Low-*k* xerogel films studied by ellipsometry and IR spectroscopy

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Abstract. Silica xerogel films with low dielectric constant were prepared by means of a sol-gel spin-coating method using different aging and hydrophobisation conditions. Non-destructive Variable Angle Spectroscopic Ellipsometry (VASE) studies allows a complete characterization of the xerogel films, in terms of thickness, optical constants and void fraction. The electronic and ionic contributions to the static dielectric constant of the xerogel films were calculated from the refractive index in the visible range and from infrared transmission spectra, respectively. The origin of the differences between the contributions to the static dielectric constant of the xerogel films produced with different preparation conditions is discussed.

1. Introduction. With the reduction of dimensions in ultra-large-scale-integration (ULSI) 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, 2]. An effective method to solve this challenge is the integration of materials with a low dielectric constant (low-*k*). Porous silica prepared as aerogels (dried supercritically) or xerogels (dried by solvent evaporation) [3-5], are particularly attractive for low dielectric constant applications. Besides the low dielectric constant which is due to the high porosity, these materials have the advantage of a good compatibility with conventional Si technology [6].
In the literature materials with a low dielectric constant are known as "low-k materials", while in this work the dielectric constant is denoted by ε.
Dielectric properties of silica xerogels are strongly influenced by the preparation conditions. In this work Variable Angle Spectroscopic Ellipsometry (VASE) investigations were carried out in order to characterize xerogel films in terms of thickness, optical constants and void fraction. On the other hand, VASE combined with Infrared spectroscopy was employed to determine the electronic and ionic contributions to the static dielectric constant.
2. Experimental. The technology to produce silica xerogels films is based on a sol-gel / spin-coating process [7, 8] and is schematically presented in figure 1. A mixture of tetraethoxysilane (TEOS), water, solvent (alcohol) and a catalyst (acid) is transformed into a gel. Since TEOS is tetrafunctional, a polymerisation phenomenon appears with the formation of three dimensional silica clusters as a result of hydrolysis and condensation reactions. The solution was spun on 4" Si wafers. The silica clusters become attached one to the other forming a porous network in a process called aging [5]. After aging the xerogel films were then annealed in vacuum at 450°C for 1h. The surfaces of porous silica obtained by sol-gel methods are covered by OH groups [7]. Owing to these OH groups the pore surfaces readily adsorb water leading to an dramatic increase of the dielectric constant because of the high polarizability of water molecules. In order to stabilize electrical properties and to get a sufficient

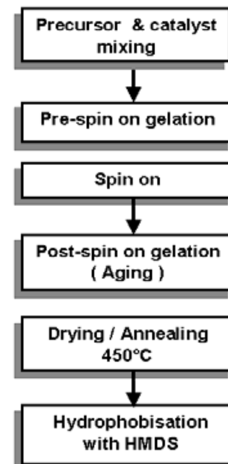

Figure 1. Scheme of the xerogel films fabrication process.

reliability for further integration steps the xerogels films have to be made hydrophobic. Hydrophobisation treatment followed immediately after annealing by exposure of the films to saturated vapors of hexamethyldisilazane (HMDS). The hydrophilic OH species can be removed from the pores and replaced with hydrophobic trimethylsilyl (TMS) [9]. Xerogel films with different porosities were produced using different aging / hydrophobisation conditions as given in table 1. As can be seen the aging was realized in air, solvent or H_2O/solvent atmosphere and the hydrophobisation was done in HMDS vapours for 10 minutes or 24 hours. According to the preparation conditions the samples were labeled A24, S10, S24 and W24, respectively.

The ellipsometric measurements were performed using a VASE Woollam Co. ellipsometer in the spectral range from 400 to 1000 nm with a step width of 5 nm. The ellipsometer is equipped with an autoretarder which allows the measurements for the ellipsometric parameter Δ in a 360° interval. The ellipsometric spectra were recorded at three angles of incidence: 65°, 70°, and 75°.

Sample	Preparation conditions	
	aging atmosphere	**HMDS hydro-phobisation time**
A24	Air	24h
S10	Solvent	10 min
S24	Solvent	24 h
W24	Water + solvent	24h

Table 1 Aging / hydrophobisation conditions for the xerogel films.

