Ellipsometry Porosimetry measurement theory

Adsorption analysis is a widely used for evaluation of porous materials. It is based on the adsorption/condensation of an appropriate adsorptive in the pores under the pressure below saturated vapor pressure. Amount of adsorbed/condensed vapor versus relative pressure of adsorptive at a constant temperature is called isotherm of adsorption. Porosity, Porous Size Distribution (PSD) are calculated from the isotherm of adsorption using Kelvin and Dubinin-Radushkevitch equations.

Ellipsometric porosimetry (EP) is a new version of adsorption porosimetry[1]. The principal feature of this method is to monitor the change of the optical characteristics of the porous film during vapor adsorption and desorption.
We use this change in optical characteristics in order to determine the mass of an adsorptive condensed/adsorbed in pores instead of direct weighing.

Ellipsometric Porosimetry (EP) measurements are performed using a high vacuum system designed for this purpose. The measurement system is based on GES5E spectroscopic ellipsometer optical arms and spectrograph (250nm-1000 nm), a dry pumping system allowing to evacuate the chamber up to 1*10-6 torr, and several sources of appropriate organic solvents and optionally water as probing gas The vacuum chamber needs to be pumped down before allowing an adsorptive into the vacuum chamber. Vapor of the organic solvent is introduced into the vacuum chamber using a precise and controllable valve. This step has to be done as slow as necessary to provide adsorption / desorption equilibrium between the adsorbed phase and the gas phase. When the adsorptive pressure reaches the saturated value, automatic pump down of the vacuum chamber is started.

Speed of the pumping also must provide adsorption / desorption equilibrium between the adsorbed and the gas phase. For this purpose the system has a special controllable valve in the bypass line. Room temperature PSD measurements can be made using EP with organic solvents and do not have the problems associated with low-temperature nitrogen porosimetry.

Total measurement time is 25 minutes for both adsorption and desorption cycles. The samples are heated on a thermal chuck for 2 minutes at 300 degrees C prior to the measurement. We use Toluene as the organic solvent.

Change of optical characteristics of porous Ultra low-K film is measured continuously during the adsorption and desorption isotherms using a cauchy dispersion law.

The amount of adsorptive inside of pores is calculated from the measured change of the optical characteristics of the porous film during the vapor adsorption / desorption. Lorentz–Lorenz equation is used to determine the porous volume of the film.
The optical characteristics of the film under ultra vacuum, at each relative pressure and the optical properties of the liquid adsorptive are used in these calculations. No information about the refractive index of the dense material is required in the calculation of the porous volume.

The PSD (Pore Size Distribution) calculation in the mesoporous films uses the phenomenon of progressive emptying of a porous system initially filled at a pressure $P=P_o$. The calculations are based on the analysis of the hysteresis loop that appears during the adsorption and desorption because the effective radius of curvature of condensed liquid meniscus is different during the adsorption and desorption. The adsorptive vapor condenses in the pores at the vapor pressure (P) lower than the equilibrium pressure of a flat liquid surface (P_o) and the dependence of the relative pressure (P/P_o) on the meniscus curvature is described by the Kelvin equation:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{f \cdot \gamma \cdot V_L}{r_K \cdot RT}$$

where γ and V_L are the surface tension and molar volume of the liquid adsorptive, respectively. f =1 for slit-shaped pores and f=2 for cylindrical pores. If the radius of a cylindrical pore is r_p, then $r_p=r_k+t$ and t is the thickness of the layer adsorbed on the pore walls.

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Values of *t* are obtained from the adsorption of the same adsorptive on a non-porous sample and are defined by the BET (Brunauer, Emmett, Teller) equation.
The primary experimental data for PSD calculation are the ellipsometric angles Δ and Ψ and the adsorptive pressure. EP software allows the calculation of the change of *n* and *d* during the adsorption and desorption, porosity and PSD.

For micropores with widths of order of a few molecular diameters, the Kelvin equation (6) is no longer valid. Not only would the values of the surface tension and the molar volume deviate from those of the bulk liquid adsorptive, but also the concept of a meniscus would eventually become meaningless. To analyze the microporous films, a method based on a theory developed by Dubinin and Radushkevitch (DR) has been chosen. The DR theory uses the change of adsorption potential when the pore diameter is comparable with the size of the adsorptive molecules (probe). The process involved is the filling of the micropore volume rather than layer-by-layer adsorption on the pore walls.

The adsorption potential A and characteristic adsorption energy Eo are dependent on the micropore size and the amount of adsorption W at the relative pressure P/P0 is given by:

$$W = W_0 \exp[-(A/E)^n]$$
$$(n = 2;\ E = \beta E_0;\ A = RT \ln(P_0/P))$$

Here, W0 is the micropore volume and β is the affinity coefficient which brings the "characteristic curves" of W vs A for different adsorptives into coincidence with the curve for some particular adsorbate taken as an arbitrary standard (benzene): for the standard adsorbate β=1. W0 and βE0 can be calculated from the linear plot of lnW versus A2 . The βE0 value provides the isosteric heat of adsorption. The pore size is then calculated from Wo = K/E0 where K ≈12 is a coefficient slightly changing with E0.
The EP5 software recognizes the presence of micropores in the film by analyzing the adsorption and desorption isotherms and calculates both the mesopore and micropore characteristics relative volume and size.

Reference:

(1) M.R.Baklanov and K.P.Mogilnikov. Non-destructive characterization of porous low-K dielectric films. Microelectronic Eng., 64, 1-4, 335 (2002).

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