Ellipsometric Porosimetry

Q&A

Question Asked	Answer
Is the vapor generator a bubbler-type or based on a contact evaporator?	The environment cell itself is at atmospheric pressure, we use an atomizing nozzle to spray solvent into a constant flow of nitrogen. The solvent amount is accurately controlled using state-of-the art mass flow controllers from Bronkhorst. The relative solvent pressure compared to the equilibrium vapor pressure is set by varying the mass flow according to standard vapor pressure equations.
In your experience, is the Bruggeman approximation more needed for mesoporous than for microporous samples? Perhaps the microporous ones can be considered 'more homogeneous'?	The Bruggeman EMA is the standard approach in the ellipsometry field for any mixed materials with mixing on the microscopic scale. It works for the entire spectral range without any further assumptions about the sample properties. In the porosimetry field it works especially well for mesoporous samples where the shape of the larger pore network tends to cause anisotropic sample properties, since it can be set up as isotropic or anisotropic version. I think the assumption that microporous samples are generally more homogeneous is valid here.
For clarity: do you do the entire measurement in the Linkam stage or only the activation? I was a bit confused since I heard you mention a transfer. If you don't, why would you not do the whole measurement in the Linkam stage?	The Environment Cell does not have a heater. So yes, the sample was moved from the Linkam after the activation. Including a heater in the environment cell would be a safety hazard that is hard for us to control from the software side. There is no guarantee that a user doesn't mix up settings selected in the software regarding a specific solvent in the tank which could cause heating of the sample above the autoignition temperature of the solvent. We therefore prefer preparing the sample outside the environment cell and transferring it afterwards.
Could you comment on the ballpark list prices of the different components?	Spectroscopic Ellipsometers (without porosimetry) cost between $50K and $150K (generally). The package for porosimetry is around $40K (as an "add-on").
How do you define an isotropic or anisotropic organic thin film?	Isotropic thin films will have the same optical properties in all directions. Anisotropic films will have different optical properties depending on the direction that the electric field is applied in. Many organics will "align" relative to each other and cause optical anisotropy. For more information on this topic please check out our Anisotropy Short Course - the first session of which is "free" on our website: https://www.jawoollam.com/resources/short-courses/on-demand-special-topic-anisotropy ; in porous samples the pore network can cause an anisotropic distribution of void space in the thin film making the sample effectively optically anisotropic, usually with larger refractive index in the surface plane than along the surface normal
Can we determine the concentration of dopant in a matrix of host materials using this technique?	Dopant characterization in the sense of modifying the conduction properties in a semiconductor is different than porosity measurements, but it can be possible by using long-wavelengths (IR-VASE) to study whether the film is highly doped. Tom Tiwald has published some papers on this and the wavelengths we measure would require quite high doping concentrations. If by "dopant" you mean adding a "filler" in an existing porous film then the answer would be yes.
Can you use it to study porosity of PECVD thin films on semiconductors?	If the pores are open towards the surface this would be exactly the situation shown in the seminar. If the pores are not connected, i.e. "closed", we can determine the volume percentage if the bulk optical properties of the skeletal material are known, e.g. from a solid film. Feel free to contact us at sales@jawoollam.com if you are interested in demo measurements.
is there capability to measure on simple patterned wafers (obviously not great for products, but could do a qual wafer if some ability to measure simple patterned structures--if yes, what would the length scale (laterally) be?	This capability depends on the spot size of your ellipsometer, our standard research ellipsometers with collimated beam have a beam diameter of about 3mm. This can be reduced using removable focusing probes down to approx. 150um, we also sell dedicated microfocus instruments with spot sizes down to 45x25um. The measurable patch size is directly related to these numbers. So in general, yes you can measure on simple patterned wafers. However, there needs to be enough space to put the lid on the cell which might require a customized solution.
Is it possible to deal with anisotropic porosity?	The anisotropic Bruggeman EMA is applicable to anisotropic pore networks and will give qualitative information about the approximate shape of the pore network, i.e. elongation along the surface normal or more oblate shape within the surface plane. If the porosity changes along the surface normal, this would be seen as a gradient in the optical properties and can also be described by a so-called parametric grading of the Bruggeman EMA layer. We actually patented this approach for the porosimetry case.
Is there a reasonable way to incorporate heating capability into the Environmental Cell?	Please see similar question above.
How tolerant is the technique to the macroscopic wetting of the surface as shown in the imaging example at high pressures? Will the droplets cause artifacts or are they too large to cause interference?	Macroscopic wetting would need to be avoided to get enough light to the detector. Droplets will cause significant scattering and the geometry in general even for small droplets would be hard to describe in a layer stack model. It was shown here to demonstrate how accurately we can control the vapor pressure.

