Measurement of Phonon Densities of States for Pure and Hydrogenated Amorphous Silicon

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Vibrational spectra for a-Si and a-SiH$_{0.12}$ have been measured by inelastic neutron scattering, directly yielding the phonon density of states for the former material, and the partial phonon density of states for H vibrations for the latter. The relevance of these results to the interpretation of infrared and Raman spectra is discussed.

Because amorphous silicon (a-Si) and amorphous germanium (a-Ge) are the simplest covalently bonded amorphous solids, they are important prototype systems for investigating the basic properties of the disordered solid state, including the vibrational properties which are the subject of the present study. In the following, we present the first detailed inelastic neutron scattering results on the vibrational spectra of a-Si and hydrogenated a-Si (a-Si:H). The potential utility of the latter material in device applications provides additional motivation for our measurements, since the local bonding configurations of H, and the corresponding influence on electronic properties, have often been characterized with the aid of optical vibrational spectroscopy. It is therefore of some interest to perform analogous neutron experiments for comparison, since the complex transition probabilities which enter into the interpretation of infrared (IR) and Raman spectra are absent in the case of neutrons. The neutron method as applied here bears a particularly close relation to theoretical work[1-4] on the vibrations of amorphous systems, yielding directly one of the most easily calculated and physically significant quantities, the phonon density of states $g(\omega)$.

The samples of a-Si and a-Si:H (5 g each) were prepared by reactive rf sputtering in an Ar/H atmosphere, using methods and apparatus that have been described in detail elsewhere.[5] Several methods were used to characterize the samples. X-ray and neutron diffraction revealed a typical amorphous elastic structure factor. By comparison of the proton NMR signal of our a-SiH$_x$ sample with a standard water sample, the H content was determined to be $x = 0.119 \pm 0.005$. The shape of the NMR line reflected a narrow component (40%) superposed on a wider component (60%), corresponding to the "distributed" and "clustered" forms of H discussed in previous NMR studies[6] on a-Si:H. IR absorption spectra obtained by photoacoustic spectroscopy will be discussed later by comparing them directly with the neutron results.

The neutron scattering measurements were carried out on two instruments—a time-of-flight (tof) spectrometer at Jülich, and a triple-axis spectrometer at the new Orphée reactor at Saclay. The tof method is preferable for measurements on amorphous materials, mainly because of a higher rate of data collection, and our primary results were obtained by this method, using neutrons with an incident energy of 3.6 meV and measuring the spectra in neutron energy gain. The tof data, obtained in 60- and 32-h runs on a-Si and a-SiH$_{0.12}$, respectively, were reduced to phonon densities of states through procedures es-

tablished over many years at Karlsruhe.[7] The results are fully corrected for multiphonon scattering contributions up to six-phonon terms.

The phonon density of states determined for a-Si is compared in Fig. 1 with $g(\omega)$ for crystalline Si (c-Si) as calculated from a model[8] which accurately reproduces the phonon dispersion curves. The four major peaks in $g(\omega)$ for c-Si at 20, 40, 50, and 60 meV are conventionally referred to as TA, LA, LO, and TO peaks, a terminology which will be followed here. The $g(\omega)$ for a-Si displays all four of these features, and over all there is a substantial similarity between the two distributions. Noteworthy differences are that (i) the peak at 27 meV at the top edge of the TA band for c-Si is absent for a-Si, (ii) the position of the LA feature is lowered in energy from 40 meV in c-Si to 35 meV in a-Si, and (iii) the 60-meV TO peak is much smaller in amplitude for a-Si, even with consideration of the effects of experimental resolution (about 7 meV full width at half maximum at $\hbar\omega = 60$ meV). Since one expects the area under the TO peak to be approximately preserved, this implies that the peak must be very asymmetric, with a long tail toward lower energies which lies under the LA and LO features. We have in fact checked that the aggregate area under the LA, LO, and TO features above 28 meV is the same (0.64 of
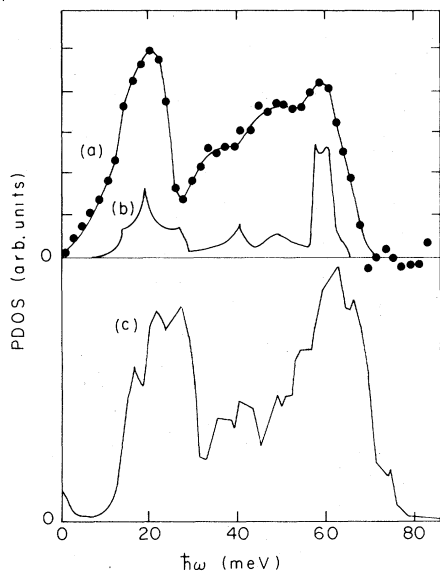
the total) for both the a-Si and c-Si distributions. Without very detailed calculations, it is difficult to explain the differences (i)–(iii), although qualitatively (iii) might have been anticipated in that the features in $g(\omega)$ for a crystalline material are expected to be sharper than for its amorphous counterpart. The observed reduction in amplitude is, however, generally greater than obtained by Alben et al.[1] in the most detailed calculations to date. As shown in Fig. 1, a representative calculated $g(\omega)$ has more weight at 60 meV and less in the 40–50-meV region. One possible explanation is that the distribution of nearest-neighbor bond angles is wider than assumed in the calculation. Lannin et al.[9] have observed that the width of the TO peak in Raman spectra is sensitive to deposition conditions, interpreting this as due to different bond angle distribution widths. Comparison of the neutron-derived $g(\omega)$ with Raman spectra[9,10] reveals that the latter do indeed reflect all the features in $g(\omega)$, albeit with a strongly ω-dependent transition probability factor.

