Determination of pore size distribution in thin films by ellipsometric porosimetry

M. R. Baklanov[a)]
IMEC, B-3001 Leuven, Belgium

K. P. Mogilnikov, V. G. Polovinkin, and F. N. Dultsev
Institute of Semiconductor Physics SB RAS, 630090 Novosibirsk, Russia

(Received 26 August 1999; accepted 28 February 2000)

We show that ellipsometric porosimetry can be used for the measurement of the pore size distribution in thin porous films deposited on top of any smooth solid substrate. In this method, *in situ* ellipsometry is used to determine the amount of adsorptive, which is adsorbed/condensed in the film. Changes in refractive index and film thickness are used to calculate the quantity of adsorptive present in the film. Room temperature porosimetry based on adsorption of vapor of organic solvents has been developed. In this article, a method of calculation of pore size distribution and results of measurements on mesoporous and microporous xerogel films is discussed. Examination of the validity of the Gurvitsch rule for various organic adsorptives (toluene, heptane, and carbon tetrachloride) is carried out to assess the reliability of measurements of pore size distributions by ellipsometric porosimetry. © *2000 American Vacuum Society.* [S0734-211X(00)06503-3]

I. INTRODUCTION

Low-dielectric-constant (low-*K*) films are in demand to reduce capacitance between interconnects and improve the switching speed in ultralarge scale integrated circuits. Popular at present, organic low-*K* polymer films without permanent dipole moment allow a reduction of the permittivity value down to 2.5–2.8. However only porous dielectric films can provide a decrease in permittivity to below 2. Porous dielectric films (both inorganic and organic) are thus becoming very important for future microelectronic technology. Film porosity and pore size distribution (PSD) define dielectric, mechanical, thermal and chemical properties of the porous films and their feasibility to be used in microelectronic technology. Increasing the porosity drives the dielectric constant down, but it degrades the mechanical and chemical properties of the film. Therefore methods are needed to reliably determine PSD and pore volume.

We show that the relative pore volume can be determined by spectroscopic ellipsometry and porosity/density simulation. X-ray reflectance, cross sectional focused ion beam combined with scanning electron microscopy technique, Rutherford backscattering spectroscopy, and small-angle neutron scattering (SANS) have also been used to determine the mean pore size.[1] Some methods of PSD measurement have already been applied to low-*k* dielectric films. These are different versions of adsorption Brunauer–Emmet–Teller[2] (BET) porosimetry, positron annihilation lifetime spectroscopy (PALS), Doppler broadening positron annihilation spectroscopy, and small angle x-ray scattering (SAXS). It has been reported that SANS also gives information about the PSD in porous dielectric films. These results were in an agreement with the nitrogen adsorption porosimetry using a powder sample.[1]

Adsorption porosimetry is considered as a reference to examine the feasibility of new techniques for PSD measurement since it is the most reliable and simple method to determine PSD. The adsorption characteristics and basic equations necessary for the PSD calculations have been analyzed and are well documented.[2] A common method to apply adsorption porosimetry is to monitor adsorption and desorption of nitrogen vapor near the boiling point by direct weighing of the adsorptive, which is adsorbed/condensed in the pores. However, the sensitivity of the traditional microbalance technique used for weighing allows us to analyze only large powder-like samples. The mass of a 1 μm thick dielectric film deposited on top of a 8 in. silicon wafer is three orders of magnitude less than the mass of the wafer. Therefore it is almost impossible to measure the change of the film mass from nitrogen adsorption using this technique. Films from several silicon substrates need to be collected in order to get enough material and prepare a powder-like sample to be analyzed by microbalance porosimetry. The low temperature of traditional nitrogen porosimetry creates additional problems. All these facts show that the development of a nondestructive and room temperature porosimetry for thin film applications is crucial for advanced microelectronic technology.

Several articles on the measurement of the pore size distribution by adsorption porosimetry in thin films have already been published. In these articles the measurement of the adsorption/desorption processes were carried out by quartz crystal microbalance (QCM),[3,4] surface acoustic wave (SAW) sensor[5,6] and by ellipsometry.[7,8] In the QCM and SAW methods the porous film must be deposited on top of a special sensor. In principle, these methods are closest to classical adsorption porosimetry because they use mass determination of the adsorbed vapors. However, the necessity to deposit the film on top of special sensors limits their application in the microelectronic industry. SANS, PALS, and SAXS can also be used to measure PSD in films deposited

[a)]Author to whom correspondence should be addressed; electronic mail: baklanov@imec.be

onto a silicon substrate, but these methods are more complicated and expensive.

