Molecular hydrogen in a-Si:H

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Recently Conradi and Norberg have proposed that a small density of molecular hydrogen in a-Si:H films provides the relaxation mechanism which is responsible for a minimum in the proton spin-lattice relaxation time T_1 at about 30 K. Although we are unable to observe an NMR line attributable to the H_2, we are able to observe the conversion of the H_2 molecules from the ortho state to the para state at 4.2 K. The process is bimolecular with a rate constant of 0.010 h^{-1}. The existence of a large number of sites able to trap such a small molecule may provide an important insight into the defect structure of these films.

Proton NMR has provided several valuable insights[1-4] into bonding of hydrogen in hydrogenated amorphous silicon (a-Si:H). For films prepared by the glow discharge of silane with $\lesssim 15$ at. % H the ^{1}H spin-lattice relaxation time T_1 has a minimum[1] at $T \approx 30$ K. This minimum in T_1 was originally interpreted in terms of a relaxation of the hydrogen atoms by a small number of hydrogen-associated disorder modes,[1] but there are difficulties with the number of these modes which is required[5] to explain the observed magnitude of T_1. In a recent Communication,[6] Conradi and Norberg (hereafter called CN) have proposed that this minimum is attributable to relaxation of the bonded hydrogen by H_2 molecules trapped in the amorphous silicon matrix.

Molecular hydrogen has been observed in SiO_2 using Raman spectroscopy,[7,8] but previous Raman investigations in a-Si:H have found[9] no evidence for H_2. However, the concentration suggested in CN is below the level of sensitivity of normal Raman spectroscopy. Raman measurements were performed on the samples employed in this study and no modes attributable to H_2 were observed. Even though trapped, molecular H_2 is not a major bonding configuration for the hydrogen in a-Si:H, it is plausible that some H_2 ($\lesssim 1\%$ of the hydrogen) is trapped in the silicon matrix during the glow discharge process. Gas evolution studies show that argon atoms, which are only $\sim 15\%$ larger than H_2, are trapped in sputtered a-Si:H films[10] and are stable up to the crystallization temperature (~ 700 °C). In this Communication we report the results of several experimental tests which probe the presence of molecular H_2 in a-Si:H.

In the CN model the bonded hydrogen is relaxed via spin diffusion to a small number of hydrogen molecules serving as relaxation centers. The coupling of the molecular hydrogen to the lattice yields the minimum in T_1. The spin-lattice relaxation time of the bonded hydrogen may be written as

$$T_1(H) = \frac{3}{8} T_1(H_2) \left[\frac{n(H)}{n(o-H_2)} \right] + T_1(SD) . \quad (1)$$

In the above, $n(H)$ is the total concentration of hydrogen in the sample and $n(o-H_2)$ is the concentration of orthohydrogen molecules in the sample. $T_1(H_2)$ is the relaxation time of the orthohydrogen molecules to the lattice and $T_1(SD)$ is the contribution to $T_1(H)$ due to the spin-diffusion process (taken by CN to be 0.16 sec). The factor of $\frac{3}{8}$ comes from the different nuclear spins of the hydrogen atoms ($I = \frac{1}{2}$) and the orthohydrogen molecules ($I = 1$). The relaxation time of the ortho molecules to the lattice is calculated to be ~ 3 msec at the T_1 minimum. Therefore, only about 1% of the total hydrogen in the amorphous silicon needs to be in H_2 molecules to give a T_1 minimum for the bonded hydrogen of ~ 0.25 sec.

The fraction of molecular hydrogen in the ortho state at room temperature is $\frac{3}{4}$. At low temperatures the orthohydrogen gradually converts to zero-spin parahydrogen which does not serve as a relaxation center. The conversion process is a slow, bimolecular process driven by the dipolar interaction of protons in adjacent H_2 molecules.[11,12] It therefore is reasonable to expect that the room temperature ortho-to-para ratio will be frozen in during a normal running time for an experiment at low temperatures. As suggested by Conradi and Norberg a first test of this model would be to hold the sample at $T = 4.2$ K for a time long enough to allow this conversion to take place, and then to check for an increase in T_1. This test was performed on a sample of a-Si:H whose deposition parameters have been published previously and whose T_1 minimum has been well characterized.[1]

