## **Amorphous Solid without Low Energy Excitations**

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We have measured the low temperature internal friction  $(Q^{-1})$  of amorphous silicon (a-Si) films. *e*-beam evaporation or <sup>28</sup>Si<sup>+</sup> implantation leads to the temperature-independent  $Q_0^{-1}$  plateau common to all amorphous solids. For hydrogenated amorphous silicon with 1 at. % H produced by hot wire chemical vapor deposition, however,  $Q_0^{-1}$  is over 200 times smaller than for *e*-beam *a*-Si. This is the first observation of an amorphous solid without any significant low energy excitations. It offers the opportunity to study amorphous solids containing controlled densities of tunneling defects, and thus to explore their nature. [S0031-9007(97)03352-8]

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The suggestion, first made 26 years ago, that all amorphous solids share low energy vibrational excitations in rather similar magnitude [1], has since been confirmed without exception in a wide range of materials [2,3]. A phenomenological model based on the assumption of atomic tunneling entities of constant spectral density  $\overline{P}$ [4,5] has also withstood the test of time, even though the physical nature of these entities, and, in particular, the nearly universal magnitude of  $\overline{P}$  in all amorphous solids has not yet been explained convincingly [6]. Undoubtedly, a major obstacle to their understanding was the very universality of these excitations, which made it impossible to modify them in some controlled way, and thus be able to study their properties. In this Letter, we report the first successful modification of these excitations: By changing the chemical composition of an amorphous solid, its low energy excitations have been essentially eliminated as measured by the low temperature internal friction they cause. This has been accomplished in amorphous silicon into which hydrogen has been introduced in small concentration.

The question whether amorphous silicon or germanium contains low energy excitations has been studied extensively in the past. However, since these solids can be produced only as thin films which are poorly suited for the standard methods of detection of those states, i.e., low temperature thermal conductivity, specific heat, and ultrasonic attenuation, the results have been controversial (for a critical review of many of the earlier investigations, see Ref. [7]). It has recently been shown that the damping of the torsional motion of double-paddle oscillators made out of high purity crystalline silicon is low enough so that the low energy excitations of thin amorphous films can be studied. Films of amorphous silica as thin as 0.75 nm could be detected, and both their internal friction and their shear modulus were found to be equal to those of bulk a-SiO<sub>2</sub> [6]. In the present investigation, the same technique will be used to study amorphous silicon films produced by different techniques, with and without hydrogen.

Hydrogen-free amorphous silicon was prepared by ebeam evaporation in a vacuum of  $10^{-7}$  Torr onto a paddle held at  $\sim 300$  K. Such films are known to be porous and grainy. These macroscopic defects can be avoided if the silicon is amorphized by ion implantation [8]. Such films were produced by <sup>28</sup>Si<sup>+</sup> implanted at room temperature at three energies, 50, 120, and 180 keV, in order to achieve uniform amorphization to a depth of 330 nm, as measured by cross-sectional transmission electron microscopy, using a Phillips CM-30 operating at 300 keV, and also by Rutherford backscattering and channeling spectroscopy. which agreed very well. Both the e-beam amorphous film and the ion-implanted amorphous layer cause a temperature independent internal friction  $(Q_{paddle}^{-1})$  of the oscillator below  $\sim 10$  K, shown in the lower part of Fig. 1, where the solid line is the background damping of a typical bare paddle. These thin films increase the damping far above the background. In the ion-implanted paddle, an additional narrow relaxation peak occurs near 50 K. It was identified as occurring in the heavily damaged crystalline region beneath the amorphous layer by removing the latter by plasma etching. This removed the damping below 10 K, but did not affect the relaxation peak. The latter will therefore be ignored in the following discussion, since it is not connected with the amorphized layer.

From the measured increase of the internal friction of the paddle, the internal friction  $(Q_{\text{film}}^{-1})$  of the amorphous film (layer) can be obtained through [6]

$$Q_{\rm film}^{-1} = \frac{G_{\rm sub} t_{\rm sub}}{3G_{\rm film} t_{\rm film}} (Q_{\rm paddle}^{-1} - Q_{\rm bare}^{-1}), \qquad (1)$$

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FIG. 1. Lower part: Internal friction of three double-paddle oscillators vibrating with a frequency of ~5 kHz one bare ("background"), one with a film (500 nm thick) of *e*-beam *a*-Si, and one with a layer 330 nm thick amorphized by  ${}^{28}\text{Si}^+$  implantation. In the upper part, the absolute value of the internal friction of film or layer has been determined, using Eq. (1). Bulk *a*-SiO<sub>2</sub> is shown for comparison. The double arrow indicates the range of temperature-independent low temperature internal friction (the plateau,  $Q_0^{-1}$ ) measured to date in bulk amorphous solids (Ref. [3]).

