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PHONON STRUCTURE OF AMORPHOUS SiO_x BY INELASTIC TUNNELLING SPECTROSCOPY

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We present phonon spectra of very thin evaporated amorphous films of SiO_x, obtained by inelastic electron tunnelling spectroscopy. The broad features of the results are similar to those found in neutron-scattering, Raman and infra-red measurements on bulk vitreous SiO_2 but there are differences of detail. The results show inelastic tunnelling spectroscopy to be a powerful technique for the study of amorphous systems.

ACCURATE KNOWLEDGE of the phonon density of states $g(\omega)$ is essential for an adequate understanding of the properties of amorphous materials [1]. Infra-red [2], Raman [2, 3] and neutron spectroscopy [4] give results for $g(\omega)$ which differ through the details of the energy dependencies of the relevant matrix elements. Inelastic electron tunnelling spectroscopy [5] provides an alternative technique which is cheap, simple and can be used on very small quantities of material.

Inelastic tunnelling spectroscopy uses electron excitation of the vibrational modes. Electrons tunnel between metallic electrodes separate by a thin (~ 2 nm) insulating barrier. The basic tunnel current arises from electrons passing without energy loss through the barrier into empty states on the other side, the number of such processes increasing with applied potential difference V to give an approximately ohmic current-voltage characteristic. However, if the energy difference eV is larger than the quantum energy $\hbar\omega$ of a mode to which it is coupled while tunnelling, it can also pass through the barrier *via* an inelastic process in which it loses energy $\hbar\omega$ to the mode. Such processes represent an additional channel for charge transfer so that, at their onset when $eV = \hbar\omega$, there is a step increase in differential conductance dI/dV and so a peak in the second differential d^2I/dV^2 of the junction characteristic. The material to be studied is either introduced as a barrier contaminant, as has been done in experiments with organic molecules [5] or, as in the present study, the material itself can be used to form the barrier.

Tunnel junctions were prepared in an oil pumped chamber by the following sequence. First an aluminium base electrode of thickness about 100 nm was deposited at 2–5 nm s^{-1} and at a pressure less than 5×10^{-6} mm Hg on a clean glass substrate at room temperature. The barrier was then formed by evaporating SiO from resistively heated boats to a nominal (mean) thickness of 3 nm at 0.3 nm s^{-1} and a pressure of about 2×10^{-6} mm Hg on a clean glass substrate at room temperature. Such thin films are not continuous so it was then necessary to oxidise the barrier to block pinholes with alumina. This was done by a glow discharge in pure oxygen at 7×10^{-2} mm Hg for 5 min. Using suitable masks, a thick layer of SiO was then deposited to define a tunnelling area that did not include edges of films. This is necessary to avoid spurious effects from film edges. Finally an aluminium counter-electrode was deposited. Electrical connections were *via* fine wires and indium pads and the measurement circuitry used standard bridge and phase-sensitive detection techniques [6]. To avoid significant instrumental line-broadening, a modulation level of 1.4 mV was used at a measurement temperature of 4.2 K. Electron diffraction measurements on the SiO_x showed that it was amorphous and electron energy-loss work gave $x = 1.4 \pm 0.1$.

Tests were made to confirm that the predominant mechanism of charge transfer was tunnelling through the SiO_x. Comparison of I–V characteristics with the aluminium in superconducting and normal states showed conduction to be by tunnelling; the absence of an – OH peak at 120 mV (which is always associated with aluminia) showed that tunnelling was not through the alumina; and absence of molecular vibrational modes in the 160–500 meV range proved that there was no significant organic contamination.

Figure 1 shows the second differential characteristic where the structure associated with the SiO_x stands out from the smoothly varying background. Substraction of the background and averaging of the structure for positive and negative biases results in the spectrum shown in Fig. 2.

It would be desirable to compare these results with neutron, Raman and infra-red measurements on similarly prepared material. We have made some Raman and infra-red measurements and these show the same broad peaks

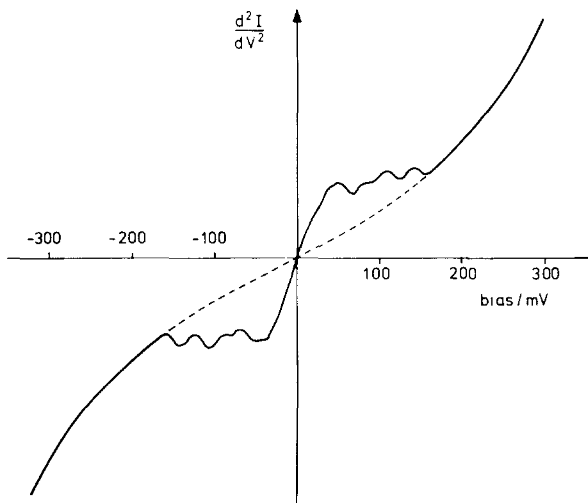

Fig. 1. Second differential of the current-voltage characteristic for tunnelling through a thin film of SiO_x between aluminium electrodes. The structure resulting from inelastic interactions in the SiO_x stands out above the smooth background.

