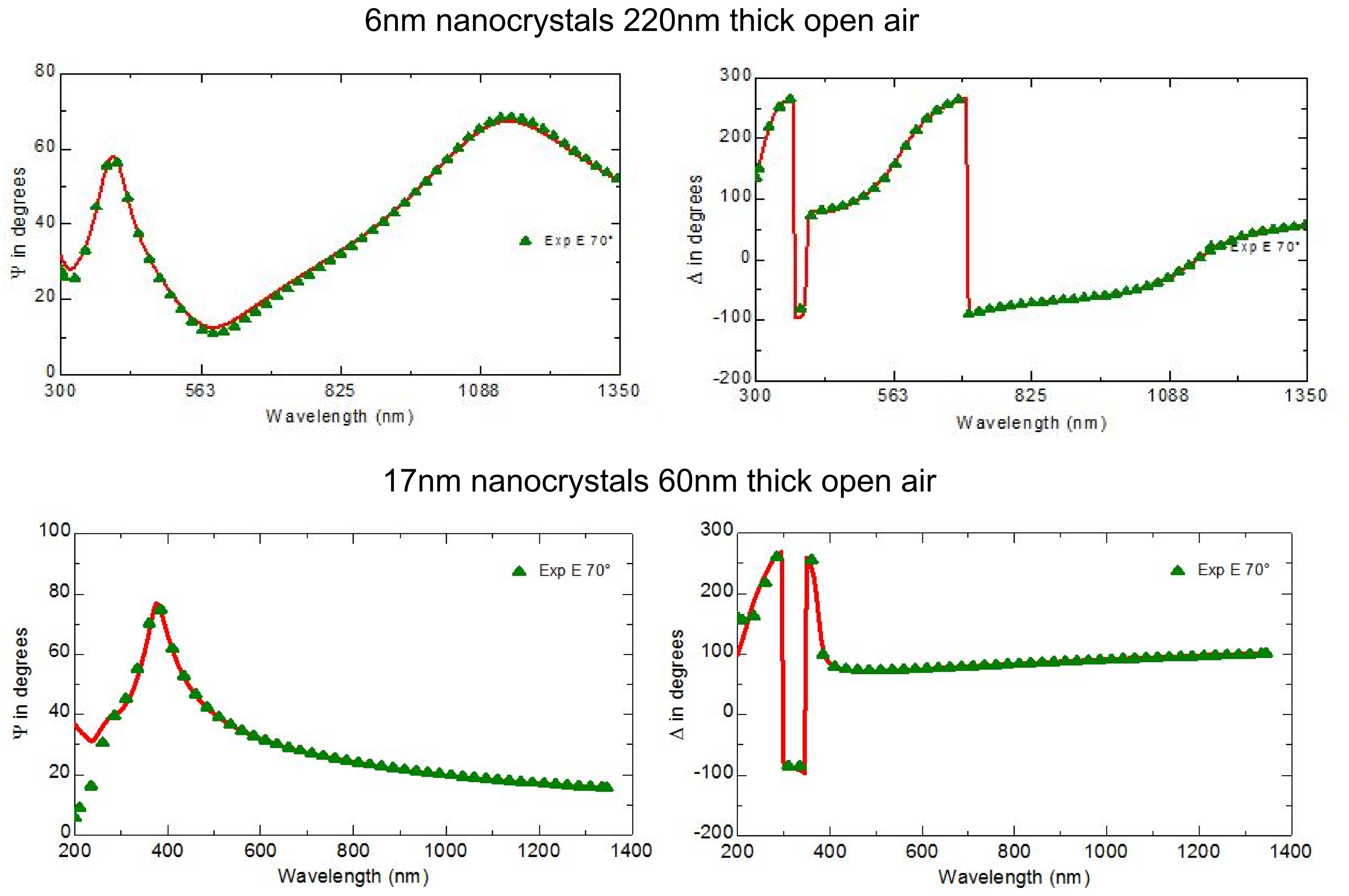
The Samples

We received ten samples from Iowa State.