where G and t refer to the shear moduli and thicknesses of the paddle and the film (layer), respectively. For the e-beam film,  $G_e = 3.63 \times 10^{11}$  dyne/cm<sup>2</sup> (55% of the shear modulus of polycrystalline silicon) was used, based on sound velocity measurements by Cox-Smith et al. [9] and the mass density  $\rho_e = 2.1$  g cm<sup>-3</sup> (=  $0.9\rho_{\rm Si}$ ) [8]. Film thickness  $t_e = 500$  nm was determined with a stylus. Similarly, for the implanted layer,  $G_i = 5.54 \times 10^{11}$  dyne/cm<sup>2</sup> was used [9],  $\rho_i =$ 2.29 g cm<sup>-3</sup>, 98.2% of that for crystalline Si [8]. The top part of Fig. 1 shows the internal frictions of both the ebeam film and the implanted layer. They show the same temperature independence (the plateau) that is typical for all amorphous solids ( $Q^{-1}$  for bulk a-SiO<sub>2</sub> is shown for comparison). According to the tunneling model [4,5], the internal friction for torsional oscillations in the plateau region is given by

$$Q_0^{-1} = \frac{\pi}{2} \frac{\overline{P} \gamma^2}{\rho v^2}, \qquad (2)$$

where  $\overline{P}$  is the spectral density of the tunneling states,  $\gamma$ their coupling energy to the lattice,  $\rho$  the mass density, and v the transverse sound velocity. The double arrow in Fig. 1 indicates the range of  $Q_0^{-1}$  found for all amorphous solids measured to date in the temperature region of the plateau [3]. We conclude that the e-beam *a*-Si film contains tunneling states, leading to an internal friction  $Q_0^{-1} \approx 1 \times 10^{-4}$  that lies close to the lower limit of the empirical range for all amorphous solids. For the silicon layer which had been amorphized by implantation, the temperature independence of the internal friction also indicates a constant  $\overline{P}$ , but the smaller value of  $Q_0^{-1}$  suggests that the spectral density is smaller.  $Q_0^{-1}$  is about 4 times smaller than for the *e*-beam film. This is a somewhat larger variation than that commonly observed in other amorphous solids prepared by different techniques. For example, in heavily neutron-irradiated bulk a-SiO<sub>2</sub>, low temperature thermal conductivity and specific heat measurements have indicated a decrease of  $Q_0^{-1}$  by a factor of 2 relative to that of well annealed, unirradiated a-SiO<sub>2</sub> [10]. The larger effect observed in a-Si is the first indication that the low energy excitations in this solid are sensitive to details of its preparation.

For use as a semiconductor, the dangling bonds found in a-Si have to be passivated by hydrogen. The most common process is plasma enhanced chemical vapor deposition (PECVD) of silane, which introduces typically 10 at. % hydrogen into the silicon. This hydrogen is not distributed uniformly throughout the amorphous lattice. In device quality material most of it is clustered in small regions, and only 20%-30% are isolated and distributed randomly throughout the material [11,12]. Recently, the National Renewable Energy Laboratory has pioneered the use of low-pressure hot-wire-assisted chemical vapor deposition (HWCVD) of silane with which semiconducting grade a-Si:H with hydrogen concentrations as small as 0.07 at. % has been produced [13,14]. This concentration is just sufficient to passivate the dangling bonds. The structural properties of the HWCVD material with small hydrogen concentration are markedly different from those of PECVD a-Si:H. For example, it contains no nanovoids, and x-ray diffraction measurements show this amorphous material to have a narrower first x-ray diffraction peak than PECVD a-Si:H, indicating improved medium range order [15]. The hydrogen microstructure of HWCVD material is also significantly different from PECVD material. For example, in HWCVD a-Si with 2 at. % H, most of the hydrogen has been observed to form clusters [16]. From their number and the mean spacing and number of the H in a cluster, we estimate that these occupy less than 0.4% of the volume [16]. Large regions which contain no hydrogen appear to be exceptionally well ordered, although they are certainly amorphous, as shown in Fig. 2. All a-Si films used in this study were also checked for amorphicity by x-ray diffraction and Raman scattering.



FIG. 2. High resolution transmission electron microscope picture of paddle/amorphous silicon interface region. The Si substrate is the paddle; the 10 nm thick epi layer was grown before the 2  $\mu$ m amorphous film (HWCVD with 1 at. % H). Inset: Electron diffraction pattern from the amorphous film.