In order to test for ortho-para conversion the sample was held in liquid helium for about three months, and the spin-lattice relaxation time of the sample between 4.2 and ~ 60 K was checked every few weeks. The results, which are shown in Fig. 1, clearly indicate the expected increase of the T_1 minimum with time spent at 4.2 K. The ortho-para conversion process is described by the bimolecular equation
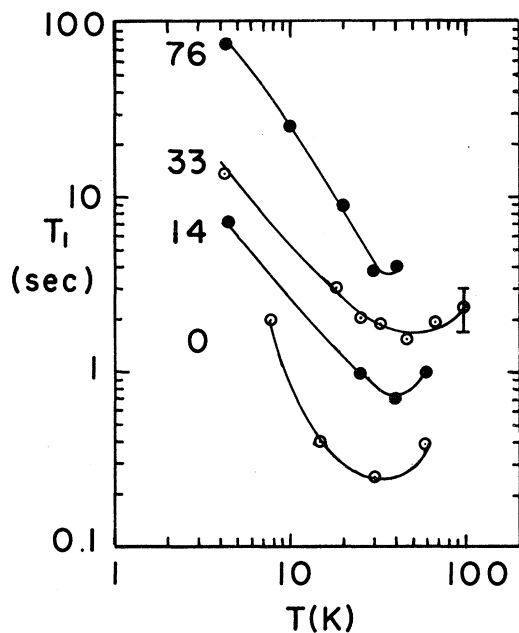
$$\frac{dx_0}{dt} = -cx_0^2 , \quad (2)$$

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FIG. 1. T_1 as a function of temperature after being held at 4.2 K for the number of days indicated on the left.

FIG. 2. The change in the value of $T_{1\,min}$ with time at 4.2 K (t_c) and effect on the $T_{1\,min}$ of annealing the sample at 300 K as a function of annealing time (t_a) (see text for details).

where x_0 is the fraction of molecular hydrogen in the ortho state and c is the rate constant. The value of T_1 at a given temperature is inversely proportional to x_0 and therefore linear in time. This behavior is illustrated in the inset to Fig. 2, for $T = 4.2$ K (solid circle) from which one may extract a rate constant of 0.010 h^{-1} for the ortho-para conversion in a-Si:H. This rate compares quite reasonably to the value[12] of ~ 0.019 h^{-1} for solid H$_2$. We cannot make a more quantitative comparison between the two systems since the rates depend on the phonon spectrum of the host lattice as well as the H$_2$-H$_2$ distance.

The open circles in Fig. 2 show the reconversion of para- to orthohydrogen measured at 30 K after annealing for the indicated time at 300 K. The dot-dashed line represents the value of T_1 observed in the usual measurements where the ortho-para ratio at 300 K is essentially maintained during the measurement time at 30 K. The only system for which an analogous rate has been determined is H$_2$ diluted in HD where the reconversion rates depend on the gas pressure at 300 K and the H$_2$ dilution factor.[13] For 0.4 at % H$_2$ in HD at atmospheric pressure, the initial rate (defined as the inverse of the time for T_1 to reach e^{-1} of its value at $t = 0$) is ~ 0.3 h^{-1} as compared with a similarly defined initial rate of ~ 3 h^{-1} in a-Si:H.

Although the CN model requires only about 1% of the hydrogen to be bonded together as H$_2$, the sensitivity of the NMR technique is such that this fraction should be observable provided that its line shape can
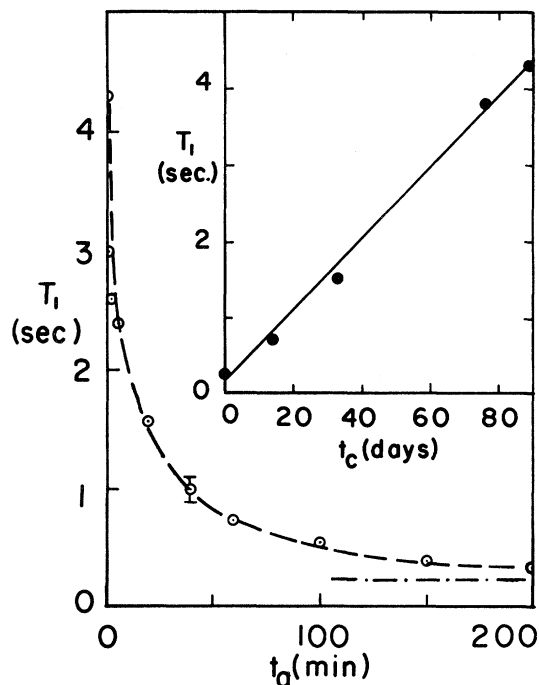
be differentiated from those of the hydrogens bonded to Si. At temperatures above the T_1 minimum the line due to H$_2$ should be motionally narrowed and clearly separable from the other broader lines. There is one caveat to this deduction. If the motion of the H$_2$ in its local site is sufficiently spatially restricted, then the surrounding hydrogen atoms might significantly broaden the H$_2$ line in spite of the local motion of this molecule.