The IR spectra were recorded using a Fourier Transform Infrared (FTIR) spectrometer Bruker IFS 66. Transmission measurements at normal incidence were performed in the spectral range of 650-4000 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussions. Spectroscopic ellipsometry is an optical technique which measures the changes of the polarization state of a polarized light beam after reflection from the sample under study. The changes are measured by the ellipsometric parameters Ψ and Δ, which are connected with the reflection Fresnel coefficients for *p* and *s* polarisation ($\boldsymbol{r_p}$ and $\boldsymbol{r_s}$) as follow:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)\cdot\exp(i\Delta) \qquad (1)$$

Since Ψ and Δ are functions of the complex refractive index: $\tilde{n} = n + ik$ (n is the refractive index and k the extinction coefficient) of the films and of the Si substrate they do not directly provide information on the xerogel films. In order to extract the information contained in the ellipsometric spectra a model describing the structure of the sample and its optical response is usually applied. Because the xerogel films are formed from a porous SiO_2 structure, they can be considered transparent in the visible region. Consequently a model describing the layer using a Cauchy dispersion relation for the refractive index ($n=a_n+b_n/\lambda^2$) on a Si substrate of known dielectric constant [10] was employed to describe the optical response of the xerogel films. The method allows the thickness and the optical constants of the films to be determined simultaneously by curve fitting of the Ψ and Δ spectra [11].

In figure 2 typical Ψ and Δ ellipsometric spectra are plotted by symbols using sample A24 as an example. The fits obtained using the Cauchy model are included as lines. The calculated thickness and refractive index for all samples are presented in table 2. The errors are calculated as a summation of the errors provided by the fitting procedure and of the statistical errors of measurements performed at four different points for each sample.

In the next step the thickness obtained from the Cauchy model was kept fixed and Maxwell-Garnet Effective Medium Approximation (EMA) was used in order to determine the void fraction. Void fraction or porosity is defined as the fraction $\boldsymbol{f}$ of the total volume of the film comprised by pores (voids): $\boldsymbol{f=V_{voids}/V_{film}}$. Maxwell-Garnet EMA was applied because this approximation assumes spherical inclusions of one medium (voids) embedded in a host material (SiO_2). In this way the porous xerogel material is seen as a mixture of SiO_2 / voids. This approach is supported by previous work [9] where ellipsometric porosimetry (EP) technique [12] was applied. Those measurements showed that the refractive index of the skeleton of the

porous structure of xerogel layers is very close to the refractive index of SiO_2 ($n_{skeleton} \approx n_{SiO2}$). The fits obtained using EMA model for the sample A24 are shown in figure 2 by dots. The determined void fraction values for the samples under study are presented in table 2.

Table 2 Thickness, refractive index and void fraction determined from VASE; as well as electronic and ionic contributions to the static dielectric constant for the samples A24, S10, S24 and W24.

Sample	Thickness/nm ± 10 nm	n (632.8 nm) $\pm 5\cdot10^{-3}$	Void fraction% ± 2%	$\Delta\varepsilon_e$ ± 0.01	$\Delta\varepsilon_i^{650}$ ± 0.1	ε_{static} ± 0.1
A24	444	1.27	39.8	0.61	0.42	2.6
S10	509	1.224	49.5	0.5	0.32	2.6
S24	509	1.237	47	0.53	0.33	2.31
W24	582	1.198	55	0.44	0.29	2