The addition of hydrogen to the a-Si during the chemical vapor deposition has a striking influence on the low temperature internal friction, with the most dramatic effect observed for the HWCVD films grown at a substrate temperature of 380 °C which leads to an incorporation of about 1 at. % H. Internal friction caused by such films is shown in Fig. 3 for three films with thicknesses ranging from 1.6 to 2.8  $\mu$ m. In contrast to the large effect of hydrogen-free films shown in Fig. 1, the films with the hydrogen cause only a very small increase of the damping of the paddles below 100 K. Note that these films are 3-9 times thicker than those in Fig. 1. If measurements of paddles carrying 2  $\mu$ m thick *e*-beam films were plotted in Fig. 3, their  $Q^{-1}$ would lie above  $10^{-6}$ . The solid curve in Fig. 3 is measured for a typical bare paddle, which has been found to be reproducible to within  $\pm 10\%$  for all the paddles machined from the same silicon ingot. This variation is probably caused predominantly by the differences in the epoxy joints used for mounting the paddle in the cryostat. With increasing thickness of the HWCVD a-Si films, the damping increases (see the inset in Fig. 3, which shows the internal friction at 4.2 K). The solid line yields an approximate variation of the internal friction of the paddle with film thickness, and is used to determine the internal friction of the films at this temperature, using Eq. (1); since the mass density of these films is close to that of  ${}^{28}\text{Si}^+$  implanted *a*-Si, we also used the shear modulus of the latter in Eq. (1). Thus, we obtain  $Q_0^{-1} =$  $5 \times 10^{-7}$  at 4.2 K for these films, which is 250 times smaller than the value of the *e*-beam *a*-Si. Consequently, either the spectral density  $\overline{P}$  of the tunneling states or the coupling energy  $\gamma$  has been drastically reduced. While



FIG. 3. Internal friction of three double-paddle oscillators carrying films of HWCVD *a*-Si:H with 1 at. % H with different thicknesses, compared to a typical background internal friction of a bare paddle. Inset: Internal friction at 4.2 K for the four paddles.

the accuracy of the measurements does not allow one to verify the temperature independence of  $Q^{-1}$  for these films, our data certainly do not disagree with such a conclusion. The only exception is observed below 2 K, where the internal friction of the paddle increases with decreasing temperatures although not with film thickness. While it cannot be ruled out that this increase is a property of the films, we suspect that it is caused by some accidental impurity, conceivably boron, which has been shown to lead to a relaxation peak at  $\sim 0.1$  K [17]. We observed similar peaks in bare wafers after they had been heat treated without following stringent cleaning procedures. However, the nature of this peak in the HWCVD a-Si film with 1 at. % H is irrelevant for the major conclusion, which is that this amorphous film does not have low energy excitations in anywhere near the concentration commonly found in all amorphous solids. The important role of the hydrogen in these films is further illustrated in Fig. 4, in which HWCVD films with 1, 3, and 6 at. % H are compared. The two higher concentrations show pronounced relaxation peaks; however, even below 2 K the nearly temperatureindependent internal friction,  $Q_0^{-1} \approx 5 \times 10^{-5}$  for the 6% film, is smaller than that of the hydrogen-free *e*beam film. In some exploratory measurements, three films prepared by HWCVD and by PECVD, all with 10 at. % H, were measured below 20 K, and showed a temperature-independent internal friction  $Q_0^{-1} \sim 10^{-5}$ , much smaller than hydrogen-free films. After removal of the hydrogen from he PECVD film through a vacuum anneal at 530 °C, the internal friction was found to increase threefold. Although these findings need to be



FIG. 4. Internal friction caused by three films of HWCVD films with different hydrogen concentrations.

confirmed, they show that the effects of the hydrogen are not restricted to the HWCVD films.

To conclude, hydrogen in small concentrations has been shown to virtually eliminate the low energy excitations in HWCVD amorphous silicon films. The cause for this anomalous and entirely unexpected behavior is unknown, and calls for a systematic study. Conceivably, the hydrogen in small concentrations leads to the formation of an amorphous network with more perfect fourfold coordination. Such a lattice may be expected to have fewer low energy excitations. This interpretation would support the major assumption made in the tunneling model, which is that the low energy excitations result from the motion of atoms which have more than one equilibrium position. For a discussion of the absence of tunneling states in overconstrained lattices, see Refs. [4,18,19]. This interpretation would also indicate that the excellent semiconducting properties in these films are caused by the low density of the dangling bonds and nanovoids, rather than by those bonds being chemically passivated by hydrogen being bonded to them. Regardless of this speculation, however, we wish to emphasize the fact that we now have, for the first time, an amorphous solid in which the low energy excitations can be modified. This offers the exciting opportunity of identifying their nature.

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