Infrared Absorption in a-Si:H: First Observation of Gaseous Molecular H_2 and Si-H Overtone

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We report the first observations of collision-induced infrared absorption of the fundamental vibrational band of molecular hydrogen incorporated in microvoids in heavily hydrogenated amorphous silicon. These results provide the first direct evidence of high-pressure gas (~ 2000 atm) occluded in a-Si:H. We also report the observation of the overtone absorption spectrum of the Si-H bond in a-Si:H, thus providing useful information regarding anharmonic potential well describing the Si-H bond in bulk amorphous silicon.

Hydrogen is commonly added to amorphous silicon during deposition process to saturate[1] the dangling silicon bonds. Formation of Si-H bonds has been inferred indirectly from the disappearance of the ESR signal[2] in a-Si and inferred directly from the observation of infrared absorption and Raman scattering[3] arising from the vibrational excitation of the Si-H bond in the bulk of a-Si:H. In addition, incorporation of molecular hydrogen in a-Si:H voids has been speculated[4] and deduced[5-8] from the anomalous proton spin-lattice relaxation time near 30 K and from thermal calorimetry indicating a conversion of orthohydrogen to parahydrogen in solidified hydrogen at $T \simeq 0.1$–5 K. In this Letter we report the first observations of infrared absorption arising from molecular gaseous hydrogen trapped within heavily hydrogenated a-Si. The infrared absorption of the fundamental vibrational band of H_2 is known to arise from the dipole moment induced through the overlap and anisotropic interactions as a result of collision processes in high-pressure gaseous hydrogen which has been extensively studied in the past.[9] We observe both single and double transitions in the molecular H_2 infrared absorption spectrum. The observation of double transitions conclusively points to the existence of more than one H_2 molecule in the microvoids in a-Si:H. Our measurements provide direct evidence of the existence of H_2 in voids at pressures approaching 2 000 atm in a-Si:H. Further, we report the first observations of the overtone spectra of Si:H vibrational absorption. These data provide information regarding the anharmonic interactions which describe the potential well for the Si-H bond in amorphous bulk silicon.

Hydrogenated amorphous silicon films of various thicknesses from 0.5 to 5.0 μm were prepared by plasma deposition from silane (30% SiH_4, 70% Ar, at a pressure of 0.36 Torr, rf power of 5 W, and a substrate temperature of 523 K) and were deposited on one half of the two flat sides of the crystalline silicon prism shown in Fig. 1 at a rate of 1 μm per hour. Hydrogen evolution data on similarly prepared samples have shown the total hydrogen content to be $\simeq 15$ at.%. Collimated light obtained from a Fourier-transform spectrometer was made incident on one of the prism edges as shown. The crystalline silicon substrate is 500 μm thick, and hence the infrared radiation travels along a zigzag path, being reflected from the silicon-vacuum boundary by total internal reflections. The refractive index of amorphous silicon being very close to that of the crystalline silicon substrate, there is no total internal reflection at the a-c interfaces. Thus at each internal reflection the infrared light samples the amorphous silicon film twice (at the angle of $\theta \simeq 37°$). We estimate that over the length of the substrate the infrared light makes fifty traversals back and forth giving a total sample thickness of amorphous silicon of

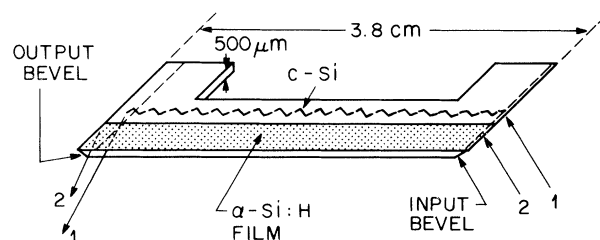$$l_{eff} = 200 l_{a\text{-Si}} \sec\theta. \tag{1}$$

FIG. 1. Schematic drawing of the silicon prism cut in a U shape to allow easy clamping without interfering with the bevelled edges. Half of the usable area is coated on both sides with an a-Si:H film while the other half remains clean. In position 1, the infrared radiation probes the clean c-Si, and in position 2, the a-Si film is probed. The internal angle of incidence is 37°.

Thus for a typical a-Si film thickness of 2 μm deposited on both sides of the c-Si substrate we have an effective thickness of about 0.5 mm. The infrared light exits at the other prism face and is measured with appropriate detectors. The absorption associated with the a-Si film was measured by subtracting from the spectrum of the coated half of the sample the spectrum obtained when probing the other half of the sample where no a-Si had been deposited. Similar multiple-reflection geometry has been used by Chabal[10] recently to study the surface reconstruction of silicon as well as to study the structural aspects of various molecules adsorbed on crystalline silicon.

