Impact of solvent and low k material surface characteristics on pore sealing efficiency and porosity measurement

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Abstract. The penetration kinetics of different solvents having various properties (size, polarity, viscosity…) inside a porous low k SiOCH material modified by plasma treatments were investigated by ellipsometric porosimetry. The solvent penetration rates and durations to reach the saturation strongly depend on both the solvent properties and on the plasma post-treatments performed on the porous low k material. Pore sealing and barrier effect were quantified from the experimental determination of permeability coefficients for sample modified by a NH₃ and Fluocarbon based plasma using a permeation model. For these samples, the best barrier effects are observed with toluene and ethanol, respectively. In absence of barrier effect (unmodified material, plasmas He and NH₃/N₂), the solvent polarity and viscosity influence the time required for the complete saturation of the porous material. The liquid volume fraction f_L at saturation is also a function of the used solvent affecting the porosity estimation. All of these results highlight the complexity of the solvent penetration mechanisms.

1. Introduction

Porous low k materials (k ≤ 2.5) are intensively studied for their integration as insulator in the Back End Of Line (BEOL) for 45 nm and beyond technology nodes. Integrate such materials requires to investigate the modifications generated during the integration processes. Our study is focused on the consequence of plasma post-treatments and more particularly on the efficiency of the resulting pore sealing and on their impact on the porosity measurement. Indeed, during plasma treatment, the structure, the morphology, the composition and the porosity of a few nanometers in material subsurface are modified. After specific plasma treatments the porosity of the material is sealed. This so-called “pore sealing” phenomenon has been previously characterized by standard adsorption/desorption isotherms measured by Ellipsometric Porosimetry (EP) [2–5].

Puyrenier et al [5] have also performed another type of EP measurement by collecting the evolution versus time of the refractive index after a sudden solvent pressure increase from residual vacuum to a relative pressure corresponding to the sample saturation. For a porous SiOCH dielectric modified by different plasmas, it was shown that solvents such as ethanol can more or less easily diffuse through the modified subsurface and fill the “buried” zone. These results also highlighted that the ethanol penetration kinetics strongly depended on the nature of the applied plasma.
It is known that vapor transport across a thin polymeric barrier (like a membrane) is governed both by sorption and diffusion [6]. The chemical nature of the barrier (organic/inorganic balance, hydrophilic/hydrophobic balance, etc) mainly influences the sorption process whereas the polymer reticulation controls the diffusion process [7]. Solvent viscosity and surface tension also affect solvent permeation in a nanoporous layer [8].

In this study, we attempted to determine if the solvent penetration is only governed by specific chemical interactions between the solvent and the modified zone or is also affected by a geometrical effect of the subsurface porosity limiting the solvent transport. Thus, we studied the penetration of several solvents exhibiting different characteristics (in term of size, polarity, viscosity, etc) in the same SiOCH porous material modified by different plasma post-treatments. The mean objective was to improve the understanding concerning the interactions between modified surface of porous material and the used solvent to quantify the low k material porosity and pore sealing efficiency.

2. Materials and Method

2.1. Experiments

Samples (20 mm x 20 mm x 1 mm sized) were cut from a 300 mm silicon wafer coated with a PECVD SiOCH porous material (k=2.5) unmodified or modified by different plasma post-treatments. The thickness and the density of the different zones in the materials were determined from X-ray reflectometry measurements. The characteristics of the samples are summarized in the table 1. More detailed information about these samples is available in [4][5].

### Table 1. Samples characteristics.

| Plasma     | Sample label | thickness (nm) | density (g.cm$^{-3}$) | water contact angle (°) |
|------------|--------------|----------------|-----------------------|-------------------------|
|            |              | Zone 1 | Zone 2 | Zone 1 | Zone 2 |             |
| no plasma  | ref          | 158   | -     | 1.23  | -     | 97          |
| He         | He           | 140   | 10    | 1.23  | 1.36  | 92          |
| NH$_3$     | NH$_3$       | 149   | 9     | 1.23  | 1.76  | 62          |
| NH$_3$/N$_2$ | NH$_3$/N$_2$ | 153   | 5     | 1.23  | 1.28  | 52          |
| C$_4$F$_8$/Ar/N$_2$ | Etch | 98    | 9     | 1.23  | 1.61  | 89          |

After annealing at 250°C during 1 hour in order to remove the residual moisture, the samples were characterised at 25°C in a closed EP cell connected to a solvent source and to a vacuum pump. The evolution versus time of the refractive index was recorded with a single wavelength ellipsometer (Plasmos SD 2300, $\lambda$ = 632.8 nm) at fixed incidence angle (70°), after a sudden pressure increase from residual vacuum to a relative solvent pressure corresponding to complete filling of the pores, later named the sample saturation. The thickness variations (less than 5%) were neglected. Several solvents presented in table 2 were used as penetrants.