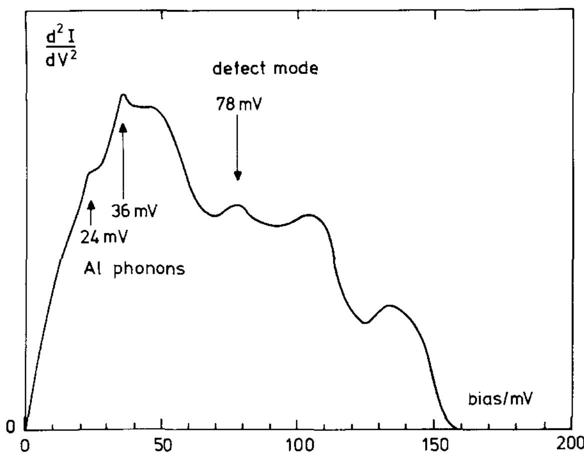

Fig. 2. The second differential spectrum after substraction of the background and averaging of the data for positive and negative biases.

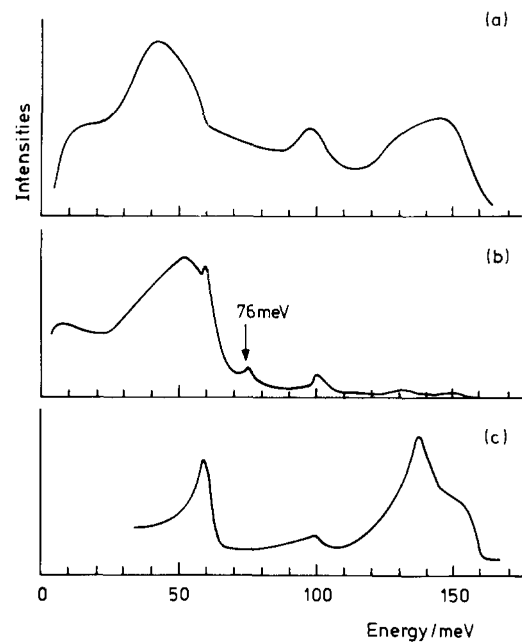

Fig. 3. Phonon spectra obtained by (a) inelastic neutron scattering, (b) Raman spectroscopy, (c) infra-red spectroscopy. Different relative sensitivities in different parts of the spectra result from the different energy-dependencies of the relevant matrix elements. (Data from [2], [3] and [4]).

but details were obscured by large noise levels resulting from the relatively thin samples that could be prepared by evaporation. Instead, we discuss the results in relation to neutron, Raman and infra-red work carried out on vitreous *bulk* SiO_2. These are shown in Fig. 3.

It must first be pointed out that the four techniques have different (and unknown) energy-dependence for their scattering matrix elements and one cannot derive quantitative values of $g(\omega)$ from any of the measurements. Differences of relative amplitudes in different parts of the spectra are therefore not significant. The three dominant peaks in SiO_2 at approximately 50, 100 and 140 meV correspond to different types of oxygen–silicon relative motion in the Si–O–Si "molecule" [3]. Similar modes should occur in SiO_x and indeed are observed in the inelastic electron tunnelling spectrum shown in Fig. 2. A comparison of the relative amplitude of the three peaks in Fig. 2 both with the neutron data and with calculated spectra [7] indicates that the matrix element linking $g(\omega)$ to the inelastic tunnelling spectrum decreases smoothly with increasing energy, and does not have the rapid variations with energy seen in the infra-red and Raman spectra. A reliable theoretical guide to this matrix element would be very valuable, as the results do not appear to support existing ideas [8].

Specific features deserve comment. The tunnelling electrons can undergo inelastic interaction not only in the barrier but also in the region of the barrier/electrode interface. This accounts for the aluminium phonon peaks at 24 mV and 36 mV visible in the tunnelling spectrum.

The peak at 78 meV is not observed in neutron or infra-red spectra of SiO_2, but almost coincides with a peak of 76 meV in the Raman spectrum. This peak has been attributed to a "defect mode" by Stolen

et al. [9] on the basis that the intensity increases when SiO_2 is irradiated with neutrons. Microscopically the mode has been ascribed to vibrations of Si–Si bonds in the SiO_2 matrix [10], and also to vibrations associated with oxygen [2, 11]. The enhancement of the mode in SiO_x, which presumably contains excess Si–Si bonds rather than excess oxygen, appears to support the former interpretation, although relative motion of two silicon atoms inevitably entrains the motion of nearby oxygen. It is noticeable that the peak in the inelastic electron spectrum is broadened in comparison to the Raman peak, a result which correlates with the more disordered structure of the vapour condensed SiO_x film as compared to SiO_2 samples formed by slow cooling from the melt.

This preliminary work establishes inelastic electron tunnelling spectroscopy as a powerful and versatile technique for the study of the amorphous state.

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