Ellipsometric porosimetry (EP) is a new version of adsorption porosimetry. The principal feature of this method is its utilization of the change of the optical characteristics of the porous film during vapor adsorption and desorption to determine the mass of an adsorptive condensed/adsorbed in pores instead of direct weighing. Ellipsometric porosimetry is more informative and promising in comparison to classical adsorption porosimetry, and is much more simple than, for example, SANS or positron annihilation methods.

The most important advantages of ellipsometric porosimetry are:

(1) All measurements can be carried out on a porous film, deposited directly on top of a silicon wafer or any smooth solid substrate. Additional layers between the silicon substrate and the porous dielectric film do not induce any problems for the measurements if their optical characteristics are known. The optical characteristics of the intermediate layers can be determined using the same ellipsometer prior to deposition of the porous film.

(2) Because a laser probe is used, small surface areas can be analyzed. Therefore EP can be used on patterned wafers, which is necessary for compatibility with microelectronic technology.

(3) Room temperature PSD measurements can be made using EP with organic solvents[7,8] and do not have the problems associated with low-temperature nitrogen porosimetry.

As mentioned above, 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. There are several methods for performing these calculations based on various equations (Lorentz–Lorenz, Newton–Laplace, Bragg–Pippard, etc.[9]). The optical characteristics of the dense part of the porous media (i.e., the frame of the porous film) and of the liquid adsorptive are used in these calculations. The various equations give similar results, however, the Lorentz–Lorenz equation is more widely used.

The correct choice of an adsorptive for room temperature porosimetry is an important issue. The adsorptive should be a volatile liquid, because of the need to work near the equilibrium pressure ($P=P_0$). If chosen correctly, the typical problems related to low temperature nitrogen porosimetry can be avoided. This advantage is more important for organic polymer films because of their sensitivity to temperature. It was shown[3,4,7,8] that some organic solvents can be used for this purpose. Nonpolar solvents, without permanent dipole moment, are preferred. Measurements by ellipsometric porosimetry with these solvents are in a good agreement with the results of microbalance porosimetry.[7,8]

In this work, results of porosity measurement and PSD calculations based on adsorption ellipsometric measurements are presented. *In situ* ellipsometric measurements were performed using a custom-built high-vacuum tool.[7,8] Two types of dielectric films were used in the experiments. Mesoporous and microporous silica films with porosity of 64% and 25%, respectively, were deposited on top of silicon wafers by sol–gel technology. [According to classification of the International Union of Pure and Applied Chemistry (IUPAC) published in a Manual ''Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity'' pores with widths between 2 and 50 nm are called *mesopores*. Pores with width not exceeding 2 nm are called *micropores*.[10]] Adsorption of toluene ($C_6H_5CH_3$), heptane (C_7H_{16}) and carbon tetrachloride (CCl_4) vapors was used for comparative analysis. All adsorption measurements were done at room temperature. We showed recently[8] that ellipsometric and microbalance porosimetry give very similar pore size distribution for the chemical vapor deposited SiO_2 films. In this work, an additional examination of reliability of the PSD measurements by ellipsometric porosimetry has been carried out. This examination is based on the validity of the Gurvitsch rule for different organic solvents, and allows us to conclude that room temperature ellipsometric porosimetry with organic solvents gives adequate information to determine the film porosity and pore size distribution in thin films.

