

Ellipsometric porosimetry

Ellipsometric porosimetry is used for measuring porosity and pore size distribution (PSD) of thin porous films. The method is based on ability of a porous film to adsorb solvent vapour inside the pores. Such adsorption is performed in a vacuum chamber and monitored by ellipsometry. The solvent for adsorption should fulfill the following requirements:

- Low contact angle with the porous film in question (to be able to penetrate into pores)
- The boiling temperature is higher than the room temperature (to be able to condense at room temperature) but not significantly higher to provide substantial saturated pressure at room temperature (to reduce the influence of the residual pressure in a vacuum chamber on pressure measurements)
- No chemical interaction with the porous film

We used toluene as a solvent for adsorption in porous film. It has boiling temperature of 110.6 °C, the saturated vapour pressure of about 24 Torr at room temperature, low (<5°) contact angle with all studied materials. Toluene molecule is non-polar that reduces interaction with pore walls.

The experimental configuration looks as follows. A sample (a porous film on a substrate) is placed in a vacuum chamber equipped with ellipsometer. The chamber is firstly pumped down to low vacuum (10^{-2} Torr) and then slowly filled with toluene vapour (up to the saturated pressure). The toluene adsorption in the porous film is monitored by *in-situ* ellipsometer. After reaching the saturated toluene pressure, the chamber is pumped down again to low vacuum while desorption of toluene from the porous film is monitored *in-situ* again. The results of the measurements are dependencies of ellipsometric angles Ψ and Δ on toluene pressure. The pressure is expressed in relative units (P/P_0 , where P_0 is the saturated toluene pressure at room temperature) from 0 to 1. The optical properties and thickness of the film are extracted and then used in calculation of porosity and pore size distribution as will be explained below.

Porosity

Porosity can be extracted from the film refractive index measured prior to adsorption and after the full adsorption (the film is completely filled with toluene at saturated pressure). The relation between the optical constants and properties of a multi component system is described by the Lorentz-Lorenz equation:

$$B_{eff} = \frac{3}{4\pi} \cdot \frac{(n_{eff}^2 - 1)}{(n_{eff}^2 + 2)} = \sum N_i \alpha_i \quad (1)$$

where B_{eff} is the effective polarizability of a unit of volume, n_{eff} is the effective refractive index of the multi component film, N_i and α_i are the number of molecules and molecular polarizability of each component, respectively. If a film consists of two components: matrix and pores and relative amount of pores (porosity, in other words) is P , then the equation (1) can be rewritten as follows:

$$B_{eff} = B_p \cdot P + B_m \cdot (1 - P) \quad (2)$$

or, taking into account the relation between polarizability and refractive index, as

$$\frac{(n_{eff}^2 - 1)}{(n_{eff}^2 + 2)} = \frac{(n_p^2 - 1)}{(n_p^2 + 2)} \cdot P + \frac{(n_m^2 - 1)}{(n_m^2 + 2)} \cdot (1 - P) \quad (3)$$

where subscripts p and m denote refractive indices of pores and matrix, respectively. The equations (2) and (3) are valid regardless presence or absence of any substance in pores. When at zero toluene pressure all pores are empty, $n_p=1$ and, therefore, $B_p=0$. In this case, the first term of equation (2) turns to 0 and the equation can be written as:

$$B_0 = B_m \cdot (1 - P) \quad (4)$$

where B_0 denotes polarizability of the film at 0 toluene pressure. At the saturated pressure, when all the pores are filled with toluene equation (2) becomes

$$B_{sat} = B_{tol} \cdot P + B_m \cdot (1 - P) \quad (5)$$

where B_{sat} is the polarizability of the film at saturated toluene pressure and B_{tol} is the polarizability of toluene. Combining equations (4) and (5) one can easily express porosity through polarizabilities:

$$P = \frac{B_{sat} - B_0}{B_{tol}} \quad (6)$$

or, taking into account the relation between polarizability and refractive index:

$$P = \frac{\frac{n_{sat}^2 - 1}{n_{sat}^2 + 2} - \frac{n_0^2 - 1}{n_0^2 + 2}}{\frac{n_{tol}^2 - 1}{n_{tol}^2 + 2}} \quad (7)$$

The last equation is used to calculate porosity. One can see that this equation does not contain unknown refractive index of the film matrix. Effective refractive indices of the empty film (n_0) and the film filled with toluene (n_{sat}) are measured while the refractive index of toluene is well known ($n_{tol}=1.4961$ at 632.8 nm at room temperature).

It should be noted that EP is able to measure porosity only if pores are interconnected and open to the surface. If a pore is disconnected from the surface, it will not change its status upon filling the film with toluene and will not contribute to total porosity obtained from the measurements. As a result, the real porosity could be higher than that measured by EP if a porous film contains closed disconnected pores.

