Modelling of fluorine based high density plasma for the etching of silica glasses

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Abstract: Etching simulator has been developed to study the etching of silica glass (Pyrex®, D263®, AF45®, and Vycor®) in SF6/Ar plasma. The etching model is based on the development of the plasma kinetic model coupled to 2D Monte Carlo surface model to predict the etched surface morphology as a function of the operating condition. The results obtained by the model are compared with experimental results: etching rate and roughness. A satisfactory agreements between experimental results and the model concerning the etching rate and the etched surface morphology have been obtained for different glasses.

Keywords: plasma etching, modelling, silica glasses

Introduction
Quartz or pure fused silica are selected materials for the fabrication of biochip devices and more specifically electrophoresis chips [1]. Indeed, these materials benefit from transparency in the UV-visible range and low dielectric breakdown. However material cost is higher in comparison to silica glass which offers similar properties with a low purity degree. Plasma deep etching techniques are well established for fused silica and quartz [2], but much more challenging for glass. The presence of metallic oxides will result in the production of non volatile moieties in fluorine-based plasmas, a slow etch rate and surface texturation, which proves to be an important issue [3,4].

In the present study, a gas phase global model of SF6/Ar plasma combined to a 2D surface model are developed to predict the submicron etching profiles as a function of the plasma parameters. On the other hand, surface analyses such as the etch rate, surface roughness (profilometry), and surface topography (AFM) of some commercially available silica glass as a function of operating conditions have been carried out.

In this study we present both experimental and modelling results concerning the silica glass etching using SF6/Ar in inductive coupled plasma (ICP).

Experimental studies
The etching studies are carried out in an inductively coupled plasma (ICP) chamber [5]. Silica glass materials investigated are: Pyrex®, D263®, AF45®, and Vycor® (Table 1). Unless noticed, typical etching conditions are: 1500 W source power (rf 13.56 MHz), 200 V substrate bias (rf 13.56 MHz), 40 sccm total gas flow and 10 mTorr gas pressure. Etching gas is SF6-Ar. A stylus profiler (Veeco Dektak 8) is used to probe the surface roughness on a large range, as well as to obtain the etched depth from step measurement and thus estimate the average etch rate. Atomic force microscopy (AFM-Veeco Nanoscope III) is used to characterize the etched surface topography and probe surface roughness in micronic and sub micronic scale.

Table 1. Glass composition as given by the supplier (wt%oxide).

<table>
<thead>
<tr>
<th></th>
<th>Vycor</th>
<th>Pyrex</th>
<th>AF45</th>
<th>D263</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>97</td>
<td>80.6</td>
<td>49.6</td>
<td>64.1</td>
</tr>
<tr>
<td>B2O3</td>
<td>3</td>
<td>13.0</td>
<td>14.2</td>
<td>8.4</td>
</tr>
<tr>
<td>Al2O3</td>
<td>2.3</td>
<td>4.0</td>
<td>11.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Na2O</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2</td>
<td></td>
<td></td>
<td></td>
<td>6.4</td>
</tr>
<tr>
<td>BaO</td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>24.1</td>
<td></td>
<td>5.9</td>
</tr>
<tr>
<td>K2O</td>
<td></td>
<td></td>
<td></td>
<td>6.9</td>
</tr>
</tbody>
</table>

Global model
The gas phase model is based on the mass balance equations of reactive species diffusing toward the surface [6,7]. The additional equation of power balance in the ICP reactor allows to determine the electron temperature evolution as a function of the plasma discharge parameters. Even if the global model does not give details about the spatial distribution of neutral and charged species in the discharge, it allows to take into account of a large number of species and reactions. Global models are therefore suited to describe the large variety of neutral, positive and negative ion species produced in SF6/Ar discharges [8]. The gas phase model allows to calculate the fluxes of reactive species participating to etching process such as atomic fluorine and positive ions. These parameters are then introduced as input parameters in the surface model.
Surface model

Surface etching model is based on the discretization of the 2D etched surface in uniform cells [9]. The later are considered as the super-sites representing a number of real surface sites. The super-sites are squares with sides one nanometre long, this allows a good compromise between computing time and spatial resolution. In the case of silica glasses, we consider only the silicon sites Si, oxygen is assumed to desorb very quickly under the effect of ion bombardment. The metal species contained in the glass are modelled by a single metal site M. The number of Si or M atoms in a cell or super-site was calculated from data densities, it is 22 (Vycor), 23 (Pyrex), 29 (D263) et 25 (AF45). In this manner, this matrix gives a specific photography of the physical state of the surface with a resolution of one nanometre at any moment. Other information could also be extracted, such as the density of metallis sites, surface coverage in fluorine. The etching process, i.e. the vertical displacement of the surface is symbolized by a cellular transition between a full state to an empty state.

Table 2. Reaction kinetics of silica glasses etching in SF₆ plasma.

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Reaction probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(s) + F(g) → SiF(s)</td>
<td>P₁</td>
</tr>
<tr>
<td>SiF(s) + F(g) → SiF₂(s)</td>
<td>P₂</td>
</tr>
<tr>
<td>SiF₂(s) + F(g) → SiF₃(s)</td>
<td>P₃</td>
</tr>
<tr>
<td>M(s) + F(g) → MF(s)</td>
<td>P₄</td>
</tr>
<tr>
<td>MF(s) + F(g) → MF₂(s)</td>
<td>P₅</td>
</tr>
</tbody>
</table>

The neutral and ion particle fluxes calculated from the gas phase model are introduced as input data in the etching model. Then, Monte-Carlo technique is used to follow the trajectory of a plasma particle from an upper plan close to the simulated etch surface until the particle encounters a full cell representing a surface site. Adsorption and desorption of reactive particles, preferential sputtering mechanisms are taken into account in the surface model.