II. METHOD OF CALCULATIONS

Adsorption porosimetry is based on analysis of the hysteresis loops that appear due to the processes of capillary condensation and desorption of a vapor out of porous adsorbents. The hysteresis loops appear because the effective radius of curvature of condensed liquid meniscus is different during the adsorption and desorption processes. The adsorptive vapor condenses in pores even if the vapor pressure P is 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

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

where γ and V_L are surface tension and molar volume of the liquid adsorptive, respectively. The principal curvature radii r_1 and r_2 define pore sizes. In the case of cylindrical pores, $r_1=r_2$ and

$$\left(\frac{1}{r_1}+\frac{1}{r_2}\right)=\frac{2}{r_k}.$$

The radius r_k is often termed the Kelvin radius.[10] 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 nonporous sample having a similar surface and is defined by the BET equation

$$t=\frac{d_0CK\cdot(P/P_0)}{[1-K(P/P_0)]\cdot[1+K(C-1)(P/P_0)]}, \tag{2}$$

where d_0 is the thickness of 1 monolayer, C is the BET constant, and K is a coefficient which satisfies the requirement that at $P=P_0$, $t\leqslant 5$–6 monolayers.[2] The BET constant is $C=\exp[(q_1-q_L)/RT]$, where q_1 and q_L are the heat of adsorption in the first monolayer and the molar heat of con-

densation, respectively. The commonly used coefficient K was introduced by Brunauer and his co-workers to obtain a better agreement between experimental isotherm data in the multilayer region (Ref. 2, p. 53).

The relation between the optical characteristics and the material composition in a multicomponent system can be described by the Lorentz–Lorenz equation

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

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. This formula, particularly, is used to calculate the density of a porous material from the measured values of the refractive indices determined by spectroscopic ellipsometry. If n_b is the refractive index of the dense part of material with the volume polarizability B_b, n_p is the measured refractive index of the porous film and B_p is the volume polarizability calculated from n_p, the pore volume is equal to

$$V=1-\frac{B_p}{B_b}=1-\left[\frac{(n_p^2-1)}{(n_p^2+2)}\right]\Big/\left[\frac{(n_b^2-1)}{(n_b^2+2)}\right]. \tag{4}$$

It is obvious that this approach is also valid if pores are completely or partially filled by a liquid (condensed adsorptive) with known refractive index. In this case the adsorptive amount in the pores can be calculated using refractive index and density values of the adsorptive.

Ellipsometry allows us to measure both the refractive index and the film thickness d (i.e., the effects of the film swelling). In this case the adsorptive volume in pores can be calculated as

$$V_{\text{ads}}=\frac{V_m}{\alpha_{\text{ads}}\cdot d_1}(B_1d_1-B_0d_0), \tag{5}$$

where V_{ads} is the volume of the liquid adsorptive in the 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 thickness before and after adsorption, respectively, V_{mol} is the molecular volume of the adsorptive and α_{ads} is the polarizability of the adsorptive molecule.

The initial experimental data for the calculation of the adsorption isotherm are the ellipsometric characteristics Δ and Ψ. Special software, developed at the Institute of Semiconductor Physics, allows us to calculate the change of the film thickness and refractive index of the film during the adsorption and desorption, the average pore size, and the pore size distribution. The change of the adsorptive volume is calculated from the change of the refractive index using Eq. (4). The dependence of the adsorptive volume on the relative pressure P/P_0 is an adsorption isotherm, which is used to calculate the PSD. Calculations of the pore size using the Kelvin equation is based on the picture of a progressive emptying of a porous system initially filled at $P=P_0$. It is also assumed[2] that all pores with radii smaller than the critical one are filled by the adsorptive. All other pores (with radii higher than the critical one) are empty but their sidewalls are covered by the adsorptive with thickness t [Eq. (2)].

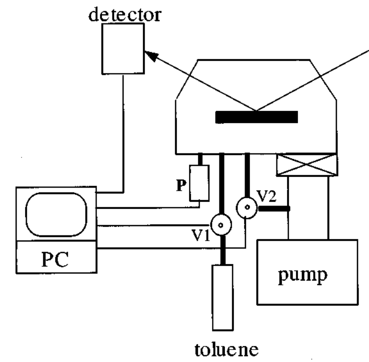

FIG. 1. Schematic of the EP tool used in this work.