The Fourier-transform infrared spectra were obtained with a Nicolet 6000 spectrometer which has been modified to accommodate samples as well as the detectors outside the conventional instrument. In the range of interest from 2000 to 5000 cm^{-1}, the signal-to-noise ratio with an InSb detector is such that a net absorption of as small as 0.1% could be measured for the light traversing the sample as shown in Fig. 1. The sample is mounted on a helium-cooled stage which allows us to reach temperatures as low as 30 K (limited by the present experimental apparatus[11]).

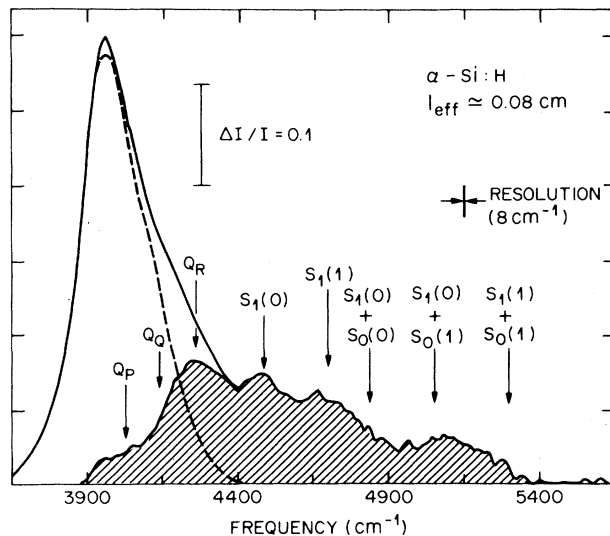A typical spectrum associated with the a-Si in the region 3650–5650 cm^{-1} is shown in Fig. 2. We

FIG. 2. Absorption spectrum of a-Si:H in the region 3700–5600 cm^{-1}. The solid line shows the raw spectrum associated with a-Si:H obtained by subtraction of the spectrum obtained in position 1 from that obtained in position 2 in Fig. 1. The dashed curve is the contribution from the SiH overtone and the hatched area the contribution from the occluded H_2 gas.

now show that it is made up from the superposition of two different contributions: (1) the strong absorption of the overtone of the SiH stretch centered around 3950 cm^{-1}, and (2) the broad and structured absorption of H_2 gas in the region 4150 cm^{-1} to 5500 cm^{-1}. The fundamental absorption of the Si-H stretch is too strong to be studied with our high-sensitivity configuration of Fig. 1. Therefore, we used data obtained with a one-bounce reflection and a one-pass transition to measure the line shape and intensity of the SiH fundamental. The line peaks at 2005 cm^{-1} with a full width at the half maximum of 140 cm^{-1} indicating that the contribution arises mainly from SiH rather than SiH_2 complexes as known for samples grown under similar conditions.[12] A reasonable fit was obtained by use of two Gaussians centered at 2000 and 2090 cm^{-1} with full width at half maximum $\sim$ 100 cm^{-1} and a respective strength ratio 2000/2090 $\sim$ 1.9 indicating, however, that $\sim$ 25% SiH_2 is present. A more accurate multiple-Gaussian fit was used in order to fit reliably the fundamental and the overtone absorption features. The latter was fitted by varying only the common linewidth of the Gaussians, $\Delta\tilde{\nu}$, keeping their relative strengths equal and multiplying the center frequency by the same factor x. The optimum fit for the region 3600 to 4000 cm^{-1} was obtained for $x = 1.97$ and $\Delta\tilde{\nu}_{overtone} = 1.9\Delta\tilde{\nu}_{fund.}$. The resulting anharmonicity parameter is $x_e = (1.4 \pm 0.1) \times 10^{-2}$, which is essentially identical to that of gas-phase SiH bonds.[13] The observed intensity ratio of the overtone to the fundamental is 5×10^{-3} and is consistent with such an anharmonicity. Both the fundamental and overtone SiH absorption do not show any temperature dependence except for a small shift toward higher frequencies ($\simeq 5$ cm^{-1} for fundamental, $\simeq 10$ cm^{-1} for overtone) in going from 300 to 80 K. The lack of narrowing of the linewidths on cooling clearly confirms that inhomogeneities are responsible for the linewidth. Hence, the similarity in anharmonicities between the SiH in a-Si and the gas-phase SiH indicates that the anharmonicity at the bottom of the well is not substantially modified by the large variations of the Si–H bond environment. When the sensitive configuration of Fig. 1 was used to study weak absorptions around the SiH fundamental, no evidence was found for phonon sidebands, thus ruling out the association of the absorption in the 4100 to 5600-cm^{-1} region to phonon sidebands of the SiH overtone.

