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ELECTRONIC STRUCTURE OF AMORPHOUS SiO$_x$

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Abstract.—The electronic structure of amorphous SiO$_x$ (0 $\leq x \leq$ 2) is studied in order to characterise the distribution of Si and O atoms in the alloy. Our results are in excellent agreement with photoemission data as well as with optical absorption measurements. Our calculations indicate that there is no short-range order such as (SiO$_4$)$_y$Si$_{1-y}$ and the distribution of silicon and oxygen atoms is random with no oxygen-oxygen bonds, the Si-O-Si bond angle for SiO being smaller (∼120°) than for SiO$_2$ (144°). The non-linear variation of the SiO$_x$ gap with concentration is related to the breaking of Si chains in the alloy. The implications of our results on the electronic properties of the Si/SiO$_2$ interface are also discussed.

We have performed a theoretical study of the electronic structure of amorphous SiO$_x$. Although the study of SiO$_x$ is very interesting by itself, our final goal is to study the interface Si-SiO$_2$ where an amorphous transition region of SiO$_x$ is formed (1).

The main questions we want to answer in this work are:

(i) Which is the local bonding in a-SiO$_x$?
(ii) Which are the bonding statistics of SiO$_x$ (i.e. random-bonding model or mixture model)?
(iii) Which is the atomic structure of the alloy and in particular which is the bond angle Si-O-Si?
(iv) What is the electronic structure at the Si-SiO$_2$ interface when there is a transition region between Si and SiO$_2$?

To describe the electronic structure of SiO$_x$, we have used a tight-binding hamiltonian which includes the 3s and 3p orbitals of Si and the 2s and 2p orbitals of O. In the case of the Si-Si bond we take into account all possible interactions between the orbitals in nearest-neighbour atoms whereas in the Si-O bond only O-like interactions are taken. This hamiltonian gives a very good description of the electronic structure of both a-Si (2) and a-SiO$_2$ (3).

We now discuss separately the four points mentioned above.

(i) To simulate the structure of SiO$_x$, we assume the following:

a) The sp$^3$ hybridisation of the Si atom is kept irrespective of the kind of their nearest-neighbour atoms. This is supported by the fact that electron diffraction measurements for a-SiO$_x$ (0 $\leq x \leq$ 2) films (4) indicate tetrahedral coordination of the Si atoms.

b) No oxygen-oxygen bonds are allowed in the structure.

c) The continuous random network of atoms forms a Bethe lattice with no
closed rings of bonds. The calculation follows the cluster-Bethe lattice model procedure (5).

ii) In order to determine the bonding statistics of \( a\text{-SiO}_x \) we have studied the variation of the optical absorption with concentration. Results of our calculations of the energy gap (\( E_g \)) for a random distribution of atoms along with the experimental results (6) are shown in Figure 1. We interpret the abrupt change of \( E_g \) at \( x \approx 1.4 \) as being related to the percolation threshold (7). It can be shown (3) that for energies near the Si gap the \( \text{SiO}_x \) structure is equivalent to the two non-interacting structures; one formed by Si and the other one by Si-0 (see Figure 2). It can also be shown (3) that as long as there are infinite (long enough) Si chains in the alloy the top of the valence band is the same as in \( a\text{-Si} \). If the distribution is random the disappearance of infinite Si chains (which is related to the percolation threshold) takes place at \( x_c = 1.33 \) in good agreement with experiments. One can also calculate the percolation threshold for distribution other than random. In particular if \( \text{SiO}_x \) is like \( \text{Si}_y(\text{Si}_4)_1\beta \) \( x_c = 1.77 \) and if it is as in \( (\text{Si-Si}_4)_y(\text{Si}_4)_1\beta \) then \( x_c = 1.87 \) in

\[ \text{Fig. 1: Variation of the optical gap of } a\text{-SiO}_x \text{ vs concentration } x. \text{ Block squares indicate theoretical results and the stars indicate experimental data (ref. } 6). \text{ The theoretical results have been shifted in energy for a better comparison with experiments.} \]

\[ \text{Fig. 2: Two-dimensional simulation of the decoupling of the } a\text{-SiO}_x \text{ network. (a) } a\text{-SiO}_x \text{ network. (b) Si-like network and (c) SiO}_2\text{-like network. Open and block circles indicate oxygen and silicon atoms respectively.} \]
disagreement with the experimental data. We can then conclude that the distribution has a strong tendency to be random since the mixture distribution (8) gives an $x_c$ much higher than that experimentally observed.

iii) The optical absorption is indeed independent of the Si-O-Si bond angle $\theta$, therefore in order to gain some insight into the structure of SiO$_x$ we have looked at photoemission measurements of SiO (9). In Figure 3(a) we have shown the photoemission spectrum of SiO and in Figures 3(b) and 3(c) our calculated densities of state for a random distribution and for $\theta = 144^\circ$ (as in $\alpha$-quartz) and $\theta=125^\circ$ respectively. We get a good agreement between theory and experiments for $\theta = 125^\circ$ in agreement with chemical shift analysis (10) at the Si-SiO$_2$ interface. The double-peak structure of the calculated density of states at $\sim 2$ eV is due to the absence of O=O and p p interaction in the Si-O bond in the Hamiltonian.

iv) In order to study the effect of the presence of an amorphous layer at the Si-SiO$_2$ interface, we have calculated the density of states when there is a layer of SiO$_{0.5}$ between Si and SiO$_2$ (see Figure 4). In our calculation, the Si-O-Si

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![Fig. 3: Electronic structure of SiO. (a) Experimental UPS data (ref. 9). (b) Calculated density of states for $\theta = 144^\circ$. (c) Calculated density of states for $\theta = 125^\circ$.]

![Fig. 4: Local density of states at a silicon atom in the SiO$_{0.5}$ layer described in the text between Si and SiO$_2$. $E_v$ indicates the top of the Si valence band.]

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bond angle at the interface is 125°. Our results are shown in Figure 4. The main effect of the presence of the interface SiO$_{0.5}$ layer is to induce localised states at the Si gap 0.1 eV above the top of the silicon valence band.

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References

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