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Ellipsometric study of the change in the porosity of silica xerogels after chemical modification of the surface with hexamethyldisilazane

Abstract Variable angle spectroscopic ellipsometry (VASE) and ellipsometric porosimetry (EP) have been used to study the effect of treatment with hexamethyldisilazane (HMDS) on the porosity of silica xerogel films. Chemical modification of the surface with HMDS was found to reduce the porosity by ~15%. This reduction was connected with changes which occur in the silica network, with further condensation or the reaction between neighbouring trimethylsilyl (TMS) surface groups being possible causes.

**Keywords** Ellipsometry · Low-k dielectric · Xerogel

Introduction

In ultra-large-scale-integration technology the performance of electronic circuits is limited by the resistance–capacitance delay associated with the parasitic capacitance of the dielectric and with the resistance of the metal [1]. Because of its low dielectric constant, ε, porous silica, prepared as aerogels (dried supercritically) or xerogels (dried by solvent evaporation) [2, 3], has become an attractive means of meeting this challenge. The surfaces of porous silica obtained by sol–gel methods are covered by OH groups [4]. Owing to these OH groups the pore surfaces readily adsorb water leading to an dramatic increase of ε, because of the high polarity of water molecules. The hydrophilic OH species can be removed from the pores, and replaced with hydrophobic trimethylsilyl (TMS) groups, by chemical modification of the surface with HMDS or

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trimethylchlorosilane (TMCS) [2, 5]. The aim of the work discussed in this paper was to study changes of the porosity of the silica xerogel films induced by reaction with HMDS. Variable angle spectroscopic ellipsometry (VASE) and ellipsometric porosimetry (EP) were used in the investigation.

Experimental

The silica xerogel films were spun on four-inch diameter Si wafers from a tetraethylorthosilicate (TEOS) solution (the TEOS:water ratio, R, was 7) in the presence of a mutual solvent and a catalyst [6]. After successive hydrolysis and condensation reactions [4] a three-dimensional siloxane (Si–O–Si) network was formed. After a gelation period the films were dried and annealed at 450 °C for 1 h. Finally the films were exposed to HMDS vapour for 24 h at room temperature. Infrared (IR) transmission measurements [7] confirmed that hydroxyl groups from the surface of the pores had been replaced with less polar methyl groups as follows:

$$2[\equiv Si - OH] + (CH_3)_3 - Si - NH - Si(CH_3)_3 \rightarrow$$
$$2[\equiv Si - O - Si(CH_3)_3] + NH_3 \tag{1}$$
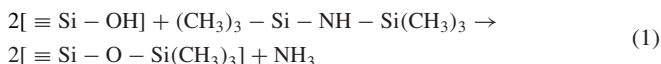
Ellipsometry was performed with a VASE Woollam ellipsometer in the spectral range from 1.5 to 4.5 eV with a step in energy of 0.02 eV. The ellipsometric spectra were recorded at four angles of incidence – 65°, 70°, 75°, and 80°. Ellipsometric porosimetry was performed with a high-vacuum system and a one-wavelength ellipsometer (λ=632.8 nm), as described elsewhere [8].
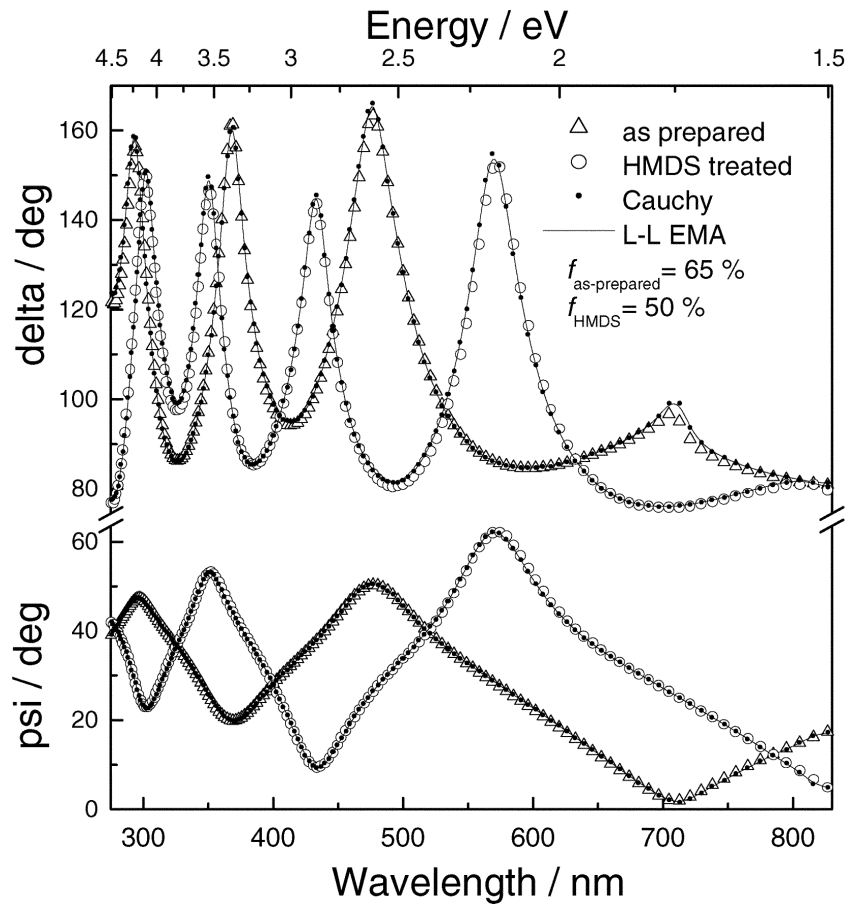
Results and discussion