The total porosity could be calculated if refractive index of the matrix is known. When pores are empty one can see from equation (3) that

$$P = 1 - \left(\frac{n_{eff}^2 - 1}{n_{eff}^2 + 2} \right) \bigg/ \left(\frac{n_m^2 - 1}{n_m^2 + 2} \right) \quad (8)$$

where n_{eff} is n_0 – refractive index of the film at zero toluene pressure. The equation (8) is also known in ellipsometry as a Bruggeman model of effective medium. This model should be used carefully as the refractive index of the matrix is not always known may differ from that of the dense material with the same chemical composition. Some materials (most of plasma deposited silicon oxycarbides SiOCH) exist in porous form only and determination of the matrix refractive index is complicated.

Pore size distribution

Pore size distribution is calculated from the isotherms (amount of the toluene adsorbed in a porous film as a function of relative pressure). Toluene is condensed in pores at pressures below saturation (P_0) because pressure in liquid below a concave meniscus (which is formed in a pore as in a capillary) is lower than that below flat surface. The meniscus curvature radius r_m and the relative pressure P/P_0 are related by the Kelvin equation:

$$\frac{1}{r_m} = \frac{RT}{\gamma_L \cos \theta} \ln \left(\frac{P}{P_0} \right) \quad (9)$$

where R is the universal gas constant, T is temperature (in K), γ and V_L are the surface tension and the molar volume of the liquid, respectively, and θ is the contact angle. By selecting solvent with small contact angle $\cos \theta$ is turned to 1. The mean radius of curvature of the meniscus is defined as:ⁱ

$$\frac{2}{r_m} = \frac{1}{r_1} + \frac{1}{r_2} \quad (10)$$

Here, r_1 and r_2 are two principal radii of the meniscus. These radii of curvature are defined by taking two planes at right angles to each other, and each of them passes through a normal vector from a point on the meniscus. Let us consider how the mean meniscus radius r_m and pore radius r are related to each other when capillary condensation occurs in pores.

During desorption, when all pores are filled with liquid, the meniscus has a hemispherical shape as depicted in Fig. 1(a). In that case two perpendicular planes containing the normal vector cross-section a pore along its axis and r_1 and r_2 are the pore radii in two perpendicular directions. If the pore has a cylindrical shape, then $r_1 = r_2 = r$ and from equation (10) it is obvious that

$$r_m = r \quad (11)$$

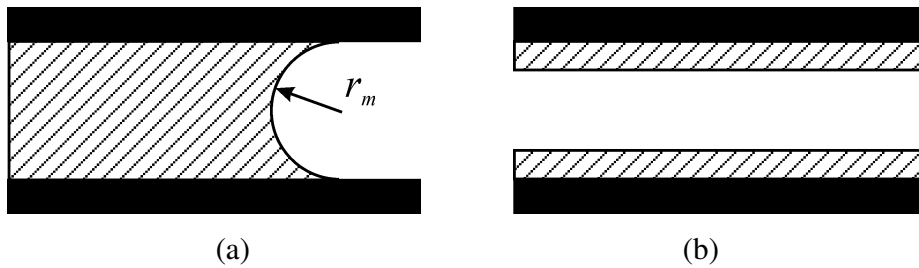


Fig. 1. The schematic diagram of the meniscus during (a) desorption and (b) adsorption.

During adsorption, when pores are initially empty, the meniscus takes the cylindrical shape as shown in Fig. 1(b). One plane containing the normal vector cuts the pore and, therefore, $r_1 = r$. Another plane perpendicular to the first one and containing the

normal vector cuts the pore along its axis and hence its principal radius $r_2 = \infty$. Using equation (10), we obtain

$$r_m = 2r \quad (12)$$

From this consideration we see that during adsorption higher pressure is needed for condensation to occur as compared to desorption. As a result of this difference, a typical adsorption-desorption isotherm usually exhibits a hysteresis loop (see Fig. 2). In EP, the relative adsorbate volume in pores is calculated from the effective refractive index of a film partially filled with solvent. Substituting refractive index at the saturated pressure n_{sat} by the refractive index at given pressure n_{pres} in equation (7), it is possible to calculate the relative volume of adsorbate at the given pressure.