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Do you provide porosity measurement services.	We generally provide measurement services, but usually avoid in-situ projects due to the long time needed to finish the projects. We charge by the engineer hour which would make this approach not very cost effective. However, we also provide free demonstrations, so feel free to e-mail or call to discuss.
What is the lowest porosity you can measure?	This depends a little on the material of the porous film. Mixing void into a bulk film changes the optical properties more dramatically the higher the refractive index is for the solid film. It just comes down to the smallest refractive index changes that can be measured without correlation. As an estimate a few single digit percent are very realistic.
Are the measured results solvent dependent?	The data will look different for different solvents due to the variation in molecule size and different refractive index values for the solvents. However, when plotting the actual adsorption isotherm in terms of adsorbed solvent volume vs relative pressure the results will be the same and thus the pore size distribution will also be identical. This is known as the Gurvich rule in the porosimetry field. However, for some solvents there might not be any changes whatsoever based on the polarity of the solvent and missing wettability. In other words based on the contact angle on a solid film, the solvent might not even penetrate into the porous film.
How do you define the saturation pressure in the experiment as it depends on the environmental conditions?	The environment cell uses temperature feedback from the sample compartment which feeds into Antoine Vapor Pressure equations to calculate the vapor pressure.
Any plan to include a vapor generator with multiple solvent tanks?	That capability is not included with our current system, but it may be added at a future date. Changing solvents is a fairly straightforward process that should only take 10-20 minutes. Contact us if you have further questions (sales@jawoollam.com)
As I understood, you still use a single-wavelength for porosity measurements. Any advantages to use multiple wavelengths?	The user can select either the single-wavelength approach based on the Lorentz-Lorenz equation and can define which wavelength to use or even can use a refractive index specific parameter in the model such as the Cauchy-A parameter. We prefer the Bruggeman EMA approach since it models the entire spectrum as we always prefer when analyzing data. This will give as an idea about non-idealities in the sample such as anisotropy or gradients. Again, the user can select the preferred method and we can even include other methods upon user requests.
Have you tried to use carbon tetrachloride (CCl4) instead toluene?	No we haven't at this point
Can you study loose particles?	This will likely not work very well with this method. There are methods used to study particles on a surface, but the sensitivity to a refractive index change in these particles due to porosity might be limited. If you refer to studying space between particles on a surface that would depend strongly on the density and size of the particles.
Do we usually single wavelength for measurement? How do you determine the wavelength you use? Is there any wavelength-dependent sensitivity for the measurements?	Please refer to similar question above. Often people use the refractive index at the HeNe laser wavelength of 632.8 nm.
Is it possible to install this chamber on the alpha-SE, or is a more advanced ellipsometer necessary.	At this time we have done measurements with our M-2000 and RC2 ellipsometers. We are open to discussions if you are interested in using this with an alpha-SE.
Can this unit be mounted on standard VASE?	Please feel free to contact us at sales@jawoollam.com for more detail. In general, the chamber can be mounted on our vertical stages, however, at this time there is no software implementation in our older WVASE software package that the VASE instruments run on.
How do you differentiate between pore condensation and material absorption? Material absorption might not impact refractive index but it would impact pore structure	If by absorption you mean reaction of the solvent with the skeletal material, this will in fact change the refractive index, there would be a permanent change of the refractive index. Measuring multiple cycles will allow us to identify such effect. We also always determine the thickness change of the film which also will show characteristic changes when a reaction with the skeletal material occurs
Is this technique intended to replace PALS for microporous samples? Have you compared PALS analysis to yours to see if the free-volume element measurements are consistent between the two methods?	It is not intend to replace PALS. Ellipsometry is relatively more accessible comparing to the advanced system requirement of PALS. There are publications on round-robin comparison among PALS, EP and Small angle neutron scattering. We have not performed the comparison yet.
Can you provide a depth profile of pore size, or are these pore diameter distributions for the entire material?	A depth profile would be seen as a variation of the refractive index within the film known as "grading". The anisotropic Bruggeman EMA in combination with the standard "parametric grading" in CompleteEASE allows us to vary the porosity in the film from top to bottom to account for that effect. In fact, we patented using the Bruggeman EMA for the porosimetry analysis with this effect and anisotropy in mind. (contact support@jawoollam.com if you have further questions)
Does your measurement technique include porosity that is closed (i.e. closed pores with no entrance or exit)? or does it ignore these pores since condensation will not occur?	Please see the answer to a similar question above. In general, if the skeletal material refractive index is known the closed pore volume can be accessed.
Have you confirmed accuracy of this technique with film porosity measurements conducted by positron annihilation lifetime spectroscopy?	We only have limited access to alternative techniques and rely on customer feedback for this purpose. We can compare the results obtained on samples of "known" porosity as we have done on porous silica. These results match well with the expected values.