The measured ellipsometric parameters ψ and Δ are connected with the reflection Fresnel coefficients for p and s polarisation (r_p and r_s) by the equation $r_p/r_s = \tan \psi \exp(i\Delta)$. Because ψ and Δ are functions of the complex refractive index: $\tilde{n} = n + ik$ (where n is the refractive index and k the extinction coefficient) of the films and of the Si substrate they do not directly provide information about the xerogel films. Because the xerogel films consist of porous silicon oxide, we suppose that they are transparent in the 1.5–4.5 eV spectral region. Consequently, a model describing the layer by use of a Cauchy dispersion relation ($n = a_n + b_n/\lambda^2$) on an Si substrate of known dielectric con-

Fig. 1 Experimental ψ and Δ spectra (for 70° incidence angle) obtained from an as-prepared (*triangles*) and HMDS-treated (*circles*) xerogel film, and the fitted spectra obtained by use of the Cauchy (*dotted lines*) and Lorentz–Lorenz EMA (*solid lines*) models

Energy / eV

Table 1 Values of, and errors in, the Cauchy parameters a_n and b_n for as-prepared and HMDS-treated films

Sample	Cauchy parameters	
	a_n	$b_n \times 10^3$
As prepared	$1.146 \pm 3 \times 10^{-3}$	1.07 ± 0.02
HMDS treated	$1.212 \pm 5 \times 10^{-3}$	1.91 ± 0.03

stant [9] was used to describe the optical response of the xerogel films. The method enables simultaneous determination of the thickness and optical constants of the films by curve fitting of the ψ and Δ spectra. The spectra simulated by use of the Cauchy model are depicted in Fig. 1 as dots, together with the experimental data (open triangles and circles) for an as-prepared and HMDS-treated xerogel film. As is readily apparent, there is a very good match between experimental and calculated spectra, indicating the reliability of the optical constants and thickness obtained in this way. The values of a_n and b_n and the errors in their determination are given in Table 1. The errors are calculated as a summation of the errors arising from the fitting procedure and of the statistical errors of measurements performed at three different points on the samples.

Figure 2 shows the refractive indices obtained by use of the method described above. For comparison purposes literature data for the refractive index of SiO_2 [10] are pre-

