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Characterization of porous dielectric films by ellipsometric porosimetry

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Ellipsometric porosimetry (EP) is a simple and effective method for characterization of porosity, average pore size, specific surface area and pore size distribution (PSD) in thin films deposited on top of any smooth solid substrate. This method is a new version of adsorption porosimetry. *In situ* ellipsometry is used to determine the amount of adsorptive adsorbed in the film. Change in refractive index is used for calculation of the quantity of adsorptive present in the film. The EP allows the study of thermal stability, adsorption and swelling properties of porous films. Room temperature EP based on the adsorption of vapour of some organic solvents and a method for calculating the porosity and PSD are discussed.

1. Introduction

Porous films are extremely important for various practical applications. These are different types of antireflective coating, gas sensors, *etc.* A new application of porous films is related to the advanced ultra large scale integrated (ULSI) circuits technology. The porous, so called low-K dielectric films, are used to reduce capacitance between interconnects and improve the switching speed in ULSI circuits. Porosity and PSD define dielectric, mechanical, thermal and chemical properties of the films. Increasing the porosity drives the dielectric constant down, but it degrades the mechanical and chemical properties of the film. Therefore, characterization of pore structure in thin films is an extremely important problem.

Porosity of bulk materials is measured by *stereology analysis* such as microscope techniques, *intrusive methods* such as gas adsorption, mercury porosimetry, *etc.*, and *nonintrusive methods* such as radiation scattering, wave propagation, *etc.*, [1]. However, most of them have limitations to be applied for the thin film characterization.

The principal feature of EP is to utilize the change of optical characteristics of the porous films during the vapour adsorption and desorption to determine the mass and adsorbate condensed/adsorbed in pores. The optical characteristics of the film skeleton and of the adsorptive are used for the calculations. The choice of an adsorptive for the room temperature porosimetry is an important issue. The adsorptive should be a volatile liquid, because of the need to work near the equilibrium pressure P_0.

In this work, fundamentals and practical applications of EP are presented. *In situ* ellipsometric measurements were performed using a custom-built high-vacuum tool. Adsorption of toluene ($C_6H_5CH_3$), heptane (C_7H_{16}), carbon tetrachloride (CCl_4) and isopropyl alcohol (IPA: $i{-}C_3H_7OH$) vapours was used for the comparative analysis.

2. Fundamentals of ellipsometric porosimetry

Relation between the optical characteristics and the material composition in a multicomponent system is described by the Lorentz–Lorenz equation

$$B = \sum N_i \alpha_i = \frac{3(n^2-1)}{4\pi(n^2+2)} \tag{1}$$

where B is the polarizability of a unit of volume, N_i and α_i are the number of molecules and the molecular polarizability of the material components, $n = \sqrt{\varepsilon_r}$ is the refractive index of the film. If n_s is the refractive index of the film skeleton with the volume polarizability B_s, n_p is the measured refractive index of the porous film and B_p is the volume polarizability calculated from n_p, the relative film porosity V is equal to

$$V = 1 - \frac{B_p}{B_s} = 1 - \left[\frac{(n_p^2-1)}{(n_p^2+2)}\right] \Big/ \left[\frac{(n_s^2-1)}{(n_s^2+2)}\right]. \tag{2}$$

This approach and Eq. (2) are also valid if a liquid with a known refractive index fills the pores. In this case the absorbate amount is calculated using the refractive index and density of the liquid adsorptive. The ellipsometry allows us to measure both the refractive index and the film thickness d (*i.e.*, the effect of the film swelling). The adsorptive volume in pores is calculated as

$$V_{ads} = \frac{V_m}{\alpha_{ads} d_1}(B_1 d_1 - B_0 d_0) \tag{3}$$

where: V_{ads} = (adsorbate volume/film volume) is the relative volume of the liquid adsorbate in the pores (volume of open pores), B_0 and B_1 are the volume polarizability of the film before and after adsorption, d_0 and d_1 are the film thicknesses before and after adsorption, respectively. The V_{mol} is the molecular volume of the adsorptive and α_{ads} is the polarizability of the adsorptive molecule. The relative volume of open and close pores, calculated by comparison of the results obtained with Eqs. (2) and (3) gives us information related to the pore interconnectivity.