In order to exclude effects of vapor condensation on top of the film, all calculations presented here were carried out for the model with cylindrical pores and for $P<0.9P_0$.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In situ ellipsometric measurements were performed using a high-vacuum system designed for this purpose (Fig. 1). The EP setup consists of an ellipsometer ($\lambda=632.8$ nm), a pumping system, and a source of an organic solvent (liquid adsorptive). The vacuum chamber needs to be pumped down before allowing an adsorptive into the vacuum chamber. The sample can be annealed up to 600 °C to empty all pores before adsorption. Vapor of the organic solvent is introduced into the vacuum chamber using a precise and controllable valve (V1). This step has to be done as slow as necessary to provide adsorption–desorption equilibrium between the adsorbed phase and the gas phase. The same requirement applies when the vapor is pumping out. For this purpose the system has a controllable valve V2 in the bypass line. Changes of optical characteristics of the sample during the adsorption/desorption processes are measured by ellipsometry. These data are used for calculation of the mean porosity and pore size distribution as described in Sec. II.

As mentioned above, the mesoporous and microporous silica films were deposited on top of silicon wafers by sol–gel technology. All adsorption measurements were done at room temperature. Special multiangle ellipsometric measurements of the as deposited films showed that the films are optically homogeneous (pore size is much less than the laser wavelength). The initial refractive indices of the films at $\lambda=632.8$ nm were 1.18 and 1.35 for the mesoporous and microporous films, respectively. Porosity of the films calculated from n_p by Eq. (4) were equal to 64% and 25%, respectively.

Figure 2 shows the typical behavior of the ellipsometric angles Δ and Ψ observed during the vapor adsorption and desorption. The arrows show how the ellipsometric angles are changed when the relative pressure of the CCl_4 vapor is varied from zero to unity (adsorption) and back from unity to zero (desorption). The initial point corresponds to the zero relative pressure ($P=0$) and the final one to the relative pres-

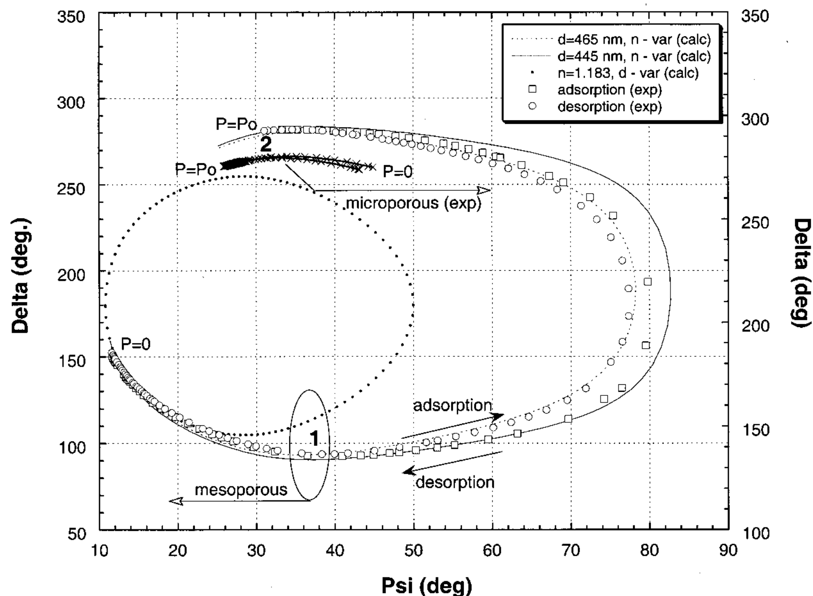

FIG. 2. Change of the ellipsometric characteristics Δ and Ψ occurring during the adsorption and desorption of CCl_4 vapor in mesoporous (1) and microporous (2) silica films. A theoretical curve assuming only change of the film thickness at a constant refractive index (dotted line) and two calculated curves for constant film thickness at varying refractive indices (continuous and dashed lines) are also shown for the mesoporous silica film.

sure equal to unity ($P=P_0$). One can see that for the silica film with 25% porosity changes of the ellipsometric characteristics are relatively small (Fig. 2, curve 2). However, these changes are significant as the sensitivity of the *in situ* ellipsometry for the determination of both polarization angles Δ and Ψ were better than 0.01°.

