Contributions to the static dielectric constant of low-\(k\) xerogel films derived from ellipsometry and IR spectroscopy

C. Himcinschi\(^a,\)*, M. Friedrich\(^a\), S. Frühauf\(^b\), S.E. Schulz\(^b\), T. Gessner\(^b\), D.R.T. Zahn\(^a\)

\(^a\)Institut für Physik, Technische Universität Chemnitz, Reichenhainerstr 70-72, D-09107 Chemnitz, Germany
\(^b\)Zentrum für Mikrotechnologien, Technische Universität, D-09107 Chemnitz, Germany

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 allow 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.

Keywords: Ellipsometry; Xerogel films; Low-\(k\) dielectric; Infrared spectroscopy

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 \(\varepsilon\).

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. However, 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 xerogel films is based on a sol–gel/spin-coating process [7,8] and is schematically presented in Fig. 1. A mixture of tetraethoxysilane (TEOS), water, solvent (alcohol) and a catalyst (acid) is transformed into a gel. Since TEOS is tetrafuctional, 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 inch 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 1 h. 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 reliability for further integration steps the xerogel films have to be made

Fig. 1. Scheme of the xerogel films fabrication process.

Aging
hydrophobisation conditions for the xerogel films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A24</td>
<td>Air 24 h</td>
</tr>
<tr>
<td>S10</td>
<td>Solvent 10 min</td>
</tr>
<tr>
<td>S24</td>
<td>Solvent 24 h</td>
</tr>
<tr>
<td>W24</td>
<td>Water + solvent 24 h</td>
</tr>
</tbody>
</table>

Table 1
Aging/hydrophobisation conditions for the xerogel films

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 $\Psi$ and $\Delta$, which are connected with the reflection Fresnel coefficients for $p$ and $s$ polarization ($r_p$ and $r_s$) as follow:

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

Since $\Psi$ and $\Delta$ 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 $\text{SiO}_2$ 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 ($n = a_0 + b_0/\lambda^2$) 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 $\Psi$ and $\Delta$ spectra [11].

In Fig. 2 typical $\Psi$ and $\Delta$ 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 $f$ of the total volume of the film comprised by pores (voids): $f = V_{\text{voids}} / V_{\text{film}}$. Maxwell–Garnet EMA was applied because this approximation assumes spherical inclusions of one medium (voids) embedded in a host material ($\text{SiO}_2$). In this way the porous xerogel material is seen as a mixture of $\text{SiO}_2$/voids. This approach is supported by previous...
The magnitude of the dielectric constant then is:

\[ \varepsilon = \sqrt{\varepsilon_1^2 + \varepsilon_2^2} \]  

(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 1 MHz. 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 Fig. 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.

The dielectric constant in the IR range \(\varepsilon_{IR}\) consists of vacuum, electronic and ionic contributions. \(\varepsilon_{IR}\) 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 Eqs. (3) and (4) the magnitude of the dielectric constant \(\varepsilon_{IR}\) in the 650–

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness/nm (\pm 10) nm</th>
<th>(n) (632.8 nm) (\pm 5 \times 10^{-3})</th>
<th>Void fraction% (\pm 2%)</th>
<th>(\Delta \varepsilon_e) (\pm 0.01)</th>
<th>(\Delta \varepsilon_e^{50}) (\pm 0.1)</th>
<th>(\varepsilon_{max}) (\pm 0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A24</td>
<td>444</td>
<td>1.27</td>
<td>39.8</td>
<td>0.61</td>
<td>0.42</td>
<td>2.6</td>
</tr>
<tr>
<td>S10</td>
<td>509</td>
<td>1.224</td>
<td>49.5</td>
<td>0.5</td>
<td>0.32</td>
<td>2.6</td>
</tr>
<tr>
<td>S24</td>
<td>509</td>
<td>1.237</td>
<td>47</td>
<td>0.53</td>
<td>0.33</td>
<td>2.31</td>
</tr>
<tr>
<td>W24</td>
<td>582</td>
<td>1.198</td>
<td>55</td>
<td>0.44</td>
<td>0.29</td>
<td>2</td>
</tr>
</tbody>
</table>
4000 cm\(^{-1}\) IR range was calculated. \(\varepsilon_{\text{IR}}\) is plotted in Fig. 4. As can be observed in this figure, \(\varepsilon_{\text{IR}}\) at 650 cm\(^{-1}\) consists of vacuum (1), electronic (\(\Delta \varepsilon_e\)) and ionic contributions (\(\Delta \varepsilon_i\)). The values for the ionic contribution at 650 cm\(^{-1}\) (\(\Delta \varepsilon_i\)) 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 approximately 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].

Fig. 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 \(\Delta \varepsilon_i\) 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 Fig. 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 min, 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. However, for sample W24 aged in H\(_2\)O/solvent the addition of water in the aging process enhances the polycondensation reaction 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 optimisation of the production process of low-k xerogel films.

Acknowledgments

This research was supported by the Deutsche Forschungsgemeinschaft Sonderforschungsbereich 379: ‘Mikromechanische Sensor- und Aktorarrays’.

References