In calculation of PSD use is made of the phenomenon of progressive emptying of pores initially filled at $P = P_0$. The calculations are based on analysis of hysteresis loop that appears due to the adsorption and desorption of vapour. The hysteresis loop appears because the radius of curvature of liquid meniscus is different during the adsorption and desorption. The vapour condenses in pores at the vapour pressure P being less than the equilibrium pressure of a flat liquid surface P_0. Dependence of the relative pressure P/P_0 on the meniscus curvature is described by the Kelvin equation

$$\frac{1}{r_1}+\frac{1}{r_2}=-\frac{RT}{\gamma V_L \cos\theta}\ln\left(\frac{P}{P_0}\right) \tag{4}$$

where γ and V_L are surface tension and molar volume of the liquid adsorptive, respectively, θ is the contact angle of the adsorptive. The curvature radii r_1 and r_2 define pore sizes. In the case of cylindrical pores $r_1 = r_2$ and $(1/r_1+1/r_2) = 2/r_k$. The radius r_k is dimension characteristic of the capillary and often termed the Kelvin radius. If the radius of a cylindrical pore is r_p, then $r_p = r_k+t$, where t is the thickness of the layer already adsorbed on the pore walls. Values of t are obtained from the data for the adsorption of the same adsorptive on a non-porous sample having a chemically similar surface and are defined by the BET equation [3].

The initial experimental data for calculating the adsorption isotherm and PSD are the ellipsometric characteristics Δ and Ψ. The computer software developed at the Institute of Semiconductor Physics allows calculating the change of the film thickness and refractive index of the film during the adsorption and desorption, PSD and cumulative surface area.

Specific surface area is an important characteristic of porous materials. The BET method for the calculation of the specific surface area A is well known. Our software directly calculates the cumulative surface area [3]. The surface areas of each small group of pores δA_i are calculated from the corresponding pore volume and pore radius as $\delta A_i = \delta V_i/r_i$. By assuming the values of δA_i over the whole pore system a value of the cumulative surface area is obtained.

A possible problem of the reliability of the PSD calculation can be related to the range of validity of the Kelvin equation. The most important problems deal with the change of surface tension of the adsorptive in fine pores and surface tensile effects inside of fine pores. Therefore, it is necessary to find additional proofs to exclude the calculation errors. A simple way to examine the reliability of measurements is the Gurvitsch test that can be carried out using the same experimental tool. The idea of the Gurvitsch rule [4] is that a volume of a liquid should be the same for all applicable adsorptives in a given porous solid. In pores equal to several molecular sizes, change of the surface tension and molecular volume of adsorbate can be significant. If we used several adsorptives with differential values of surface tension and molecular volume, and if they gave us the same value of pore size, this would be a proof that the adsorptives used are still outside of these limitations.

3. Experimental results and discussion

Figure 1 shows a typical change in the ellipsometric angles Δ and Ψ observed during the vapour adsorption and desorption in a mesoporous film. The initial point corresponds to $P = 0$ and the final one to the relative pressure equal to unity $(P = P_0)$. The experimental points are far from the theoretical curve calculated for

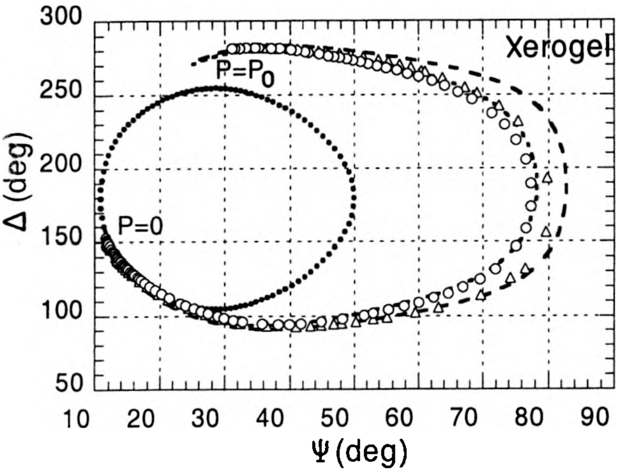

Fig. 1. Change of the ellipsometric angles Δ and Ψ during adsorption and desorption of the toluene vapour in mesoporous xerogel and HSSQ films. .... $n = 1.183$, d — various; oooo adsorption, △ — desorption; —— $d = 465$ nm, n — various; - - - - $d = 445$ nm, n — various.

the change of the film thickness at a constant refractive index ($n = 1.183$ for this xerogel film). All experimental data were well described by a model using the change of the refractive index without remarkable change of the film thickness. Some difference in the Δ and Ψ values during the adsorption and desorption deals with insignificant and reversible swelling and shrinkage. Full porosity of the xerogel film was determined by multiangle ellipsometric measurements before adsorption (at $P = 0$) and calculated by Eq. (2). This value was equal to 0.57 (57%). Concentration of open pores was determined by the solvent adsorption and Eq. (3).