sented in the same plot. After treatment with HMDS the refractive index increases from 1.148 ± 0.005 to 1.216 ± 0.005 (values at $\lambda = 632.8$ nm). The reason for this increase will be given later. At the same time, the thickness of the
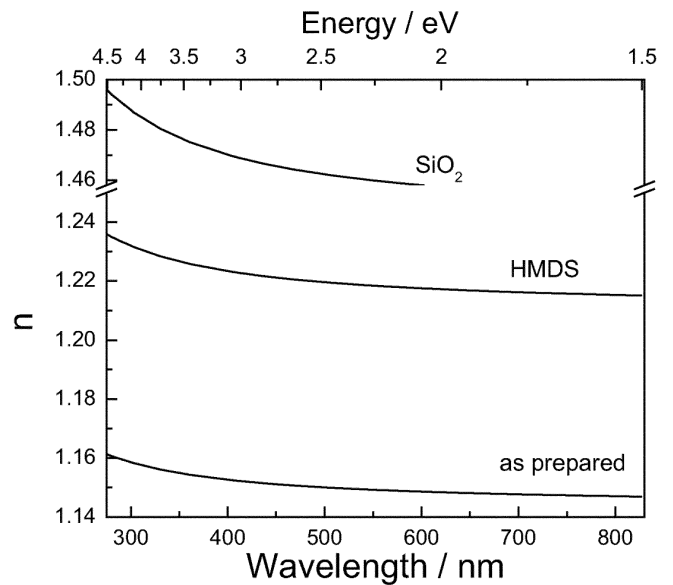
Fig. 2 Refractive indices obtained by use of the Cauchy model for the as-prepared and HMDS-treated xerogel films, compared with the literature refractive index of SiO_2

xerogel remains almost the same for as-prepared (570±5 nm) and HMDS (582±8 nm) films.

The dielectric constant of a porous dielectric, ε_r, can be determined by use of the Lorentz–Lorenz effective medium approximation (EMA) [11]:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = f \frac{\varepsilon_a - 1}{\varepsilon_a + 2} + (1 - f) \frac{\varepsilon_s - 1}{\varepsilon_s + 2} \qquad (2)$$

where f (=pore volume/film volume) is the relative film porosity and ε_a and ε_s are the dielectric constants of air and the film skeleton, respectively. Because $\varepsilon = n^2$ and $\varepsilon_a = 1$ the porosity of the films can be calculated from:

$$f = 1 - \left[\frac{n_r^2 - 1}{n_r^2 + 2}\right] / \left[\frac{n_s^2 - 1}{n_s^2 + 2}\right] \qquad (3)$$

where n_r is the measured refractive index of the porous film and n_s the refractive index of the skeleton.

Taking $n_s = n_{SiO2}$, the porosity, f, of the xerogel films can be determined by curve fitting of the experimental ψ and Δ spectra. From the simulated spectra for the EMA model, shown in Fig. 1 by continuous lines, values for the porosity of $f_{as-prepared} = 65 \pm 3\%$ and $f_{HMDS} = 50 \pm 3\%$ were obtained. Very similar values (differences <2%) were obtained when other EMA models were used (Bruggeman and Maxwell-Garnet). Reduction of the porosity by ~15% also explains the increase of the refractive index by ~0.07, as is apparent from Fig. 2.

Ellipsometric porosimetry was used to confirm the values obtained by use of VASE. The principle behind EP is to use changes in the optical characteristics of porous films during adsorption and/or desorption of an adsorbate in/from the pores, and to determine the amount of adsorbate (toluene in our work) inside the pores. Besides porosity values, important information about pore-size distribution (PSD) and pore interconnectivity can be obtained. A detailed description of the method can be found elsewhere [8, 12]. In practice Eq. (2) can again be used, because the pores are filled with an adsorptive liquid of known refractive index. Measurements performed for different adsorbates showed that the approximation $n_s \cong n_{SiO2}$ was reasonable. The dependence of adsorptive volume on the relative pressure P/P_0 is an adsorptive isotherm, which is used to calculate PSD [8]. Figure 3a shows the adsorption and desorption isotherms of the toluene in/from the as-prepared and HMDS-treated xerogel films. Toluene was used as adsorbed species, because it has a contact angle close to zero for the xerogel films under study. The hysteresis behaviour observed is because of capillary condensation and desorption of the toluene from the porous film [12]. The porosity is determined from the saturation values of the isotherms in Fig. 3a, and is called the "open" porosity, because it refers to the open pores which are accessible to toluene. The values of the open porosity from Fig. 3a are very close to the values of the "full" porosity obtained by use of VASE, which means that nearly all the pores are interconnected. The skeleton refractive index was, moreover, found to be equal to that of silicon oxide ($n_{skeleton} \approx n_{SiO2} = 1.46$) for both untreated and HMDS-treated films. This means there is at most a negligible number of closed pores in the films, because their presence would reduce the skeleton refractive index (the toluene cannot penetrate the closed pores). This is another indication of the interconnectivity between the pores. Figure 3b shows the PSD obtained from the desorption isotherms by use of the Kelvin and BET equations (a commonly used approach in adsorption porosimetry [8]). It is apparent that some micropores in the as-prepared sample disappear after treatment with HMDS. Pores with dimensions smaller than 2 nm were analysed by use of Dubinin–Radushkevich theory [13] which enables determination of the mean pore size of the micropores.