### Table 2. Characteristics of the solvents used as penetrants.

| Formula          | H$_2$O | OH | OH | OH | OH | H | O     |
|------------------|--------|----|----|----|----|---|-------|
| Vapour pressure at 25°C (mbar) | 31.67  | 169.9 | 75.9 | 58.01 | 37.05 | 130.7 |
| Refractive index  | 1.333  | 1.329 | 1.361 | 1.377 | 1.496 | 1.426 |
| Dipole moment (Debye) | 1.85 | 1.71 | 1.69 | 1.66 | 0.38-0.43 | 0.04 |
| kinetic diameter (nm) | 0.27 | 0.38-0.41 | 0.44 | 0.47 | 0.59 | 0.60 |
| Viscosity at 25°C (mPa.s) | 1.00 | 0.56 | 1.04 | 1.98 | 0.55 | 0.88 |
| Surface tension against air at 20°C (mN·m$^{-1}$) | 72.9 | 22.5 | 22.4 | 23 | 28.5 | 25 |
The solvent volume fraction in the material $f_L$ was determined using the Lorentz-Lorenz formula (1):

$$f_L = \frac{n^2 - 1}{n^2 + 2} \frac{n_0^2 - 1}{n_0^2 + 2} \frac{n_{\text{sol}}^2 - 1}{n_{\text{sol}}^2 + 2}$$

(1)

with $n$ the low k material refractive index, $n_0$ the initial refractive index and $n_{\text{sol}}$, the solvent refractive index.

2.2. Permeation model

The solvent penetration rate in the mesoporous thin layer through the top zone acting as a barrier layer/membrane was investigated from the evolution versus time of the refractive index. Gas transport in a polymeric membrane can be decomposed into three consecutive steps: sorption in the membrane, diffusion through the membrane and desorption on its opposite side. Sorption usually occurs very fast and is difficult to observe [5]. In our study, permeation which appeared as the time-limiting process was more precisely investigated. Solvent transport in the porous layer with thickness $d$ and across a barrier with a thickness $e$ (figure 1) was quantified using a permeation model. The samples were considered as bilayer systems (table 1) corresponding to a dead-end cell setup: the modified top layer and the “buried” porous material act as membrane and closed reception tank, respectively. The permeability coefficient $P_e$ was determined from the permeance $P$ (2) and permeance $P$ was evaluated using (3), derived from Fick and Crank equation [5].

$$P_e = P \times e$$

(2)

$$P = \frac{d}{V_{ML}} \frac{\Delta f_L}{\Delta t} \frac{1}{\Delta P}$$

(3)

with $V_{ML}$, the solvent molar volume; $\Delta P$, the transmembrane pressure and, $\Delta f_L/\Delta t$, the initial slope of the curve giving the evolution versus time of the solvent volume fraction in the material, $f_L$.

\[ \text{Figure 1. Bilayer model} \]
3. Results and discussion
The evolutions versus time of the refractive index for the different samples and the different solvents are shown in figure 2. The origin of the abscissa axis (t = 0) corresponds to the sudden increase of solvent pressure in the EP cell.

Whatever the solvent, these results highlight two types of sample behaviors. For the unmodified material (sample ref) and for samples He and NH$_3$/N$_2$, a fast solvent penetration (less than 2 minutes) is observed, excepted for water. For samples Etch and NH$_3$, the penetration kinetics are significantly longer and the barrier effect is thus potentially measurable.

3.1. Barrier effect of the zone modified by plasma
The barrier effect for samples NH$_3$ and Etch samples was quantified by calculating the permeability coefficient of the modified top layer (table 3).

| Sample | methanol | ethanol | isopropanol | toluene | cyclohexane |
|--------|----------|---------|-------------|---------|-------------|
| NH$_3$ | 1.9.10$^{-19}$ | 7.4.10$^{-20}$ | 4.3.10$^{-19}$ | 5.1.10$^{-19}$ | 3.9.10$^{-18}$ |
| Etch  | 5.3.10$^{-18}$ | 2.1.10$^{-18}$ | 1.3.10$^{-19}$ | 3.7.10$^{-20}$ | 3.5.10$^{-19}$ |

The measured values of Pe are ranging in the same order of magnitude as that of vitreous polymers with ethanol [10] and strongly depend on the used solvent. For instance, the barrier effect of the sample NH$_3$ with the ethanol is from one to two orders of magnitude higher than that with the other solvents. For sample Etch, the permeability of the modified layer is the lowest with toluene.