Note that the adsorption and desorption curves in the $\Delta-\Psi$ plot sometimes show a hysteresis loop (Fig. 2, experimental data 1). This hysteresis loop is related to a reversible swelling and shrinkage of the silica film during the adsorption/desorption cycle. These effects do not significantly affect the PSD calculation for the mesoporous xerogel films. However, they can give additional information about the elastic properties of the porous film, which is an important capability of the ellipsometric porosimetry in comparison with classic microbalance porosimetry. Microbalance porosimetry cannot provide this information, while the film swelling can be significant even with low temperature adsorption. These phenomena are related to a decrease of surface free energy during adsorption and were observed for the first time by Amberg and McIntosh,[11] and Yates.[12] For instance, Yates observed the swelling of porous glasses during the adsorption of Ar, N_2, and O_2 at 79 and 90 K. These conditions are typical for the traditional nitrogen porosimetry. The effect of swelling is especially crucial for porous organic films. Results of such kinds of investigations will be presented in a future publication.

The experimental data of Fig. 2 are well described by a model based on the change of the refractive index without significant change of the film thickness. However, it was established that the calculated adsorptive volume is slightly higher than the film porosity calculated from the multiangle ellipsometric measurements and the porosity/density simulation for the xerogel film before vapor adsorption. Multiangle ellipsometric measurements of the xerogel film in a vacuum chamber completely filled by saturated toluene vapor showed that the xerogel film had swelled during the adsorption by $\approx 5\%$. This value is in a good agreement with the difference of film porosity calculated from the change of the refractive index and the adsorptive volume.

Adsorption isotherms calculated from the experimental data presented in Fig. 2 are shown in Fig. 3. One can see that the saturation point for the different adsorptives is very

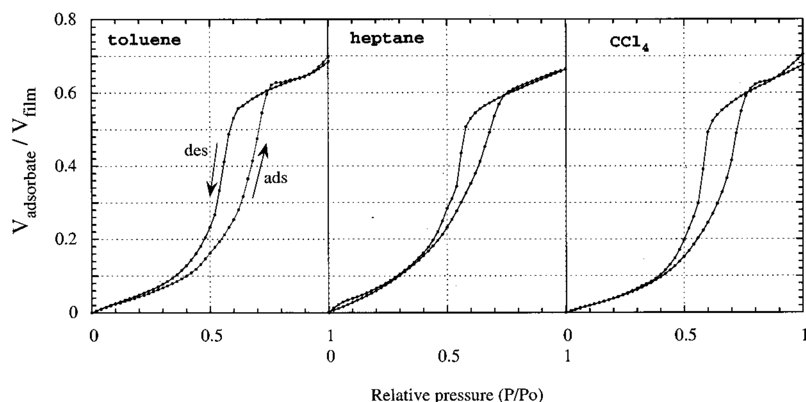

FIG. 3. Adsorption/desorption isotherms of toluene, heptane, and CCl_4 vapors in the mesoporous silica (xerogel) film.

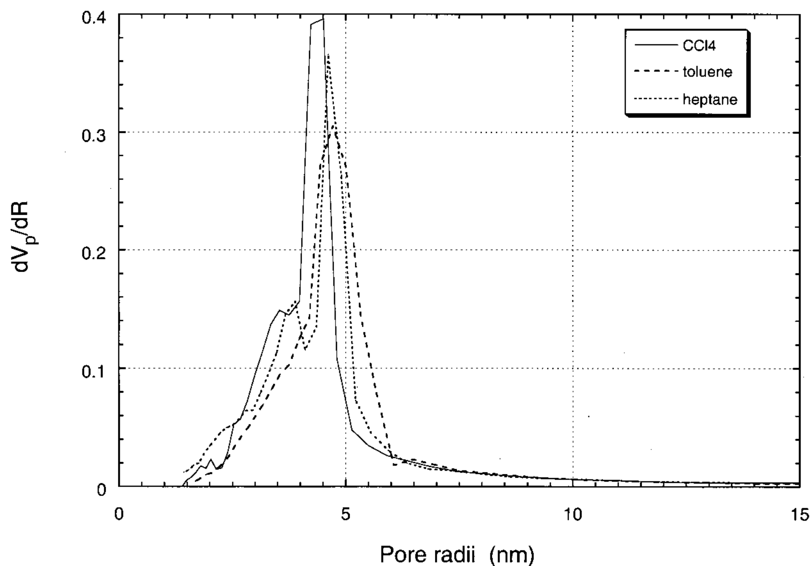

FIG. 4. Pore size distribution in the mesoporous silica film calculated from the desorption isotherms.

close; therefore the Gurvitsch rule[2,13] is valid in these cases. The idea of the Gurvitsch rule, embodied many years ago,[13] is that a volume of a liquid (by use of the normal liquid density) should be the same for all applicable adsorptives in a given porous solid. Therefore this experimental observation allows us to conclude that the chosen adsorptives give adequate information about the film porosity. This fact also proves the feasibility of ellipsometric measurements for the PSD determination at room temperature.