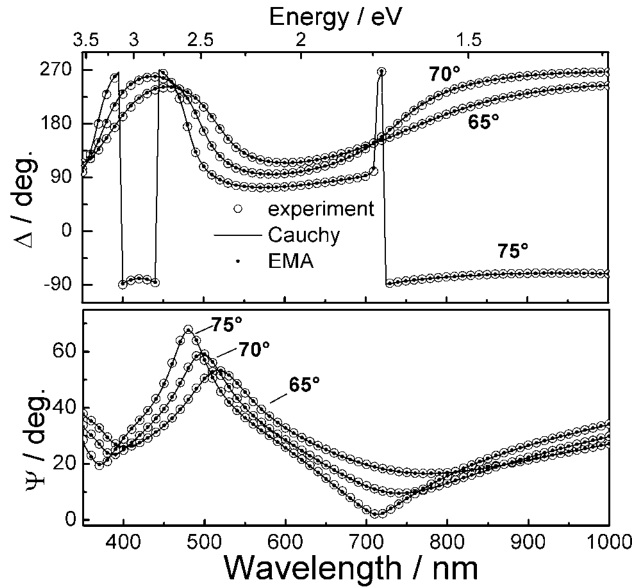

Figure 2. Ψ and Δ ellipsometric spectra of a silica xerogel film on Si substrate. Open circles are the experimental points, continuous lines are the fits obtained using Cauchy model and dots are the fits obtained using EMA model. The spectra refer to sample A24.

The static dielectric constant ε_{static}, determined by capacitance-voltage (C-V) measurements at 1 MHz consists of electronic $\Delta\varepsilon_e$, ionic $\Delta\varepsilon_i$ and configurational $\Delta\varepsilon_c$ contributions [13]:

$$\varepsilon_{static} = 1 + \Delta\varepsilon_e + \Delta\varepsilon_i + \Delta\varepsilon_c \qquad (2)$$

where 1 is the dielectric constant of vacuum. The electronic contribution $\Delta\varepsilon_e$ arises from the polarization generated by the distortion of the electron clouds, the ionic contribution $\Delta\varepsilon_i$ is caused by the ionic motions and the configurational contribution $\Delta\varepsilon_c$ stems from polar molecules which try to align with the applied electric field [13]. When the frequency of the applied radiation will exceed the characteristic frequency of the motion which contributes to the polarization, this motion cannot further follow the electric field and consequently the dielectric constant is reduced with increasing frequency. In the infrared range the dielectric constant above vacuum dielectric constant consists of ionic and electronic contributions while in visible range only the electronic part contributes [14].

The value of the dielectric function of a material at a certain energy is related to its optical constants as follows:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = (n + ik)^2 = n^2 - k^2 + i2nk \quad (3)$$

where ε_1 and ε_2 are the real and imaginary part of ε, n is the refractive index and k the extinction coefficient. The magnitude of the dielectric constant then is:

$$\bar{\varepsilon} = \sqrt{\varepsilon_1^2 + \varepsilon_2^2} \quad (4)$$

Xerogel films produced using different aging / hydrophobisation conditions according to table 1 were used to investigate the contributions to the static dielectric constant determined from C-V measurements at 1MHz. Because the films are transparent (k=0) in the visible range, the dielectric constant is the square of the refractive index ($\varepsilon = n^2$) so that the electronic contribution can be written as: $\Delta\varepsilon_e = n^2 - 1$. In the calculation of $\Delta\varepsilon_e$ the refractive index of the porous xerogel films at 632.8 nm was used for consistence with literature (632.8 nm is a wavelength commonly used in one-wavelength ellipsometry) [13-15].

The dielectric constant in the visible range determined from the refractive index is plotted in figure 3 together with the films void fraction. It can be observed that the electronic contribution is directly influenced by the void fraction, because it is calculated using the refractive index: samples with higher void fraction will have a lower electronic contribution to the dielectric constants.

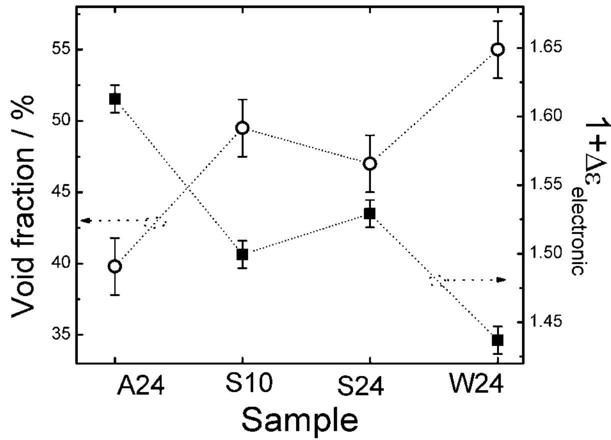

Figure 3. Void fraction (circles) and electronic contribution including vacuum dielectric constant (squares) calculated from the refractive index for the samples A24, S10, S24 and W24 respectively.