Because Si is a predominantly coherent scatterer of neutrons, the cross section of a-Si depends strongly on wave vector Q for $Q \lesssim 4$ Å^{-1}, but becomes[1] nearly Q-independent and representative of the phonon density of states at larger Q. In our tof neutron experiment, we sample a fairly wide range of Q for each value of the phonon energy $\hbar\omega$ and although some of the Q values are small, the averaging process is sufficient to provide $g(\omega)$ of a-Si within a few percent for $\hbar\omega > 12$ meV. This point has been carefully checked by direct comparison with the Q-dependent neutron cross sections calculated in Ref. 1. For small $\hbar\omega$, the Q-averaging is less satisfactory, and the fact that $g(\omega)$ does not go as ω^2 below 10 meV could be due to this, although it is more likely to arise from extra low-frequency modes which are not present in the crystalline state. Because H has a large (~ 80 b) and primarily incoherent cross section, the data for a-SiH$_{0.12}$ involve no problem of Q averaging, but the function obtained is the partial phonon density of states for H vibrations (H-PDOS) rather than the total $g(\omega)$. This is true even for $\hbar\omega \leq 65$ meV, where the kinetic energy is mostly that of the Si atoms, but the H atoms still provide about 80% of the neutron cross section.[4]

The H-PDOS for a-SiH$_{0.12}$ (Fig. 2) shows a number of interesting characteristics. In the Si-mode region below 65 meV, we can see TA, LO, and TO peaks, but the 60-meV TO peak is much
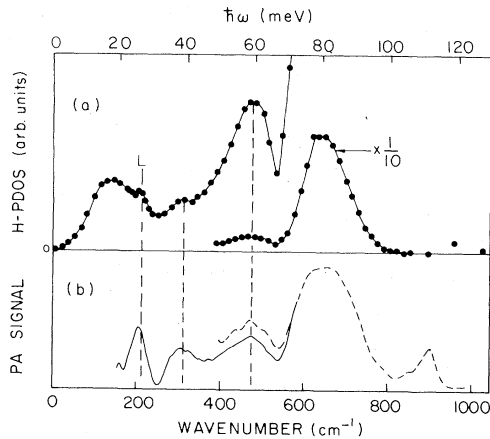

FIG. 1. Curve (a): experimental phonon density of states (PDOS) for pure a-Si, (b) PDOS of c-Si calculated from bond charge model (Ref. 8), and (c) PDOS for 61-atom model of a-Si (Ref. 1).

FIG. 2. (a) Partial phonon density of states for H modes (H-PDOS) in a-SiH$_{0.12}$. (b) Infrared absorption measured by photoacoustic (PA) spectroscopy. The zeros and scales of the IR spectra have been adjusted for convenience.

FIG. 3. (Top) Triple-axis data on a-SiH$_{0.12}$. A Be filter was used as analyzer. (Bottom) IR absorption spectrum.

stronger than the TA or LO features. If the H atoms were merely passive "riders" on the Si vibrations, this asymmetry would not develop, and this part of the spectrum would look very much like $g(\omega)$ for pure a-Si. Evidently at higher frequencies H atoms have greater vibrational amplitudes than Si atoms. The enhancement has been noted in independent measurements by Axe and Passell,[11] who have been able to account for it quantitatively as a resonant response to the H wagging mode at 80 meV. Another noteworthy feature in the Si-mode region is the appearance of a small peak (L in Fig. 2) which is not present in pure a-Si. The IR absorption spectrum on the same a-Si:H sample shows a prominent peak at this energy. The 27-meV mode has been previously observed as a very strong feature in IR spectra by Shen et al.[12] and as a very weak feature in Raman spectra by Bermejo and Cardona.[13] The neutron peak is intermediate in strength. The most recent interpretation[2,3] of this feature is that it is an "acoustic local mode" in which a Si-H atomic pair vibrates together against the network back-boned to the Si atom.

