Internal Friction of Subnanometer a-SiO$_2$ Films

B. E. White, Jr. and R. O. Pohl

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501
(Received 24 August 1995)

In order to determine whether strong interactions between defects are responsible for the spectral distribution of the low energy excitations that are believed to exist in all amorphous solids, we have measured the low temperature internal friction of thin a-SiO$_2$ films with thicknesses ranging from 0.75 to 1000 nm. The internal friction of these films is found to be identical to that of bulk a-SiO$_2$. From this it is concluded that interactions, if significant at all, are limited to distances less than 0.75 nm.

The internal friction of amorphous solids at temperatures below $\sim$5 K is remarkably similar, despite the wide range of chemical and physical properties present in these solids [1]. In this temperature range, the internal friction, Q^{-1}, becomes independent of temperature with a magnitude, Q_0^{-1}, between 10^{-4} and 10^{-3}. Similar universality is also seen in the thermal conductivity of amorphous solids. In terms of the tunneling model [2], which has been rather successful in describing the anomalous low temperature thermal and elastic properties of amorphous solids, the universal quantity that appears in expressions for both the thermal conductivity and internal friction is

$$C_{l,t} = \frac{\overline{P}\gamma_{l,t}^2}{\rho v_{l,t}^2}, \qquad (1)$$

where $\overline{P}$ is the spectral density of states of the tunneling entities, $\gamma_{l,t}$ is the coupling energy of the phonons to the tunneling entities, where the subscripts denote the differences in the coupling energy of transverse (t) and longitudinal (l) phonons, $v_{l,t}$ is the speed of sound in the amorphous solid, and ρ is the mass density. The internal friction in the plateau region, Q_0^{-1}, is a direct measure of C (omitting the subscripts here and in the following) with

$$Q_0^{-1} = \frac{\pi}{2} C. \qquad (2)$$

Despite its success, the tunneling model offers no explanation as to why C should have a nearly universal value. Recently, several workers [3] have postulated the existence of strong interactions between the defects as a means of explaining the universal value of C. We have tested this assumption by looking for size effects in the internal friction of thin amorphous films. From the observations presented here, we conclude that if strong interactions play any role they must be limited to length scales less than 0.75 nm, the minimum thickness of the films studied. This is only 3 times the size of the SiO$_4$ tetrahedron, which is 0.26 nm.

For the purpose of this study, we have developed a technique for measuring the internal friction of thin films, which has been described in detail elsewhere [4] and will only be briefly summarized here. The internal friction of a thin film can be determined from the change in

the internal friction of an oscillator, which acts as a substrate for the thin film, after deposition of the film. In our technique, the oscillator is a modification of one developed by Kleiman *et al.* [5] and is known as a double paddle oscillator (see inset of Fig. 1). It is etched from an ultrapure $\langle 100 \rangle$ silicon wafer. Because of its complicated geometry, the oscillator has many modes of vibration. We are primarily interested in the mode, known as the antisymmetric mode, in which the head (H) and wings (W) vibrate out of phase with each other, twisting the neck (N). In this mode, the change in the internal friction of the oscillator, ΔQ^{-1}, after deposition of a thin film is given by

$$\Delta Q^{-1} = \frac{3G_{\text{film}}t_{\text{film}}}{G_{\text{sub}}t_{\text{sub}}} Q_{\text{film}}^{-1}, \qquad (3)$$

where Q_{film}^{-1} is the internal friction of the film; t_{film} and t_{sub} are the thicknesses of the film and substrate, respectively; and G_{film} and G_{sub} are the corresponding shear moduli. In our experiments, $G_{\text{sub}} = G_{\text{si}} = 6.2 \times 10^{11}$ dyn cm^{-2} and t_{sub} was 300 or 385 μm. Through the proper choice of silicon wafer, paddle geometry, etching, and paddle mounting, a background (bare paddle) internal friction of $\sim$3 $\times$ 10^{-8} at 1 K could be achieved for the antisymmetric mode. More importantly, the background could be made to be reproducible to within 1% upon thermally cycling the oscillator to room temperature and removing it from the cryostat. With these paddles, we were able to measure the internal friction of amorphous thin films as small as 0.7 nm.

