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A STRUCTURAL INVESTIGATION OF SOME EVAPORATED SiO$_x$ FILMS

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Résumé.- La structure des films minces SiO$_x$ formés par évaporation du silicium ou de silice dans différentes pressions parcielles d’oxygène a été investiguée en utilisant EXAFS, au seuil d’absorption K du silicium, et XPS. L’évaporation a été obtenue par la fusion du cible de silicium ou silice en la bombardant à l’aide d’un faisceau électronique et les vapeurs ont été déposées sur un substrat de mica fraîchement clivé et chauffé. Les résultats obtenus dans cette étude sont en accord avec le model du mélange aléatoire pour la structure de SiO$_x$ et ne montrent aucune consistance avec le modèle de distribution aléatoire de liaisons atomiques.

Abstract.- The structure of thin SiO$_x$ films formed by the electron beam evaporation of silicon, or silica, on to heated mica substrates in various partial pressures of oxygen has been investigated using both EXAFS, at the Si K edge, and X-ray photoelectron spectroscopy. The data obtained from these studies are consistent with the random mixture model for the structure of SiO$_x$ and inconsistent with the random bond model.

1. Introduction

Probably the most important substrates in microelectronic device technology consist of silicon wafers covered with amorphous silicon oxide films, these oxide films being used both for surface passivation and diffusion masking. In view of this application there is considerable interest in the structure of these films and in particular of the non-stoichiometric oxides such as are formed at the silicon/silicon oxide interface.

Over recent years there has been much debate in the literature concerning the structure of SiO$_x$ ($0 < x < 2$) powders and films, particularly of 'SiO'. It is well established that whilst SiO is a stable species in the gas phase[1] solid SiO is thermodynamically unstable and therefore does not exist in any defined crystalline form[2], and at one time it was even thought that 'SiO' was simply a macro mixture of Si and SiO$_2$. This is clearly not the case and there are currently two principal models that are used to describe the amorphous structure of SiO$_x$: the random bond (RB) model first discussed by Phillip[3] and the random mixture (RM) model proposed by Temkin[4]. In the former SiO$_x$Si$_{(4-x)}$ tetrahedra are randomly distributed throughout the material and thus five distinct silicon environments can be identified. In the latter there are microregions (linear dimensions ~1nm) of Si(Si)$_4$ tetrahedra and Si(0)$_4$ tetrahedra and thus there are two distinct environments plus a small amount of interfacial material.
There have been many investigations of amorphous Si$_x$ aimed at elucidating its structure and it now appears that for commercial SiO powder it is the PM model that is appropriate. This has been shown by various studies including X-ray diffraction and most recently magic angle spinning nmr. For Si$_x$ thin films the situation is less clear-cut and it appears that the structure of the film is extremely sensitive to the method of preparation. For example XPS studies of films formed by the evaporation of SiO powder suggest that the use of a cold substrate favours a film with the RB structure whilst a heated substrate favours the PM structure. 

Most of the techniques that have been used to study Si$_x$ films do not provide direct structural information whilst such a technique would clearly be very helpful. X-ray diffraction is unlikely to be sufficiently sensitive to these thin layers whilst the quality of electron diffraction data has been poor. One technique that should prove useful is EXAFS and indeed Greaves has used this approach to study films formed by glow discharge of SiH$_4$ and N$_2$O on Be foil substrates at 290°C. On the basis of bond length measurements and absorption edge shifts it was shown that the films were of the random bond type.

In this paper we report the results of an XPS and EXAFS study of the Si$_x$ films formed by the evaporation of either Si or SiO$_2$ in oxygen containing atmospheres.

2. Experimental

The samples used in this study were prepared as thin films by electron beam evaporation of either silica or silicon. The base pressure of the deposition chamber was $10^{-8}$ Pa and during evaporation various oxygen partial pressures were maintained in it. The substrate, which was maintained at 325°C, consisted of a thin layer (10nm) of carbon vapour deposited on a strip of freshly cleaved mica. The oxide film thickness of 200nm was chosen to be greater than the electron escape depth so that there would be no interference from the substrate in the total electron yield EXAFS measurements. After deposition the films were transferred within the vacuum system to an XPS spectrometer for analysis. The details of the films used are given in Table 1. EXAFS measurements at the Si K edge were made using the storage ring ACO at LURE (Orsay, France).