- These samples were all created by synthesizing hafnium dioxide nanocrystals of sizes 6nm, 12nm, and 17nm.
- They were then spin coated on top of silicon substrates.
- They were produced in various thicknesses of hafnia from 50-300nm.
- Higher thickness samples tended to have coagulation and more of a variation across the sample due to the spin coating.
- These images are of a 12nm nanocrystal sample at the center and its edge



Ellipsometry

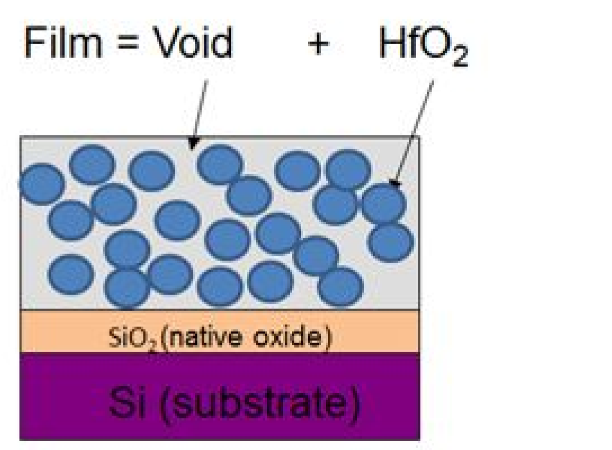


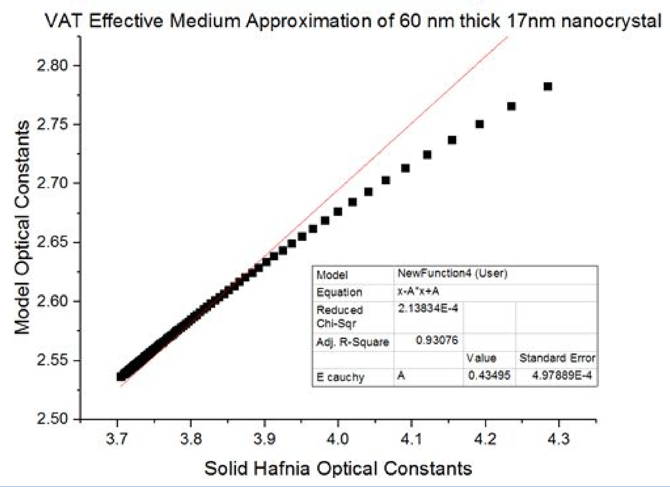
The ellipsometer measures the psi and delta values which can be modeled to find the thickness and optical constants of a material. These are the results of scans of two samples with varying thicknesses; 220 nm and 60nm. Since both samples were produced with Hafnia, they should have very similar optical constants which is mostly a factor of their porosity which should be similar since they were constructed the same way. The models of these scans give us the thicknesses reported and also very similar optical constants with the index of refraction of the 6nm sample being 1.60 at 650 nm, and the 17nm sample having an index of refraction of 1.63 at 650 nm. These curves however are very different, but all that difference is from the thickness which the model does an excellent job of tracking.