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Will choosing different solvents allow for higher resolution measurement in certain pore ranges?	In general the solvent properties shift the position of data features and more viscous solvents are easier to control by the flow controller which can become relevant at very low relative pressures when studying microporous samples. Also, the wettability of a solvent on a specific material is important, in other words the polarity of the solvent could prevent the solvent from entering the pores all together which then of course would not change the film refractive index with relative pressure changes.
Have you conducted analyses of materials with known more diameter distributions and porosity to verify accuracy of the technique?	please see similar question above.
Can we get information about the porosity variations within the sample or are we getting effective porosity of the sample?	Porosity variation along the surface normal can be studied to some extent, lateral variations over the measurement spot are not detectible and an average value would be given. See also some answer for similar question above.
The Brunauer, Emmett and Teller (BET) technique is the most common method for determining Porosity measurements. How does Ellipsometer porosimetry compare with BET?	The underlying theory is very similar to the BET method. The adsorption and desorption isotherms obtained by plotting the solvent volume with respect to relative solvent pressure will show the same characteristics as for BET techniques. The way the solvent volume is determined is simply different as here we determine it from an induced refractive index change rather than measuring a weight change or volume change. Note that this has some advantages as very thin films can be studied and a swelling of the film does not influence the result since the refractive index is a volume property and the determined solvent volume in the pores is always given per unit thickness
Can you modify an existing VASE ellipsometer to function as ellipsometric porosimetry? If so, then can you please mention what are the major components required? Can the company help in setting it up?	Please check similar question above and feel free to contact us at support@jawoollam.com
Could gases, such as CO2, be used to probe microporous samples?	Suitable solvents must be liquid at room temperature so that condensation can occur in the pores and the relative pressure can be varied by mixing the solvent with nitrogen.
What range of film thickness are required?	We rely on determination of refractive index changes. For ultra-thin films below 15nm, there is correlation between the optical properties of a thin film and its thickness. Just like in any ellipsometry measurement in the NIR-VIV-UV spectral range, good sensitivity to refractive index and thickness variation are achieved for films above about 20nm up to multiple microns depending on the exact instrument and film thickness homogeneity.
Is it possible to determine the micro-porosity of organic films? If so, what's the principle for selecting solvent/gas for the test?	in general yes, the solvent would depend on the wetting properties of the organic and should not react with the film
Could this method be used to study filling pores with a melt of an organic material?	Filling porous films with any material can be studied even without an environment cell if the skeletal and filler bulk optical properties are known. Otherwise a standard porosimetry cycle would need to be performed prior to filling of the pores with a "melt" using a different solvent
Could the Lorentz-Lorenz approach provide different answers for porosity/pore sizes depending on the wavelength of light used for the refractive index?	Technically speaking, the results should be consistent regardless of the wavelength. In our software, the model allows you to choose the wavelength.
What if the solvent swells the porous coating? Can that be handled in some way, or is it recommended to only use a solvent that will not cause swelling?	We always determine refractive index and thickness independently, so you can characterize both effects. The relevant parameter for volume of solvent in the pores is only related to the refractive index, the determined volume is always per unit thickness and the actual film thickness does not matter, that said, some form of swelling will always occur but does not influence the pore characteristics determined
A more general question on ellipsometry. If the coating surface has some roughness such that there is scattering, but enough specular reflection for a signal, does this artificially inflate the extinction coefficient, k?	This depends on the scale of the roughness. When modeling ellipsometry data, we can add surface roughness as a separate layer if the roughness is on the nanometer scale, in this case k will not be inflated. If macroscopic scattering occurs, the Psi values will be changed in a similar way as would be expected if absorption was present in the film and the perceived k values would be inflated. This would usually not be a good regime for ellipsometry measurements, however, since we determine relative changes here while changing the solvent pressure, the pore size distribution would likely still be accurate.
What solvents are typically used?	Standard solvents would be water as polar solvent and toluene for non-polar, but a wide variety can be used in the environment cell as inert materials are used for chamber and hoses
Does the in situ cell have a fixed incident angle, or can that be changed?	The incidence angle is determined by the window position and is currently fixed at 70deg
Does a greater difference in (n, k) between solvent and film material help in sensitivity?	Since we determine the refractive index change, a higher contrast between film and solvent typically means better sensitivity, that is correct. (contact support@jawoollam.com if you have further questions)

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I note that your microporous sample gave desorption with virtually no irreversible character between adsorption and desorption- is that normal?		This behavior is expected, only mesopores show a hysteresis.
What is the temperature measurement range?		The environment cell does not have a heater for reasons mentioned above. Our Linkam Heat Cell is rated from -70 to 600 C.
The pore size distributions for absorption and desorption have different shapes. What does it mean in a sense of physical (real?) pore size distribution?		A hysteresis is expected for mesoporous samples since solvent can easier condense in empty pores during the adsorption process then evaporation can occur in the presence of still filled adjacent pores of smaller size through which the solvent would need to escape to empty the pores in the desorption cycle.
Can the method be applied to the anisotropic film with thickness at around 5-10 um? Also, can the closed pores be measured by any method?		This method can be applied to any porous material - even a film that is anisotropic. The key is that you need to first find a good model for the film - if it is anisotropic, then you need to be able to model this even with the porous index of refraction. Then, as the solvent is added you should see changes in the optical constants (even the anisotropic optical constants). A good example of this would be porous silicon films, which can be created as large pillars and will have strong anisotropy., closed pores are accessible if you know the refractive index of your skeletal material when deposited as bulk film