When the SiH overtone contribution is subtracted from the raw spectrum, the resulting spectrum (hatched) is characteristic of high-pressure H_2 with

a broad Q branch split into Q_P at 4035 cm^{-1} and Q_R centered at 4275 cm^{-1}, the vibrational-rotational $S_1(0)$ and $S_1(1)$ single transitions at 4485 cm^{-1} and 4700 cm^{-1}, respectively, and a weaker double transition $S_1(0) + S_1(1)$ at 5100 cm^{-1} (notation as well as definition of single and double transitions is described in Ref. 9). The width of the Q_R branch and the separation between Q_P and Q_R (240 cm^{-1}) indicate that high-density H_2 gas is present ($\rho \sim 800$ amagats) corresponding to a pressure of 2000 atm.[14] The strength and breadth of the double transitions $Q_1(0) + S_0(0)$, $Q_1(1) + S_0(1)$, and $S_1(0) + S_0(1)$ relative to the Q branch confirm that the spectrum is due to H_2 gas rather than isolated H_2 in the silicon matrix. Isolated H_2 in a foreign gas,[14] a liquid, or a solid[15] typically displays a very strong Q_R branch with weak $S_1(0)$ and $S_1(1)$ bands. Further, the characteristic temperature dependence of the peaks labeled Q_P and Q_R, presented below, rules out any association of the bands labeled Q_R, $S_1(0)$, and $S_1(1)$ to a phonon spectrum of isolated H_2.

Having determined that the spectrum arises primarily from high-pressure H_2 gas (~ 2000 atm), the concentration of H_2 within the a-Si sample can now be established. The intrinsic absorption coefficient, α_{H_2}, of the enclosed H_2 may be related to the observed extinction ratio (I/I_0) through

$$[(\epsilon+2)/3]^2 \epsilon^{-1/2} \int_{\text{band}} \alpha_{H_2} d\tilde{\nu}$$

$$= -l_{\text{eff}}^{-1} \int \ln(I/I_0) d\tilde{\nu}, \qquad (2)$$

where ϵ is the dielectric constant of the a-Si ($\epsilon \sim 12$) and $\tilde{\nu}$ the wave number. Our data give $\alpha_{H_2} \simeq 0.2$ cm^{-1}. Comparison with gas-phase data[14] yields a H_2 concentration within the a-Si sample $n_{H_2} \simeq 10^{21} H_2$/cm^3. This concentration is an order of magnitude larger than that found in the unannealed samples of Graebner $et\ al.$[8] and roughly a factor of 4 more than in their annealed samples.

The temperature dependence of the spectrum is shown in Fig. 3. The low-temperature spectrum (80 K) is characterized by a much reduced Q_P branch:

$$\int_{Q_P} \alpha(80\ \text{K}) d\tilde{\nu} / \int_{Q_P} \alpha(300\ \text{K}) d\tilde{\nu}$$

$$= 0.2 \pm 0.1. \qquad (3)$$

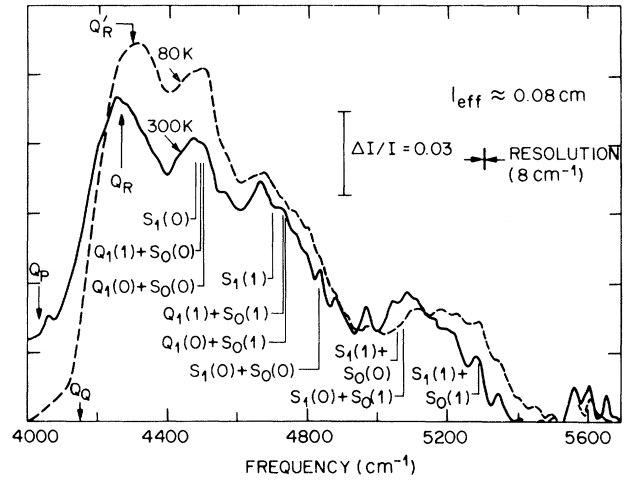The large error bar is a result of the uncertainties associated with the overtone subtraction and the

FIG. 3. Infrared absorption spectra of occluded H_2 gas in a-Si:H at 300 and 80 K.

narrowing of the strong Q_R branch. However, the intensity reduction is consistent with Boltzmann statistics,[17]

$$\int_{Q_P} \alpha(80\ \text{K}) d\tilde{\nu} / \int_{Q_P} \alpha(300\ \text{K}) d\tilde{\nu}$$

$$\simeq \exp\left[\left(\frac{\overline{\Delta\nu}hc}{k}\right)\left(\frac{1}{80} - \frac{1}{300}\right)\right], \qquad (4)$$

which, for a peak separation $\overline{\Delta\nu} = 120$ cm^{-1}, has a value of 0.21. The fact that the widths of the $Q_{P,R}$, $S_1(0)$, and $S_1(1)$ lines do not decrease upon cooling to the same extent observed with high-pressure H_2 gas[17] indicates that there is a $distribution$ of pressures in the microvoids. The spectra in Figs. 2 and 3 show weak oscillatory features which result from subtraction of the Fourier-transformed interferogram after some drift in the system has taken place and should not be associated with fine structure.[10]