Attempts were made for explaining these experimental results by the chemical affinity of the solvent with the modified subsurface and also by a plasma densification of this top zone (geometrical restriction). In order to estimate each contribution, the initial rates of solvent volume fraction variation, $\Delta f_L/\Delta t$, were plotted as a function of two parameters: $A$, defined as the “affinity parameter” (eq. 4) and $S$, defined as the “size parameter” (5):

$$A = \frac{\theta_{H2O}}{P_{sol}}$$

(eq. 4)

$$S = \frac{1}{\phi_{sol} \cdot \rho_{surf}}$$

(5)

with $\theta_{H2O}$, the water contact angle (°); $P_{sol}$ the dipole moment of the solvent (Debye); $\phi_{sol}$ (nm), the solvent kinetic diameter; $\rho_{surf}$ (g.cm$^{-3}$), the mass density of the plasma-modified top zone [5].
Figure 2. Evolution versus time of the refractive index for the different samples using: (a) cyclohexane; (b) toluene; (c) isopropanol; (d) methanol; (e) water; (f) ethanol.

The evolution of $\Delta f_l/\Delta t$ as a function of these two parameters is presented in figure 3. From figure 3, no overall trend can be extracted between penetration rate, subsurface properties and solvent characteristics. Indeed, the most favourable cases, i.e. low density surface coupled with small size solvent, hydrophobic surface coupled with apolar solvent, hydrophilic surface coupled with polar solvent do not present the highest solvent penetration rates. Meanwhile, figure 3 highlights specific trends for each sample. For Etch sample the increase of size parameter $S$ is in good agreement with the increase of the solvent penetration rate, meaning that the barrier effect of the modified zone is mainly
due to a geometrical restriction. For the NH$_3$ sample, the penetration rate of the solvent increases with the increase of the A parameter, i.e. with the decrease of the solvent polarity. This phenomenon can demonstrate that, for this sample, the penetration rate of the solvent is mainly driven by the affinity of the “buried” zone.

Figure 3. Evolutions of $\Delta f_L/\Delta t$ as a function of A and S.

3.2. Impact of solvent properties in absence of barrier effect

For the unmodified material (sample ref) and for samples He and NH$_3$/N$_2$, the fast solvent penetration is due to the absence of significant plasma densification of the subsurface. Consequently parameters which could influence the solvent flow inside the mesoporous low k material should be the solvent polarity and the solvent viscosity as previously discussed by Yang et al [8].

The time required to reach saturation equilibrium, later named “solvent penetration duration”, was determined from the different curves shown in figure 2. The evolution of the solvent penetration duration as a function of the solvent polarity and viscosity is presented in figure 4. These data highlight that the solvent transport inside the material is mainly driven by affinity of the “buried” zone located underneath the modified zone: apolar solvents penetrate faster than polar and/or small-size solvents. Viscosity influences also the solvent penetration duration: solvent such IPA presents some stabilization duration higher than one minute.

Figure 4. Evolution of the stabilization duration to reach the sample saturation as a function of the solvent polarity and viscosity for samples ref, He and NH$_3$/N$_2$. 

[Diagram showing solvent properties and their impact on penetration rate and duration]
3.3. Impact on porosity determination

Usually the porosity is determined by EP from the calculation of the liquid fraction $f_L$ at saturation. However for a given sample, this value also depends on the solvent nature as shown in figure 5. Water is also a specific case. The water amount inside the material at saturation increases with the material hydrophilicity induced by some plasma treatments: NH$_3$/N$_2$ and NH$_3$. This phenomenon can be explained by the filling with water of the chemically modified zone. This phenomenon has been already characterized using neutron reflectometry and deuterated water [11].

![Figure 5. Solvent volume fraction at saturation for the different samples.](image)

4. Conclusion

The penetration kinetics of different solvents inside a porous low k material modified by plasma treatments were investigated by ellipsometric porosimetry. The results shown that the solvent penetration rates and durations to reach the saturation strongly depend on both the solvent properties and on the plasma post-treatments performed on the porous low k material. NH$_3$ and Etch plasmas induce significant pore sealing and barrier effect which was quantified from the experimental determination of permeability coefficients for the different used solvents. For samples Etch and NH$_3$, the best barrier effects are observed with toluene and ethanol, respectively. In absence of barrier effect (unmodified material, plasmas He and NH$_3$/N$_2$), the solvent polarity and the solvent viscosity influence the time required for the complete saturation of the porous material. The liquid volume fraction $f_L$ at saturation is also a function of the used solvent affecting the porosity estimation from EP measurements.

All of these results highlight the complexity of the solvent penetration mechanisms. Profilometric analyses during solvent penetration should be very useful in order to model the solvent penetration as already shown by promising preliminary results obtained using neutron reflectometry coupled with solvent adsorption [11].

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