3. Results and Discussion

The photoelectron spectroscopy was used primarily to determine the film stoichiometry but additionally it can provide information about chemical environment. For most of the films only a single peak was observed in the Si 2p region but, as shown in fig. 1, for SiO there are two implying that there are two distinct silicon environments. A similar result was obtained by Hollinger et al. for films deposited onto a heated substrate and this was taken as evidence for the structure being of the PM type (for the RB model only a single Si 2p peak would be anticipated though the binding energy would shift with composition). Further support for this conclusion comes from the X-ray absorption edge data. Fig. 2 shows the X-ray absorption spectrum for three films, SiO$_{0.04}$, SiO and SiO$_{1.9}$ and the edge energies are tabulated in Table 1. It is immediately clear that for low

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stoichiometry</th>
<th>Edge Energy (eV)</th>
<th>Si-O</th>
<th>Si-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si no O$_2$</td>
<td>SiO$_{0.04}$</td>
<td>1835</td>
<td>0.181</td>
<td>0.235</td>
</tr>
<tr>
<td>Si + 6 x 10$^{-6}$PaO$_2$</td>
<td>SiO$_{0.19}$</td>
<td>1835</td>
<td>0.181</td>
<td>0.235</td>
</tr>
<tr>
<td>Si + 8.5 x 10$^{-5}$PaO$_2$</td>
<td>SiO</td>
<td>1837/1841</td>
<td>0.161</td>
<td>0.240</td>
</tr>
<tr>
<td>SiO$_2$ no O$_2$</td>
<td>SiO$_{1.8}$</td>
<td>1842</td>
<td>0.161</td>
<td>0.306</td>
</tr>
<tr>
<td>SiO$_2$ + 8.5 x 10$^{-5}$O$_2$</td>
<td>SiO$_{1.91}$</td>
<td>1842</td>
<td>0.161</td>
<td>0.306</td>
</tr>
<tr>
<td>a quartz</td>
<td>SiO$_2$</td>
<td>1841</td>
<td>0.161</td>
<td>0.306</td>
</tr>
</tbody>
</table>
Fig. 1 XPS spectrum for SiO film

Fig. 2 X-ray absorption spectra for
(a)SiO$_{0.04}$, (b)SiO$_{0.1}$, (c)SiO$_{1.9}$

oxygen content films the edge lies close to that for silicon whilst for the high oxygen content ones it is close to that for silica. Interestingly for SiO the edge is not well defined but instead appears to be a superposition of two edges, that for Si and that for SiO$_2$. This is in contrast to the observation of Greaves[9] who found that for his films the edge energy shifted smoothly with composition. Clearly despite the similar substrate temperatures (325°C and 293°C) used here and by Greaves the different method of film preparation has resulted in films of very different structure.

Fig. 3 shows the Fourier Transforms of the EXAFS functions $k^2\chi(k)$ extracted from the X-ray absorption spectra for the 5 films and the $\alpha$-quartz model compound. These distribution functions have not been corrected for phase shift. In discussing these it is helpful to start by considering $\alpha$-quartz as its structure is well known.[10] The largest peak at 0.10 nm is clearly due to the shell of four tetrahedrally bonded O atoms (crystallographic distance 0.161 nm) whilst that at 0.28 nm can be attributed to the second shell consisting of Si atoms (distance 0.306 nm). The distribution functions for the two oxygen rich films, Figs. 3d and e are very similar and the main peaks appear at the same positions. For the silicon rich films, Fig. 3a and b, the structure is clearly different. The largest peak is due to the first shell in a Si(Si)$_4$ configuration whilst that at 0.12 nm must be due to a shell of O atoms around Si. In view of the low oxygen content of these films, and the similarity between these two distribution functions despite the change in composition, it is probable that these oxygen atoms are in a surface oxide layer. The electron yield EXAFS technique is particularly sensitive to such surface layers. The peak at 0.28 nm also probably arises from surface oxide. The distribution function for SiO, Fig. 3c, is best described as a mixture of the results for the two other types of film, i.e. the largest peak arises from a Si(O)$_4$ configuration whereas the second peak is due to Si(Si)$_4$. These results therefore again imply that there are two Si environments present and that the film is of the RM type. The phase corrected shell distances are given in Table 1.
Fig. 3 Radial distribution functions for (a) SiO$_{0.04}$, (b) SiO$_{0.19}$, (c) SiO, (d) SiO$_{1.8}$ and (e) SiO$_{1.91}$ films and (f) α-quartz.

The results reported here lend further support to the observation that SiO film structure is extremely sensitive to the method of preparation. Indeed it appears that the method of evaporation is important as well as the substrate temperature. More work is required before the situation is fully explained.

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