Amorphous SiO$_2$ films were produced by electron beam evaporation, thermal oxidation at 1300 K, and oxidation at room temperature (native oxide). Electron beam evaporated films were deposited at a rate of $\sim$0.1 nm/s onto a double paddle oscillator, at room temperature in a vacuum of 1 $\times$ 10^{-6} torr. Before deposition, the native silicon oxide was removed from the oscillator and the surface hydrogen terminated using a 1% solution of HF. Thicknesses of the deposited films were determined by a quartz crystal balance and ranged from 0.75 to 1000 nm. Independent verification of the thicknesses was obtained, on films deposited under similar conditions, for thick films
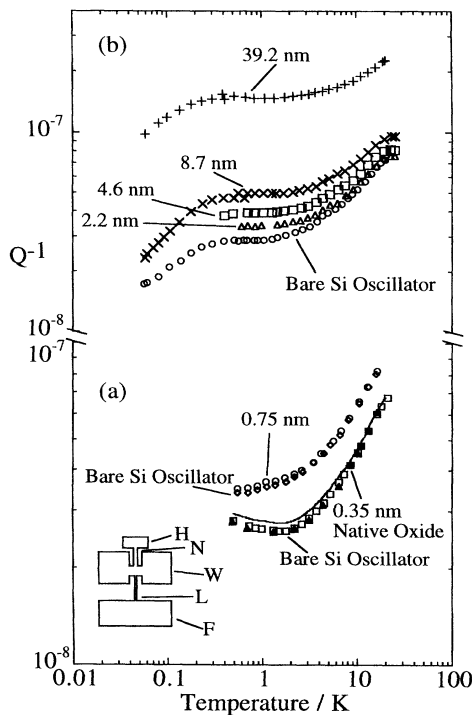
FIG. 1. The internal friction, Q^{-1}, as a function of temperature for three silicon double paddle oscillators both before and after deposition of thin a-SiO_2 films. The frequency of the oscillator is 5.5 kHz. (a) The 0.75 nm film was produced by electron beam evaporation onto a double paddle oscillator while the 0.35 nm was produced by oxidizing a bare silicon oscillator at room temperature. The solid line is explained in the text. (b) The internal friction as a function of temperature for one silicon double paddle oscillator carrying a series of a-SiO_2 films deposited consecutively by electron beam evaporation. Cumulative thicknesses are indicated. Inset: Geometry of the double paddle oscillators used in this work, height 35 mm, width 20 mm, thickness 0.3 mm. H: head, N: neck, W: wings, L: leg, F: foot.

using a stylus while for thin films through x-ray photoelectron spectroscopy (XPS). These thicknesses were found to agree with those measured by the quartz crystal balance to within 20%, with the quartz crystal balance always indicating a slightly thicker film. One film of a-SiO_2 was produced by wet thermal oxidation at 1300 K. Its thickness was determined from ellipsometry to be 500 nm. Another a-SiO_2 film was produced by room temperature oxidation of the hydrogen terminated surface, without removing the oscillator from the cryostat. The thickness of the native oxide was determined to be 0.35 nm by XPS. Atomic force microscopy measurements of an electron beam evaporated film with a thickness of 2.2 nm revealed that the film could be characterized by a rms roughness of only 0.1 nm, unchanged from the unoxidized, polished, surface. We therefore assumed that in all cases the films are continuous and of uniform thickness.

Figure 1 shows the effect of various a-SiO_2 films on the internal friction of the bare (H terminated) silicon oscillator. The thicknesses of the films shown range from 0.35 nm for the native oxide to 39.2 nm for the electron beam evaporated films. As can be seen, even an electron beam evaporated film with a thickness of 0.75 nm produces a measurable change in the internal friction of the oscillator. This is in contrast to the 0.35 nm native oxide film, which produces no change in the damping to within our experimental limits. The solid line in Fig. 1(a) shows the expected change in the internal friction of the oscillator due to the native oxide, calculated under the assumption that this film has the same internal friction as the thicker ones. Note that the effect should be comparable to that produced by the 0.75 nm e-beam film because the native oxide is present on both sides of the oscillator, which effectively doubles its thickness. Obviously, the native oxide has a smaller internal friction than a-SiO_2.

Using Eq. (3) we can predict the expected change in the internal friction of the oscillator if we assume that the shear moduli and internal friction of the films are those of bulk a-SiO_2. This is indicated by the straight line shown in Fig. 2, where we have plotted ΔQ^{-1} at 1.3 K as a function of the ratio of film thickness to substrate thickness. In addition to the data shown in Fig. 1, we have also included other data (shown as open squares) taken with earlier versions of the double paddle oscillator. Data taken on a 500 nm thermal oxide film are also shown, as well as the data taken for the 0.35 nm
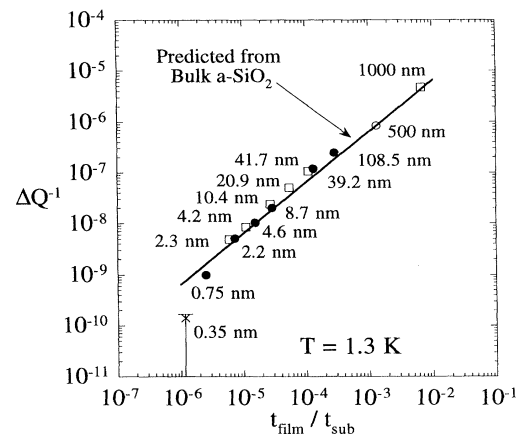