Adsorption isotherms calculated from the experimental data presented in Fig. 1 are shown in Fig. 2. One can see that the saturation points for the different adsorptives are very close to one another and correspond to open porosity equal to 0.64. Therefore the Gurvitsch rule is valid in this case. Comparing this value with full film porosity allows us to conclude that all pores in this film are interconnected. The fact that the measured "open porosity" is greater than "full porosity" is connected with the film swelling that can also be observed from Δ/Ψ behaviour. These results allow us to conclude that the chosen adsorptives give adequate information about the film porosity in the mesoporous films. The data presented in Fig. 2 were used for the calculation of PSD (Fig. 3). One can see that all adsorptives give very similar PSD.

The average pore radius in these films was calculated from the adsorption and desorption curves. In the case of cylindrical meniscus that forms during the adsorption, r_2 in Eq. (4) is equal to ∞ and the mean pore size calculated from the adsorption curve should be twice as high as the value calculated from the desorption curve. One can see that this suggestion is valid in these films. Therefore, the pores are almost cylindrical.

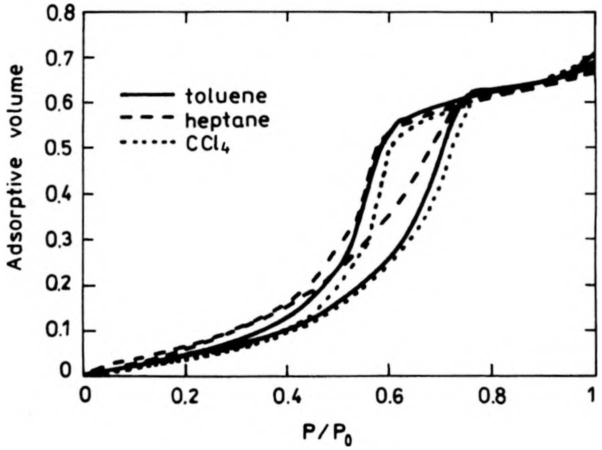

Fig. 2. Adsorption/desorption isotherms of different adsorbates in mesoporous xerogel film.

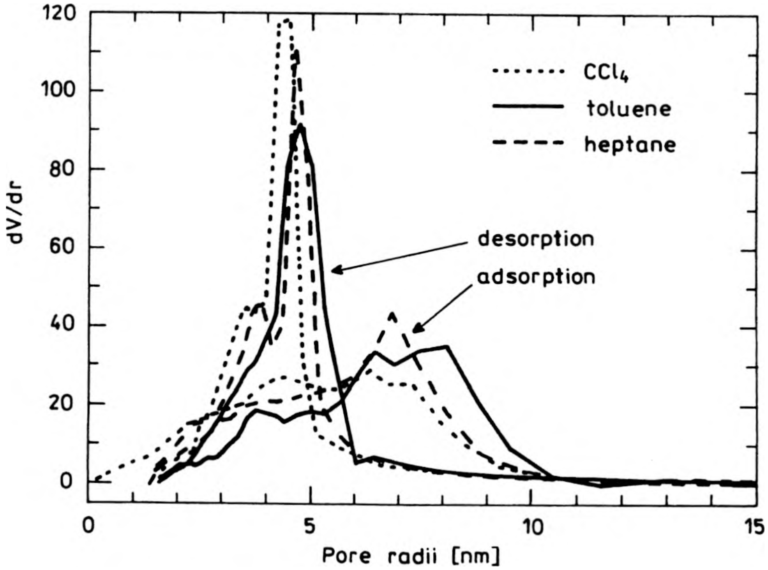

Fig. 3. Pore size distribution in mesoporous xerogel film calculated from the adsorption and desorption isotherms of different solvents.

The PSD widths obtained from the desorption and adsorption curves are quite different. This phenomenon is related to the branched distribution of pores inside the film. While the solvent desorption occurs through definite effective necks characterizing a surface region of the film, the adsorbate is distributed in the pore branches inside the film during the adsorption and a wide range of different types of meniscus can form at the same time. Therefore, the desorption curves provide a simplified image and are more straightforward for a standard characterization of the effective porosity of the film.

4. Conclusions

A new modification of the adsorption porosimetry (ellipsometric porosimetry) has been develped for the thin film application. It is a reliable and simple method for non-destructive characterization of porous dielectric films. This method allows the measurement of pore size distribution at room temperature in thin films directly deposited on top of any smooth solid substrate. A small external surface area ($< 1\ \mathrm{mm}^2$) is sufficient to carry out this analysis, making the method well suited for the microelectronic industry.

The EP provides similar information as the microbalance porosimetry. However, it is more informative than the traditional microbalance porosimetry: structural chnges (swelling) during the adsorption/desorption processes can also be analyzed.

Experimental tool and software for the PSD analysis by ellipsometric measurements of the adsorption of the organic solvents vapours in porous films have been developed. Round robin evaluation of various porous films and several different techniques such as EP, nitrogen porosimetry, SANS and SAXS have shown a good agreement between the results of the analysis. These results were reported in our previous publication [5].

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