For this model, we have considered fluorine atoms as the main neutral precursor interacting with the glass surface. For each neutral particle, the initial properties (position and incidence angle) are randomly generated. Particle energy is assumed to be equal to thermal energy. Flux is assumed to be isotropic and trajectory is realized in straight lines.

Table 2 presents the various reactions considered in the model, the reaction probability corresponds to the adsorption probability of the F atom. For the Si sites the model considers that fluorination stops on SiF₃, and that there is no spontaneous chemical etching. The desorption of a Si site requiring ion bombardment. For the metal sites, it is considered that the fluorination leads to MF₂. Indeed, two fluorides is the average fluorine atoms accepted by the various metal species in the various silica glasses (NaF, BaF₂, AlF₃, KF ...). The adsorption probability of the F atom on the Si sites is estimated at 0.05, as reported by Kota et al [10]. The same adsorption probability is used for all silica glasses and for silicon and metallic sites.

Ion incident energy and angle of incidence are determined by energy and angular distribution functions. These are calculated using a sheath model. The latter is based on Monte Carlo techniques and takes sheath characteristics into account that are, in particular, controlled by pressure and dc bias. The angular part exhibits a narrow distribution with a majority of normal incident ions.

Ion interaction with the substrate is treated according to two mechanisms: specular reflection and preferential sputtering [11]. In order to determine the sputtering yields, as it has already been shown elsewhere, the collision cascade model derived by Sigmung is not useful. For the range of low energy, a sputtering threshold and a linear function of the square root of ion energy are accurate [11]:

\[
Y_{sput} = A\times(\sqrt{E_i} - \sqrt{E_0})
\]

where A is a constant, Eᵢ is the incident ion energy determined by the transport model in the sheath, and E₀ is the threshold energy. The sputtering threshold is calculated separately for the Si and the M sites.

Redeposition of etched species is considered also in the model. The angle chosen for the trajectory of the etched species is taken randomly.

Results

The threshold energy E₀ is taken as 0 eV for the Si site [12] and 70 eV for the M site. Indeed our etching D263 and AF45, show a threshold at 70 eV [13].
Parameter A is estimated from SiO₂ for the Si site and from each glass for the M site. This determination is made for only one plasma condition (SF₆, 1500 W, 10 mTorr, 200 V, 40 sccm) by comparing the simulated etch rate to the experiment. For Si $A_S=0.04$, Table 3 gives the parameter $A_M$ for each glass and the percentage of M sites.

Table 3. Reaction kinetics of silica glasses etching in SF₆ plasma.

<table>
<thead>
<tr>
<th></th>
<th>Pyrex</th>
<th>D263</th>
<th>AF45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic sites (% at)</td>
<td>9</td>
<td>30</td>
<td>24</td>
</tr>
<tr>
<td>Parameter $A_M$</td>
<td>0.07</td>
<td>0.05</td>
<td>0.013</td>
</tr>
<tr>
<td>$E_{0M}$ (eV)</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

Fig. 2 shows the sputtering yields of Si ($Y_S$) and M ($Y_M$) sites for the various glass. In the case of Pyrex, $Y_M$ very close to $Y_S$ at 300 eV and is equivalent at 350 eV. Our experimental measurements and those made by Li et al [4] provide roughness results that meet results of sputtering yield. It has shown that the surface roughness in the case of Pyrex decreases sharply beyond 300 eV. The sputtering yield of metal contained in the AF45 is significantly less than that of Pyrex and D263. Indeed, the barium content in this glass forms a fluorinated compound BaF₂ with an evaporation temperatures higher than all other fluorinated compounds formed.

Fig. 3: Etching rate as a function of pressure for a SF₆ plasma (1500W, 200V, 40sccm): (E) experiment and (M) model.

Fig. 4 presents the etching rate evolution with dc bias. The increase of the etching rate with dc bias is due to the increase of the sputtering yield with the ion energy. Let us note the good agreement between the simulation and the experimental results for a large plasma conditions and for the various glass (Fig. 3, Fig. 4).

Fig. 4: Etching rate as a function of dc bias for a SF₆ plasma (1500W, 10mTorr, 40sccm): (E) experiment and (M) model.

One of the advantages of the 2D etching model is its ability to give information about the 2D surface morphology. For Pyrex material we have taken into account for the redeposition mechanism of the metal sites. The simulation results (Fig. 5-b) suggest that the formation of the peaks on the surface, as shown by AFM analyses (Fig. 5-a) is due to the redeposition of the metal leading to a micro-masking effect. A good agreement is obtained between the simulation and the experiment when taking the adsorption probability of the metal sites as equal to 1.
Fig. 5 : Surface morphology for Pyrex by AFM (a) and by the model with redeposition of M sites (b) after 3 min of etching (SF$_6$, 10mTorr, 1500W, 200V, 40sccm).

Fig. 6 : Density of M sites on the Pyrex surface for the model after 3 min of etching (SF$_6$, 10mTorr, 1500W, 200V, 40sccm).

Fig. 6 presents the density of metal sites on the surface of Pyrex. This results has to be compared to Fig. 5-b. One clearly sees that the metallic species accumulate on the peak E and that etching is stopped at this point. Peak F that is less pronounced than Peak E, does not present an accumulation of metallic species. This can be explained by the competition between redeposition, which stops the etching, and ion bombardment which allows to remove the redeposition metallic sites.

**Conclusion**

The surface model combined with the global kinetic model allows a better understanding of the mechanism of silica glass etching. The etching rate depends on the percentage of metallic sites and the sputtering yield of these sites. Surface roughness depends on the redeposition of metallic species which accumulate to some places and form peaks. A satisfactory agreement between the simulation and the experiment for a large operating condition range and for different glass types.

**References**