The observed hysteresis loops (Fig. 3) have a shape intermediate between so-called type H1 and H2.[10] (We use the IUPAC classification of the adsorption isotherms and hysteresis loops.[10] According to this classification six types of physisorption isotherms and four types of hysteresis loops reflect the different types of adsorbents. This classification allows us to obtain some preliminary information about the nature of the solid adsorbent.) Type H1 adsorption/desorption hysteresis loops are often associated with porous materials that consist of agglomerates or compacts of approximately uniform spheres in a fairly regular array, and hence have narrow distributions of pore size. Many porous adsorbents (e.g., inorganic oxide gels and porous glasses) tend to give type H2 loops, but in such systems the distribution of pore size and shape is not well defined. These conclusions are in agreement with transmission electron microscopy (TEM)/cross-sectional TEM analysis of xerogel and aerogel films.[14]

All isotherms shown in Fig. 3 correspond to the type 5 (IUPAC classification) of adsorption isotherm.[2] This type of adsorption isotherm is typical for weak substrate–adsorptive interaction. It is known that this type of adsorptive normally cannot provide an accurate calculation of the inner surface area because changes of the adsorption characteristics after saturation by the first monolayer are not pronounced [small value of the BET constant C in Eq. (5)]. This is probably a feature of interaction of the used solvents with the porous silica films. However, organic solvents more suitable for this purpose can be found. For example, a better shape of the adsorption isotherms (close to type 4) was obtained using benzene vapor on silica.[6]

The data presented in Fig. 3 were used for the calculation of PSD (Fig. 4). One can see that all three adsorptives give very similar PSD values. This fact also proves the method reliability. Desorption curves are normally used for the PSD calculations.[2] Therefore, the average pore radius in the mesoporous silica film was close to 4.5 nm (Fig. 4). In the case of cylindrical meniscus, r_2 in Eq. (1) is equal to ∞ and the mean pore size calculated from the adsorption curve should be two times higher than the value calculated from the desorption curve.[2] The experimental data are in an agreement with this theoretical prediction for cylindrical pores (Figs. 4 and 5). While the actual pore geometry in the xerogel film is more complicated, this result suggests that a cylindrical pore model is an acceptable approach for the PSD calculations.

An additional observation is that 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 desorption of the adsorptive occurs through definite necks characterizing a surface region of the film, the vapor is distributed in 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 are more straightforward for characterization of the film porosity, which is the traditional approach in all types of adsorption porosimetry.

The adsorption isotherm for the 25% porous silica film is shown in Fig. 6. As mentioned above this film was microporous (mean pore size less than 2 nm). The adsorption isotherm is of type 1 and is typical for a microporous material. In this case, the vapor condensation occurs at pressures where the liquid adsorptive meniscus cannot form. It has already been realized that in very fine pores with widths on the order of a few molecular diameters, the Kelvin equation no longer remains strictly valid. Not only would the values of the surface tension and the molar volume deviate from