The free-induction decay following a $\pi/2$ pulse is shown for spacings between pulses of 1 sec [T_1(H) at 77 K $\cong 0.6$ sec] in Fig. 3. Although the ^{1}H NMR line in a-Si:H consists of both a broad and a narrow component, only the narrow component of the proton line is seen since a low-frequency filter was used to reduce noise. Although we can follow the narrow line down to at least about 0.003 of its maximum (less than 0.001 of the total hydrogen line), no third narrower line is seen. This upper bound for the motionally narrowed line represents about an order of magnitude fewer hydrogen atoms than are required by the CN model to fit the data. If these data are to be consistent with the CN model, then one must assume that the H$_2$ molecules are trapped in spatially small regions of the a-Si:H network which are sufficiently close to stationary hydrogens so that motional narrowing does not occur.
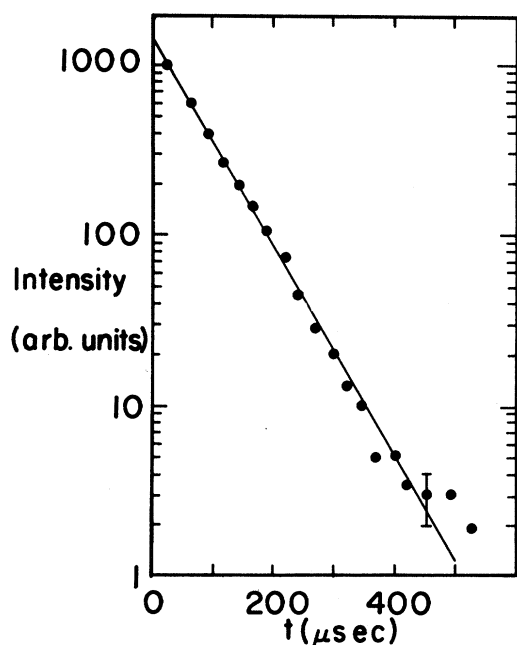
FIG. 3. The free-induction decay following a $\pi/2$ pulse. The broad line has been suppressed by a low-pass filter.

Solid echoes have been observed for pairs of closely coupled protons which are isolated from other protons (pseudo spin of 1) using a 90°, τ, 144° pulse sequence.[14] We attempted to see such an echo for the hydrogen in amorphous silicon; however, no echo signal was observable. This null result again suggests that the H_2 molecules are trapped sufficiently close to stationary, bonded hydrogens so that a solid echo is inhibited.

The ortho-para conversion results are quite convincing, since it is difficult to imagine another type of relaxation center which would "freeze out" on such a long time scale. From the null results of the H_2 free-induction decay and solid-echo experiments, one is forced to conclude that either the molecular hydrogen is trapped in a highly localized region of the a-Si:H matrix close to bonded hydrogen atoms or the number of hydrogen molecules is less than that sug-

gested by Conradi and Norberg who assumed that the hydrogen molecules sit at sites of low symmetry. If we assume that the molecules are in highly symmetric locations only about $\frac{1}{4}$ of the amount[15] of H_2 originally estimated would be necessary to provide the observed relaxation. This assumption would reduce the quantity of H_2 required to a level which would have been only marginally detectable in our attempt to see the H_2 NMR line directly.

Annealing studies show[16] that the relaxation centers evolve over a well-defined temperature range (500–530 °C). At these temperatures over half of the hydrogen which is bonded to silicon has already evolved. This result indicates that the H_2 molecules reside at well-defined sites rather than at a distribution of sites.

The existence of a small amount of molecular hydrogen trapped in the amorphous silicon films is consistent with recent models for the growth of these films[17,18] in which hydrogen is removed from the film as H_2 molecules are created at the surface. It is not surprising then to find some of the H_2 trapped within the film. Even the best a-Si:H films contain some microvoids. Some of these microstructures may be small enough to trap a molecule as small as H_2 and to ensure its stability at temperatures up to 500 °C. One possibility for this site is a hydrogenated divacancy. As the bonded hydrogen from this site is annealed out, the molecular hydrogen would become less tightly trapped and would also evolve. A fully hydrogenated divacancy would have six bonded hydrogens which would provide dipolar fields to modulate the dipolar field felt by the rotating molecular hydrogen. This mechanism would allow the H_2 to relax rapidly. Although this possibility for the H_2 site is not unique, it is clear that the H_2 molecules are trapped in identical or nearly identical sites and that these sites are fairly abundant in a-Si:H ($\sim 10^{19}/cm^3$).

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