Effective Medium Approximation

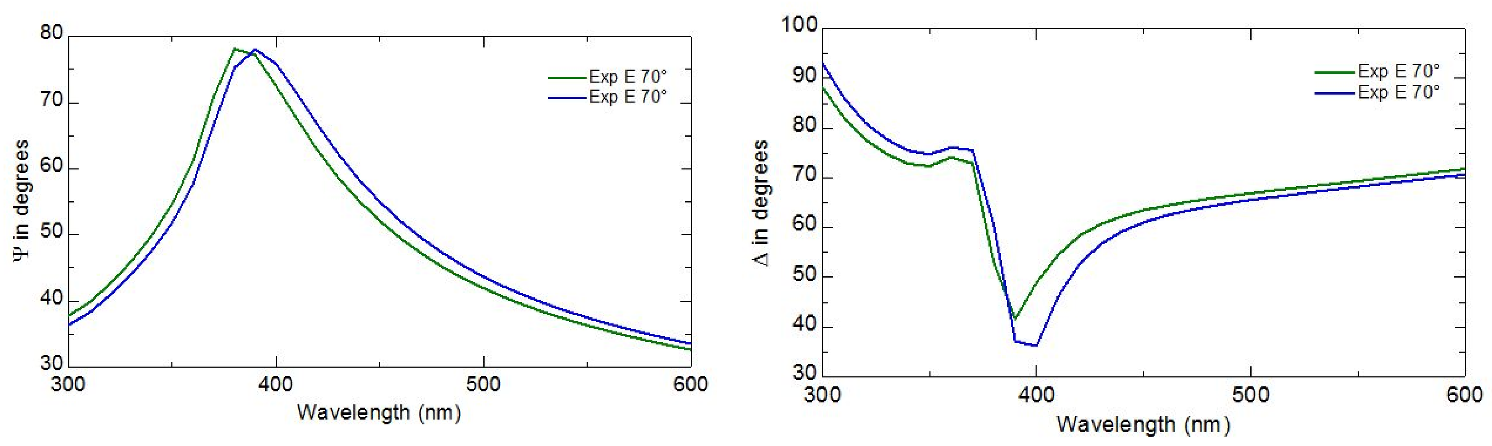
The porosity can be found by putting these optical constants through an effective medium analysis. This assumes that the hafnia is in a single layer with spaces of void mixed in. The Volume Averaging Theory (VAT), a model well suited for porosity measurements, calculates the porosity based on how the optical constants of the data compare with the known optical constants of solid hafnia and void.[3]

$$\epsilon_T = (1-\phi)\epsilon_S + \phi\epsilon_V$$





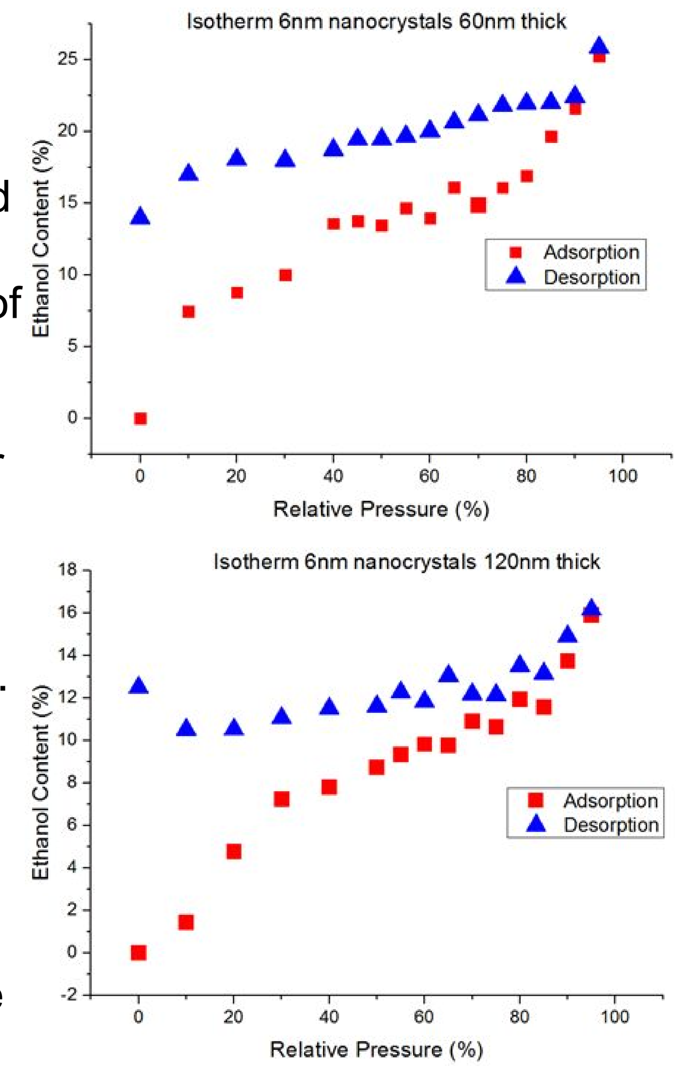
Ellipsometric Porosimetry



Ellipsometric Porosimetry involves controlling the pressure of a solvent from vacuum up to saturation pressure where the pores are filled with it. We used ethanol, and these show the difference between the ellipsometry scans, which can measure ethanol content with the VAT, at vacuum and saturation.