The dielectric constant in the IR range ε_{IR} consists of vacuum, electronic and ionic contributions. ε_{IR} was calculated from IR transmission spectra describing the film as a Lorentz layer consisting of several absorption peaks. In this way the optical constants of the films in the IR range were determined. Using equations 3 and 4 the magnitude of the dielectric constant ε_{IR} in the 650-4000 cm^{-1} IR range was calculated. ε_{IR} is plotted in figure 4. As can be observed in this figure ε_{IR} at 650 cm^{-1} consist of vacuum (1), electronic ($\Delta\varepsilon_e$) and ionic contributions ($\Delta\varepsilon_i^{650}$). The values for the ionic contribution at 650 cm^{-1} ($\Delta\varepsilon_i^{650}$) are provided in table 2. It should be noted that these values do not contain the whole ionic contribution because vibrations with characteristic frequencies below 650 cm^{-1} are not included in the model (measurements in far IR range were not performed). It can be observed that the ionic contribution decreases slightly with increasing void fraction because the films with higher void fraction have a smaller density. It can also be pointed out that the ionic contribution is smaller than the electronic one for all the films. The region at about 1100-1200 cm^{-1} where the dielectric constant is slightly

smaller than 1 corresponds to the strong absorptions by Si-O vibrations. Such effect was also observed for fluorinated and carbon-incorporated silicon oxide films [13-15].

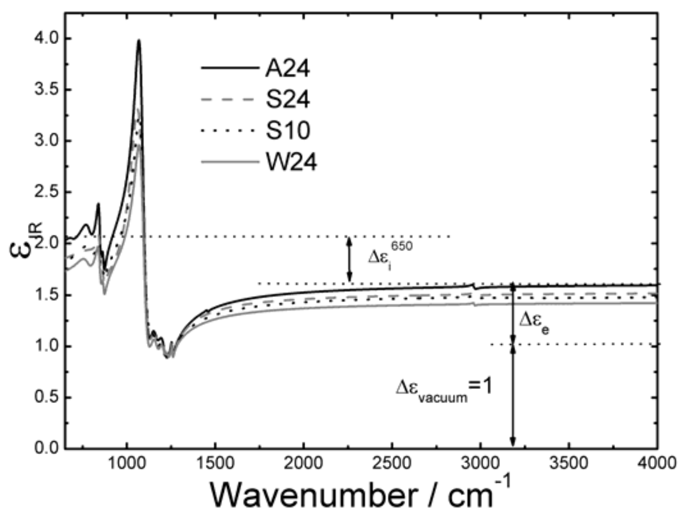

Figure 4. Dielectric constant in IR range derived from IR transmission spectra.

Figure 5 summarizes in the form of a histogram the contributions to the static dielectric. constant. The difference between the level of static dielectric constant and the upper level of $\Delta\varepsilon_i^{650}$ consists of the remaining ionic contribution in far IR range and the configurational contribution. Because the ionic contributions at 650 cm^{-1} have close values (minimum 0.29 and maximum 0.42) it is expected that the additional ionic contribution in the far IR range have close values, too. Consequently the main difference between static dielectric constants (minimum 2 and maximum 2.6) must arise from different configurational contributions. From figure 5 the highest configurational contribution is expected for sample S10 and the lowest for sample W24. This is in good agreement with the fact that for sample S10, which was hydrophobised only for 10 minutes, more –OH groups are likely to be present in the pores. Consequently the configurational contribution is expected to be high due to polarity of these groups. On the other hand, for sample W24 aged in H_2O/solvent the addition of water in the aging process enhances the polycondensation reaction [16] so that the number of "unlinked" edges is expected to be reduced. For such a sample the configurational contribution is thus lower because of a considerably smaller number of polar –OH species.