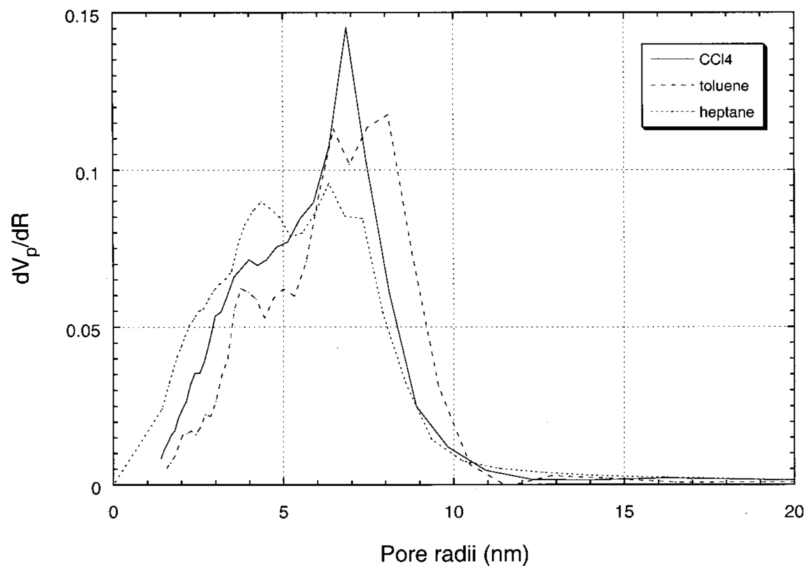

FIG. 5. Pore size distribution in the mesoporous silica film calculated from the adsorption isotherms.

those of the bulk liquid adsorptive, but the concept of a meniscus would eventually become meaningless.[2] In this case, calculation of PSD is not straightforward because it can give significant errors (even if the hysteresis loop is observed). Figure 6 shows that the adsorption/desorption isotherms for the chosen adsorptives are different for the microporous films while they are very similar for the mesoporous film (Fig. 3). This phenomenon results from the different adsorptive/surface interactions and is a general limitation of adsorption porosimetry for microporous materials. A quite large difference between the porosity value calculated from the refractive index and from the volume of the adsorbed vapors (25% and $\geqslant 12\%$, respectively) is another feature of microporous films. Porosity calculated from the condensed liquid was equal to 15.2% for toluene, 13.4% for CCl_4 and 12.7% for heptane. As mentioned above this difference is related to different adsorptive/surface interactions and also to problems with the liquid penetration into fine micropores. Therefore the Gurvitsch rule does not work well in this case. This is of little concern to the microelectronic industry, since only relative pore volume of microporous films is important because it defines the value of the dielectric constant. The relative pore volume can be calculated with a high accuracy (several percent) from the spectroscopic or the multiangle ellipsometric measurements.

These observations also suggest that ellipsometric porosimetry can be used to estimate a percentage of closed and open pores. This can be simply done by comparing the average porosity calculated from the porosity/density simulation (without an adsorptive) and the volume of the adsorbed liquid after saturation. These applications of the EP are important when the film porosity is below the percolation threshold or when the simple percolation law does not describe the porosity (as in the case of the ordered porosity).

IV. CONCLUSION

A new modification of adsorption porosimetry, ellipsometric porosimetry, has been developed for thin film application. It is a reliable and simple method for nondestructive characterization of mesoporous dielectric films. This method allows the measurement of pore size distribution at room temperature in thin films directly deposited on Si or any smooth solid substrate. Intermediate layers between the silicon substrate and the porous film do not create any problem for the measurements if their optical characteristics are

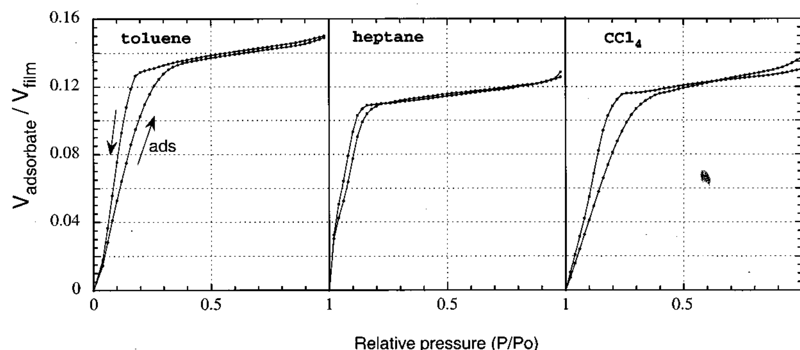

FIG. 6. Adsorption/desorption isotherms of toluene, heptane, and CCl_4 vapors in the microporous silica film.

TABLE I. Comparison of realized possibilities of different types of adsorption porosimeters.

	Method of PSD analysis (type of porosimeter)		
	Classic microbalance	Surface sensor	Ellipsometric
Temperature	Liquid nitrogen temperature	Liquid nitrogen and room temperature	Room temperature
Adsorptive	Nitrogen	Nitrogen Organic vapors	Organic vapors
Pore size (nm)	2–25	2–25	2–25
Ability to analyze a film on top of Si wafer	Very limited (depends on the tool sensitivity)	No	**Yes**
Surface area required	Very large	Area of surface sensor	**Less than 1 mm^2**
Measurement errors related to film swelling	Can be significant	Can be significant	**Film swelling can be measured and taken into account**
Compatibility with microelectronic technology	No	No	**Yes**

known. A small surface area (<1 mm^2) is sufficient to carry out this analysis, making the method well suited for the microelectronic industry.