The most prominent feature in the H-PDOS, the strong peak at 80 meV arising from wagging modes of the H atoms, has roughly the same shape as the corresponding IR absorption peak, thus merely confirming that the latter does in fact reflect the distribution of H modes in this region. Rather more interesting is the absence in the H-PDOS of a peak at 110 meV, where the IR spectrum displays a sharp peak. This feature is as-
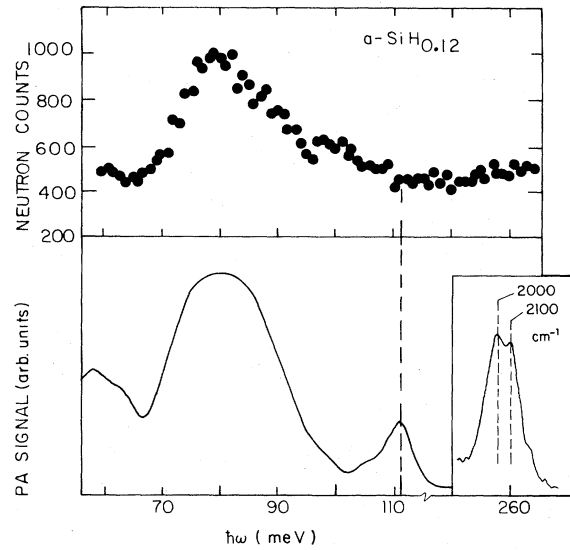
sociated with the so-called SiH$_2$ configuration, in which two H atoms are bonded to the same Si atom. The "bending" mode[4] of the configuration, in which the bond angle H-Si-H is modulated, has a somewhat higher energy (110 meV) than the "rocking" or "wagging" modes[4] in which the angle is not modulated, and which have nearly the same energy (80 meV) as the wagging mode of a H atom bonded in isolation to a Si atom. The 110-meV peak is not visible in the tof neutron data of Fig. 2, nor in the triple-axis spectrum of Fig. 3. The latter gives somewhat better sensitivity at these higher phonon energies because it was obtained in neutron energy loss rather than energy gain. Thus it appears that the actual amount of SiH$_2$ in a typical sputtered sample is much less than one would initially conclude from its IR absorption spectrum, i.e., the transition probabilities for the 110-meV SiH$_2$ bending mode are much larger than those of the 80-meV SiH wagging mode. In the near future, we plan to test this conclusion by measuring neutron spectra on sputtered samples specifically prepared to have strong absorption at 110 meV. The transition probabilities for the 2100-cm^{-1} (260-meV) stretching mode of SiH$_2$ must also be greatly enhanced over the 2000-cm^{-1} SiH stretching mode, since the absorption of our sample for both modes is comparable, as shown in the inset in Fig. 3, where the two components are not completely resolved but are clearly about equal in strength.

Perhaps the most desirable procedure for theoretical analysis of spectra such as we have measured lies in detailed computer simulations along the lines of Ref. 1, but with more atoms in the simulation, so that fine details in the theoretical and experimental spectra can be meaningfully compared. However, calculations by simpler methods[2-4] will also be useful when it is specifically H motions and the effects of H environments and clustering that are of interest. Barrio, Elliott, and Thorpe[4] have recently calculated neutron scattering cross sections for hydrogen in SiH, SiH_2, and SiH_3 complexes and have shown that the H vibrations are little affected by the modes of the Si network, which can be reasonably represented by a Bethe lattice of Si atoms to which the H complexes are attached.

Our experiment demonstrates that neutron scattering is an informative method for the spectroscopy of vibrational modes in pure and hydrogenated a-Si and a-Ge, particularly if optical spectra are obtained on the same samples. In the future, it would be very desirable to undertake systematic measurements involving all three of neutron, Raman, and IR spectroscopy, using samples prepared under a variety of conditions. It would also be of interest to examine the Q dependence of the scattering law $S(Q, \omega)$ for unhydrogenated samples, paying special attention to the region of low-energy excitations[14] near the first peak in the static structure factor $S(Q)$.

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