4. Conclusions. Optical and dielectric properties of silica xerogels films were studied by spectroscopic ellipsometry and IR spectroscopy in dependence of their preparation conditions. The void fraction determined from the ellipsometric data for the films under study is in the range 40-55%. The samples with higher void fraction have lower electronic and ionic contributions to the static dielectric constant because of their lower refractive index and lower density. The main difference between static dielectric constants of the investigated samples was found to arise from the configurational contribution. The method presented here for the characterization of the static dielectric constant brings valuable information which should be exploited for further optimization of the production process of low-k xerogel films.

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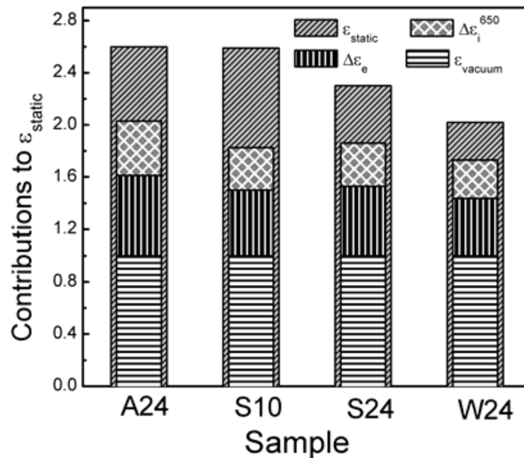

Figure 5. Contributions to the static dielectric constant.

References

[1] R. H. Havemann *et al.* – Mater. Res. Soc. Symp. Proc. 511, (1998), 3.

[2] K. Maex, M.R. Baklanov, D. Shamiryan, F. Iacopi, S.H. Brongersma, and Z.S. Yanovitskaya – J. Appl. Phys. 93, (2003), 8793.

[3] C. Jin, J.D. Luttmer, D.M. Smith, and T.A. Ramos – MRS Bull., October, (1997), 39.

[4] J.-K. Hong, H.-S. Yang, M.-H. Jo, H.-H. Park, and S.-Y. Choi – Thin Solid Films 308-309, (1997), 495.

[5] S.V. Nitta, V. Pisupatti, A. Jain, P.C. Wayner Jr., W.N. Gill and J.L. Plawsky – J. Vac. Sci. Technol. B 17, (1999), 205.

[6] N. Aoi – Jpn. J. Appl. Phys. 36, (1997), 1355.

[7] C.J. Brinker and G.W. Scherer – Sol-Gel Science: Physics and Chemistry of Sol-Gel Processing, (Academic, New York, 1990).

[8] S.E. Schulz, H. Koerner, C. Murray, I. Streiter, and T. Gessner – Microelectronic Engineering 55, (2001), 45.

[9] C. Himcinschi, M. Friedrich, S. Frühauf, I. Streiter, S. E. Schulz, T. Gessner, M.R. Baklanov, K.P. Mogilnikov, and D.R.T. Zahn – Analytical Bioanalytical Chem. 374, (2002), 654.

[10] Handbook of optical constants of Solids, edited by E.D. Palik, Academic Press, New York, (1985).

[11] C. Himcinschi, M. Friedrich, C. Murray, I. Streiter, S. E. Schulz, T. Gessner, and D.R.T. Zahn – Semicond. Sci. Technol. 16, (2001), 806.

[12] M.R. Baklanov, K.P. Mogilnikov, V.G. Polovinkin, and F.N. Dultsev – J. Vac. Sci. Technol. B 18, (2000), 1385.

[13] S.M. Han, and E.S. Aydil – J. Appl. Phys. 83, (1998), 2172.

[14] S.W. Lim, Y. Shimogaki, Y. Nakano, K. Tada, and H. Komiyama – Jpn. J. Appl. Phys. 35, (1996), 1468.

[15] J.Y. Kim, M.S. Hwang, Y.H. Kim, H.J. Kim, and Y. Lee – J. Appl. Phys. 90, (2001), 2469.

[16] S. Fruehauf, I. Streiter, R. Puschmann, S.E. Schulz, C. Himcinschi, C.M. Flannery, T. Gessner, D.R.T. Zahn - Advanced Metallization Conference (AMC) 2002, San Diego, USA, Conference Proceedings ULSI XVIII, (2003), 507.