The most interesting feature of the low-temperature spectrum is the increase in intensity of the Q_R branch and its shift toward higher frequencies (peak ~ 4300 cm^{-1}). This behavior can only be assigned to an increase of density to about $\rho \sim 1000$ amagats (2.7×10^{22} H_2/cm^3) corresponding to a pressure of about 4000 atm.[14] Consistent with that pressure increase is the increase in the relative strengths of the combination bands, $S_1(0) + S_0(0)$ and $S_1(1) + S_0(1)$, as seen in Fig. 3. Such a large change in microvoid volume ($\Delta V/V \simeq 20\%$) cannot be accounted for by an isotropic contraction of the a-Si structure. However, large anisotropies are shown to exist in the heavily

hydrogenated a-Si samples leading to anisotropic contractions. Leadbetter et $al.$[18] have shown with small-angle neutron-scattering experiments that the morphology of a-Si:H is more anisotropic (weak columnar growth) for samples prepared from a SiH_4/Ar mixture than in pure SiH_4 for a 503-K substrate temperature. It is therefore expected that the samples studied in the present work should have a higher concentration of voids and should be more anisotropic than those studied by Löhneysen, Schink, and Beyer[7] and by Graebner et $al.$[8] In the course of our studies, we have found that the concentration of molecular hydrogen varies with growth rate, e.g., the lower growth rates (1 Å/sec) yield a higher H_2 concentration. Further, our samples did not withstand annealing to 750 K without forming small craters and peeling, presumably due to high stress relaxations. Hence, the overall picture which emerges from this study is that microvoids are created during plasma growth of a-Si:H and these microvoids are filled with H_2 gas. The volume of these voids may change during the growth as a result of anisotropic relaxation of the amorphous material, resulting in high pressures. Such anisotropic relaxation capable of occluding hydrogen at such high pressures is not inconsistent with the large compressive film stresses measured in a-Si by Harbison, Williams, and Lang,[19] and may be responsible for some of the permanent changes observed in this intriguing material.

[1] See for example the review article by S. Iselborn, H. Rubel, J. Geiger, and B. Schroder, Philos. Mag. **48**, 561 (1983), and references cited therein.

[2] G. A. N. Connel and J. R. Pawlik, Phys. Rev. B **13**, 787 (1976).

[3] M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).

[4] M. S. Conradi and R. E. Norberg, Phys. Rev. B **24**, 2285 (1981).

[5] W. E. Carlos and P. C. Taylor, Phys. Rev. B **25**, 1435 (1982).

[6] D. J. Leopold, J. B. Boyce, P. A. Fedders, and R. E. Norberg, Phys. Rev. B **26**, 6053 (1982).

[7] H. v. Löhneysen, H. J. Schink, and W. Beyer, Phys. Rev. Lett. **52**, 549 (1984).

[8] J. E. Graebner, B. Golding, L. C. Allen, D. K. Biegelsen, and M. Stutzmann, Phys. Rev. Lett. **52**, 553 (1984).

[9] See, for example, H. L. Welsh, J. Atmos. Sci. **26**, 835 (1969).

[10] Y. J. Chabal, Phys. Rev. Lett. **50**, 850 (1983).

[11] E. E. Chaban and Y. J. Chabal, Rev. Sci. Instrum. **54**, 1031 (1983).

[12] G. Lucovsky, R. J. Nemanich, and J. C. Knights, Phys. Rev. B **19**, 2064 (1979).

[13] L. Halonen and M. S. Child, Mol. Phys. **46**, 239 (1982).

[14] W. F. J. Hare and H. L. Welsh, Can. J. Phys. **36**, 88 (1958).

[15] R. J. Kriegler and H. L. Welsh, Can. J. Phys. **46**, 1181 (1968).

[16] D. L. Dexter, Phys. Rev. **101**, 48 (1955).

[17] J. L. Hunt and H. L. Welsh, Can. J. Phys. **42**, 873 (1964).

[18] A. J. Leadbetter, A. A. M. Rashid, N. Colenutt, A. F. Wright, and J. C. Knights, Solid State Commun. **38**, 957 (1981).

[19] J. P. Harbison, A. J. Williams, and D. V. Lang, J. Appl. Phys. **55**, 946 (1984).