We have shown that the ellipsometric porosimetry provides similar information to microbalance porosimetry. However, it is more informative than the traditional microbalance porosimetry, because structural changes (film swelling) during the adsorption/desorption processes can also be analyzed. This last information is extremely important in advanced microelectronic technology, for instance, for optimization of the wet postetch cleaning conditions and chemistries in the organic low-*K* dielectric/Cu assemblies.[15] A comparison of the most important characteristics of different types of adsorption porosimetry is presented in Table I.

Various adsorptives for room temperature porosimetry have been selected and examined. The molecular and optical characteristics of various organic solvents have been studied in relation to the PSD calculation. Verification of the Gurvitsch rule proves that these adsorptives are applicable for room temperature porosimetry and that the corresponding data obtained by the room temperature ellipsometric porosimetry are reliable.

Estimation of the mean pore length can also be carried out by measurement of the effective pore volume in films with different thickness. This method was realized for surface sensor-based microbalance porosimetry and discussed in detail in our previous article.[4]

In summary, experimental tools and advanced software for the PSD calculations from the results of the ellipsometric measurements of the adsorption of the organic solvent vapors in porous films have been successfully developed.

ACKNOWLEDGMENTS

The authors would like to thank I. Leonov for help in the experimental work and G. Vereecke for useful discussions.

[1]E. Todd Ryan, H.-M. Ho, W.-L. Wu, P. S. Ho, D. W. Gidley, and J. Drage, Proceeding of the International Interconnect Technology Conference (IITC), San Francisco, CA, 1999, p. 187 (unpublished).
[2]S. J. Gregg and S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed. (Academic, New York, 1982).
[3]M. R. Baklanov, F. N. Dultsev, and S. M. Repinsky, Poverkhnost **11**, 1445 (1988) (in Russian).
[4]M. R. Baklanov, L. L. Vasilyeva, T. A. Gavrilova, F. N. Dultsev, K. P. Mogilnikov, and L. A. Nenasheva, Thin Solid Films **171**, 43 (1989).
[5]Y. Spooner, presented at 1999 SEMATECH Workshop, Orlando, FL, 1999 (unpublished).
[6]J. D. F. Ramsay, MRS Bull. **24**, 36 (1999).
[7]M. R.Baklanov, F. N. Dultsev, E. Kondoh, K. P. Mogilnikov, K. Maex, S.-Q. Wang, and L. Forester, *Proceeding of Advanced Metallisation Conference*, 1998, edited by G. S. Sandhu, H. Koerner, M. Murakami, Y. Yasuda, and N. Kobayashi (Materials Research Society, Pittsburgh, PA, 1999), p. 507.
[8]F. N. Dultsev and M. R. Baklanov, Electrochem. Solid State Lett. **2**, 192 (1999).
[9]G. A. Muranova and A. F. Perveev, Sov. J. Opt. Technol. **60**, 92 (1993).
[10]K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska, Pure Appl. Chem. **57**, 603 (1985).
[11]C. H. Amberg and R. McIntosh, Can. J. Chem. **30**, 1012 (1952).
[12]D. J. C. Yates, Proc. R. Soc. London, Ser. A **224**, 526 (1954).
[13]L. Gurvitsch, J. Phys. Chem. Russ. **47**, 805 (1915).
[14]S. E. Schulz, A. Bertz, W. Leyffer, M. Rennau, I. Streiter, M. Uhlig, T. Winkler, and T. Gessner, *Proceeding of Advanced Metallisation Conference*, 1998, edited by G. S. Sandhu, H. Koerner, M. Murakami, Y. Yasuda, and N. Kobayashi (Materials Research Society, Pittsburgh, PA, 1999), p. 485.
[15]M. R. Baklanov and K. P. Mogilnikov. Abstracts of the Spring Materials Research Society Symposium, San Francisco, CA, April 2000 (unpublished).