The reduced porosity of HMDS-treated films is assumed to be the result of several chemical reactions occurring in the presence of HMDS and its by-products.

Fig. 3 (**a**) Adsorption–desorption isotherms of toluene in/from the pores of the xerogel films. The toluene condenses in the pores at vapour pressures (P) less than the equilibrium pressure (P_0). (**b**) Pore-size distributions in the xerogel films before and after HMDS-treatment, calculated from the desorption isotherms
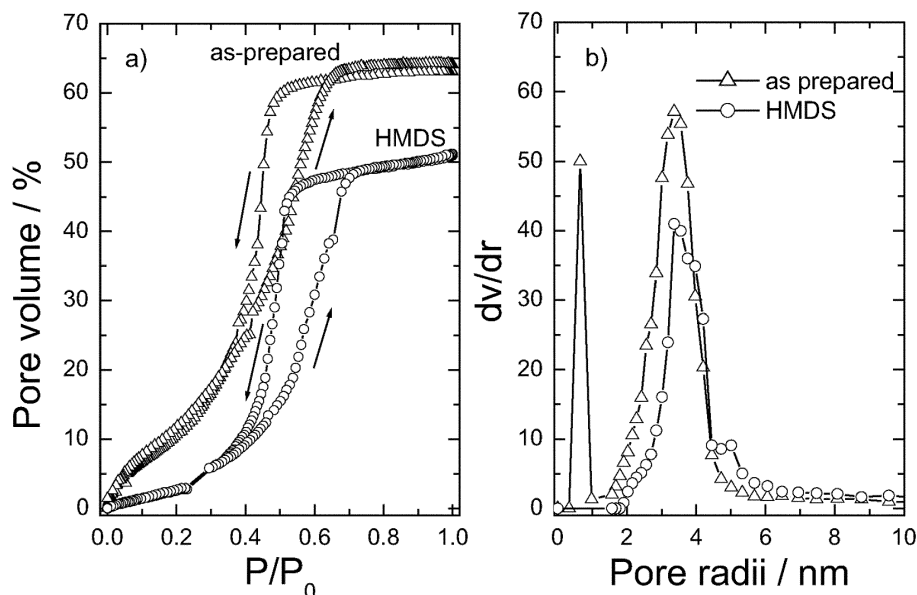
Ammonia, in particular, is known for its catalytic effect, for instance on the condensation reaction which could occur during HMDS treatment. The reaction of neighbouring TMS groups liberating hexamethyldilisoxane (HMDSO) and forming Si–O–Si bridges was observed by Slavov et al. [5] during the reaction of HMDS with silica at 200 °C:

$$2[\equiv Si - O - Si(CH_3)_3] \rightarrow ((CH_3)_3Si)_2O + \equiv Si - O - Si \equiv$$
$$(4)$$
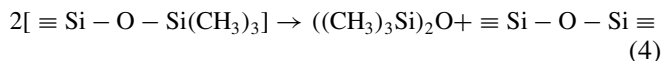
This might explain the reduction in the porosity in our films, because the pendant Si–O–Si(CH$_3$)$_3$ groups are transformed into siloxane species. Thus the structure of the xerogel becomes more compact, reflecting the reduction of porosity found by use of VASE and EP. The reaction described by Eq. (4) is, moreover, more likely for TMS groups located very close to each other, so the micropores seen in the as-prepared sample disappear after HMDS treatment. Further investigations are needed to establish the contributions of the condensation reaction and of the reaction described by Eq. (4) to the formation of Si–O–Si bridges.

Conclusions

The porosity of silica xerogel films is reduced by ~15% after HMDS treatment, because of chemical reactions that form more Si–O–Si bridges, hence a more compact silica network. As a consequence, the micropores observed in the as-prepared samples disappear after HMDS treatment and the refractive index of the films increases by ~0.07. Agreement between "full" porosity (from VASE) and "open" porosity (from EP) values suggests that most of the pores are interconnected.

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