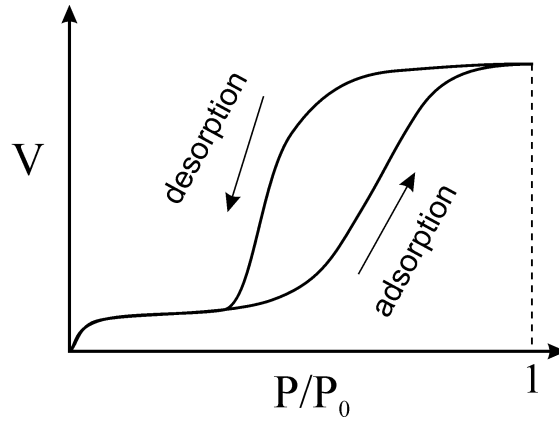


Fig. 2. Adsorption/desorption isotherm in mesoporous solids.

It should be noted that the meniscus radius is not exactly equal to the pore radius as some molecules could be adsorbed at pore walls prior to capillary condensation (the branch at low P/P_0 in Fig. 2). In this case, the meniscus radius will be smaller than the pore radius by the thickness t of the layer already adsorbed on pore walls:

$$r_m = r - t \quad (13)$$

The thickness t can be obtained from measurements of adsorption on non-porous flat surfaces having the same chemical composition as the porous material in question. The BET equation (named after developers of the adsorption theory Brunauer, Emmett and Tellerⁱⁱ) is used to estimate the t value:

$$t = \frac{t_0 \cdot C \cdot K \frac{P}{P_0}}{\left(1 - K \frac{P}{P_0}\right) \cdot \left(1 + K \cdot (C-1) \frac{P}{P_0}\right)} \quad (14)$$

where t_0 is the thickness of one monolayer of adsorbate, C is the BET constant, K is a coefficient satisfying the requirements that at $P=P_0$ $t \leq 5-6$ monolayers.ⁱⁱⁱ Equations (13) and (14) are used for correction of the pore radii calculated using the Kelvin equation (9). The correction becomes significant when pore radii are smaller than 5 nm.

Another approach is used for measuring radius of micropores (pores with sizes less than 2 nm). For such sizes comparable with size of adsorptive molecule (0.6 nm for toluene) the Kelvin equation 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. A method based on a semi-empirical theory developed by Dubinin and Radushkevich^{iv} (DR) is used to analyse films containing micropores. The DR method uses change in adsorption potential when the pore diameter is comparable with the size of the adsorptive molecules. The process involved is the micropore volume filling rather than layer-by-layer adsorption on the pore walls. The dependence of the adsorbate volume V on adsorption potential A

$$A = RT \ln \left(\frac{P_0}{P} \right) \quad (15)$$

is expressed by the following equation (known as the Dubinin-Radushkevich equation):

$$\ln V = \ln V_0 - BA^2 \quad (16)$$

where the logarithm of the amount adsorbed is linearly proportional to the square of the adsorption potential (B is a constant). Writing this equation explicitly in terms of pressure, we have:

$$V = V_0 \exp \left[-\frac{1}{(\beta E_0)^2} \left(RT \ln \frac{P}{P_0} \right)^2 \right] \quad (17)$$

where E_0 is called the solid characteristic energy towards a reference adsorbate, the parameter β is a function of the adsorptive only. The linear plot of $\ln V$ versus A^2 leads to determination of V_0 , which has the meaning of the total micropore volume, and βE_0 ,

which is the isosteric heat of adsorption. It was shown that micropore radius and the energy E_0 related to each other as

$$r = \frac{K}{2E_0} \quad (18)$$

where $K \approx 12$ is an empirical constant slightly changing with E_0 .^{iii,iv} Therefore, it is possible to extract the pore radius from the aforementioned linear plot. It should be noted, though, that the constant β is unknown and measurement of the absolute pore size could be ambiguous. As β , however, depends only on adsorptive, the comparison between porous materials is possible if the same adsorptive is used. The absolute pore size determination requires calibration with other methods. One should bear yet in mind that the meaning of a mean pore size becomes vague as pore sizes reach size of the molecule composing the porous solid.

Summary

Summarizing the described techniques we see that ellipsometry (especially SE) is able to determine refractive index, extinction coefficient and thickness of a thin film. Measuring change of refractive index of the porous film due to adsorption of solvent (toluene), ellipsometric porosimetry is able to determine

- **Porosity** using equation (7) derived from the Lorentz-Lorenz equation
- **Mesopore size** using the Kelvin equation (9) taking into account BET correction (14)
- **Micropore size** using Dubinin-Radushkevich equations (17,18)

ⁱ Defay and Prigogine, *Surface tension and adsorption*, Longman, London (1966).

ⁱⁱ S. Brunauer, P. H. Emmet, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

ⁱⁱⁱ S. J. Gregg and S. W. Sing, *Adsorption, surface area and porosity*, 2nd ed., (Academic press, NY, 1982).

^{iv} M. M. Dubinin, *Chem. Rev.*, **60**, 235 (1960).