Ellipsometric Porosoimetry

- The amount of ethanol filling the pores is calculated for each value of relative pressure of the ethanol.
- The optical constants of water are nearly the same as ethanol and are used for the approximation.
- The difference between the adsorption and desorption is important for the calculation of pore sizes.

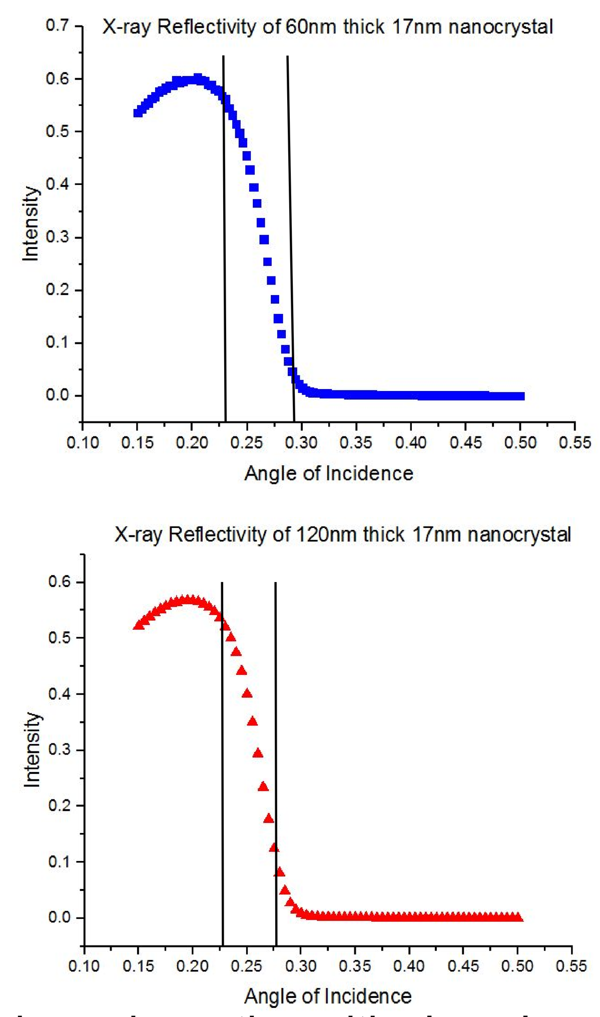


X-ray Reflectivity

The most interesting data from x-ray diffraction is the placement of the critical angle. This is the angle at which there is a significant drop in intensity from total reflection to far less. For the Hafnium samples, this was around .25 degrees.

$$\theta_c = \lambda(\rho_e r_e/\pi)^{0.5}$$

In this formula θ_c is the critical angle, λ is the x-ray wavelength, r_e is the classical electron radius and ρ_e is the electron density.[4]



From the data we can get bounds on the critical angle. Using these bounds in the formula we can get bounds on the density and from that the porosity. This was a really important check to make sure that the models we were using for ellipsometry were giving us fair values. For these samples the porosity was found to be 41-51% for the first and 46-53% for the second samples.

Refrences

1. Rouessac V, Coustel R, Bosc F, Durand J, Ayral A. Characterisation of mesostructured TiO2 thin layers by ellipsometric porosimetry. Thin Solid Films. 2005
2. X-Ray Reflectivity. Organic thin film laboratory. Valporaiso University. http://physics.valpo.edu/staff/arichter/XRR.htm
3. Braun MM, Pilon L. Effective optical properties of non-absorbing nanoporous thin films. Thin Solid Films. 2006;496(2):505–514.
4. Lee H, Soles C, Liu D, Bauer B, Wu W. Pore Size Distributions in Low-k Dielectric Thin Films from X-ray Porosimetry. 2002

Acknowledgments

This work was funded by the Kenyon College Summer Science Scholars program.