FIG. 2. The change in the internal friction of silicon double paddle oscillators at 1.3 K due to the deposition of thin a-SiO_2 films as a function of the ratio of the film thickness to substrate thickness. The solid line represents the expected result based on Eq. (3) and the shear moduli and internal friction of bulk a-SiO_2. Film thicknesses are indicated in the figure. The solid circles are from data shown in Fig. 1 (thicknesses are below the line), while the open squares are from data taken on other double paddle oscillators (thicknesses above the line). The open circle is from data taken on a 500 nm a-SiO_2 film produced by wet oxidation. The × marks the upper limit for the 0.35 nm native oxide film.

native oxide. In the case of the native oxide, the data point shown corresponds to the maximum change in the internal friction that is not detectable with our technique. Remarkably, the measured values of the change in internal friction, down to thicknesses of 0.75 nm, agree very well with the predicted values based on bulk a-SiO_2. From these results, we draw two important conclusions. First, the internal friction of these films in the plateau region agrees closely with that of bulk a-SiO_2. Thus, there is no evidence that the damping depends on film thickness. Secondly, the shear moduli of these films, even at a thickness of 0.75 nm, is also in good agreement with that of bulk a-SiO_2. This is further supported by the agreement of the measured thicknesses of these films as determined by XPS and the quartz crystal balance, since for the latter method the shear modulus of the film is needed to obtain the thickness. Note that in recent measurements on thin films of InAs and Ge it was observed that the bulk elastic properties of these materials are established within thicknesses of three monolayers [6].

In Fig. 3, we show the measured internal friction of the electron beam deposited films as well as the wet thermal oxide film. For all of these data, the appropriate background internal friction has been subtracted and the data have been scaled according to Eq. (3), assuming that the shear moduli of the films is that of bulk a-SiO_2. As can be seen, even in the thinnest films, the internal friction approaches a temperature independent value at temperatures below 5 K, which is very close to that of bulk a-SiO_2. For the 8.7 nm film, we have extended the measurements to lower temperatures and observe the same decrease of the internal friction from the plateau value as observed in bulk a-SiO_2. Finally, while the low

temperature properties of the thin films we have measured are consistent with bulk a-SiO_2, differences do occur at higher temperatures. For example, the characteristic peak in the internal friction seen in bulk a-SiO_2, and also in the wet thermal oxide film, is not present in the films deposited by electron beam evaporation. These differences, as well as the negligible damping found in the native oxide, will be discussed in a subsequent publication.

In conclusion, we have measured the internal friction of thin a-SiO_2 films with thicknesses ranging from 0.35 to 1000 nm. We find that the low temperature internal friction of these thin films is nearly identical to that of bulk a-SiO_2. This indicates that, if interactions play a role at all in determining the universal nature of the thermal conductivity and internal friction in a-SiO_2, the interaction is limited to distances not exceeding the smallest film thickness studied here, which is 0.75 nm. On such small length scales, one should probably not talk about interactions, but rather about intermolecular forces.
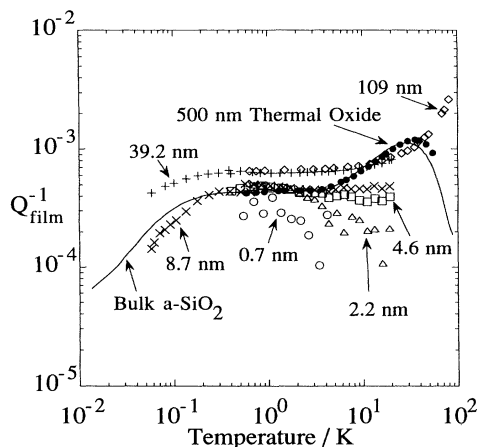
FIG. 3. The internal friction of the a-SiO_2 films shown in Fig. 1 as a function of temperature, as well as a 500 nm wet thermal oxide film. The low temperature internal friction of these films ($T \leq 1$ K, tunneling regime) is nearly identical to that of bulk a-SiO_2 (solid line), regardless of their thickness. Note that above ~ 10 K the e-beam films do not show the peak seen in thermally oxidized and bulk a-SiO_2.

[1] See, for example, J. F. Berret and M. Meissner, Z. Phys. B **70**, 65 (1988); B. E. White, Jr. and R. O. Pohl, Z. Phys. B (to be published).

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