Orientational Ordering and Melting of Molecular H_2 in an *a*-Si Matrix: NMR Studies

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Molecular hydrogen in hydrogenated amorphous silicon has been observed directly in the NMR spectrum, occurring as a powder-averaged Pake doublet in the orientationally ordered state. The molecular H_2 content is found to be approximately 0.25 at.% and to increase on annealing to about 1 at.%. In both cases, the H_2 orientationally orders and solidifies at temperatures considerably higher than in pure, normal H_2, because of the additional forces exterted on the H_2 by the *a*-Si container.

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Molecular hydrogen in amorphous silicon (*a*-Si) has recently attracted attention because of the interesting properties displayed by these quantum rotors interacting with each other and with their *a*-Si container. About 10 at.% H is incorporated in the *a*-Si when prepared by plasma decomposition of silane. Most of this H is bonded to the Si, and its important role in determining many of the properties of *a*-Si has been well documented.[1] But in addition to the bonded H, there is a small amount of molecular H_2 in voids in the *a*-Si matrix. This was originally inferred[2] from an analysis of the hydrogen NMR spin-lattice relaxation time (T_1) versus temperature,[3] which showed that about 1% of the total H was in the molecular state, i.e., 0.1 at.% H_2. This interpretation was later confirmed by additional NMR experiments,[4,5] but no direct observation of the H_2 was obtained. More recently, calorimetry experiments[6,7] and infrared-absorption experiments[8] have observed the molecular H_2 and have begun to elucidate some of its interesting properties. Also, a narrow spectral line in magic-angle spinning NMR experiments[9] at room temperature has been interpreted as being primarily due to mobile hydrogen molecules rather than due to unclustered, bonded hydrogen, the conventional interpretation.[10]

We have directly observed the NMR signal due to molecular H_2 in plasma-deposited *a*-Si below the orientational ordering temperature, T_c, of the H_2 molecules. In this ordered state, the NMR spectrum consists of a Pake doublet[11] with a splitting of 175 ± 10 kHz, similar to that observed in solid, normal H_2.[12] This unambiguously identifies the molecular H_2 in the material and differentiates it from the H bonded to the Si, which gives rise to an unsplit central line with two components having different linewidths. From this spectrum and its variation with temperature, we determine the following properties of molecular H_2 in plasma-deposited *a*-Si. First, the concentration of H_2, $n(H_2)$, in an as-deposited film is 0.25 at.% (H_2 molecules relative to Si atoms) and is increased to 1 at.% by annealing. Both of these values are comparable to those from calorimetry[6] and infrared[8] studies but are larger than inferred from T_1 measurements (≈ 0.1 at.%), thereby allowing[13] an estimate of the mean size of the H_2-containing voids of order 20 Å. Secondly, an orientational order-disorder transition for the H_2 molecules is observed at $T_c \approx 20$ K in the as-deposited film, considerably higher than $T_c \simeq 1.6$ K for pure solid H_2, an increase due to the additional crystal field from the *a*-Si matrix. This transition temperature is lowered to $T_c \approx 10$ K when the average void size is increased by annealing. Third, a gradual melting of the solid H_2 in the voids is observed between 15 and 40 K, implying a distribution of densities corresponding to internal pressures on the H_2 of 0–2 kbar.[14] Fourth, an analysis of the narrow NMR line at room temperature, in the light of this direct observation of H_2, agrees with the original conclusion[10] that the narrow line is due primarily to unclustered H bonded to Si for normal, plasma-deposited material.

The *a*-Si:H samples were prepared by plasma decomposition of pure SiH_4 gas, with use of low power density (0.025 W/cm^2) and Al substrates heated to 230 °C. One sample was then annealed at 500 °C for $\frac{1}{2}$ h to increase the molecular H_2 content, and is similar to the sample used for calorimetry experiments.[6] The NMR experiments were performed at a Larmor frequency of 92 MHz for temperatures ranging from 1.43 to 500 K, with standard pulsed NMR techniques. The spectral results at room temperature are listed in Table I. At this temperature, the spectrum for both samples consists of a central, unsplit line with two width components. The unannealed sample (U) exhibits a line shape consistent with that observed[10] on a variety of plasma-deposited films. The annealed sample (A) shows a drop in the total hydrogen content, almost all of which comes from the broad line, as well as a narrowing of both components, again consistent with earlier studies.[15]

When the sample is cooled to low temperatures, the NMR spectrum evolves into a three-component line: the central line with two width components, as observed at room temperature, plus a Pake doublet, shown in Fig. 1 for $T = 1.43$ K, with a splitting of 175 ± 10 kHz. The observed doublet is due to orientationally ordered molecular H_2 and is very similar to

TABLE I. The total hydrogen content, $n(\mathrm{H})$, and the line-shape parameters for the broad and narrow components of the NMR line at room temperature for both a-Si:H samples studied. Also given is the concentration of molecular H_2, $n(H_2)$, from the NMR spectrum (Pake doublet), which yields all the H_2, and from T_1 measurements, which samples only the H_2 on the surfaces of the voids. (FWHM denotes full width at half maximum.)

Sample	Total n(H) (at.%)	Broad n(H) (at.%)	Broad FWHM (kHz)	Narrow n(H) (at.%)	Narrow FWHM (kHz)	$n(H_2)$ from Pake doublet (at.%)	$n(H_2)$ from T_1 (at.%)
Unannealed	12.7	7.9	26	4.8	3.1	0.25	0.1
Annealed	7.5	2.9	18	4.6	1.2	1.0	~0.2

that seen in solid, normal H_2 (n-H_2, $\frac{3}{4}$ ortho and $\frac{1}{4}$ para) with a Pake splitting of 165 kHz.[12] Only the orthohydrogen (nuclear spin $I=1$, rotational spin $J=1$) contributes to the NMR spectrum and T_1 since parahydrogen has $I=0$. When placed in a crystal field, the degeneracy of the three m_J levels ($J=1$, $m_J=0, \pm 1$) can be lifted.[16] For H_2 in a-Si, the anisotropic part of the crystalline potential, V_c, consists of two components: the electrostatic quadrupole-quadrupole interaction between the o-H_2 molecules and the interaction of the electric field gradients (EFG) due to the electronic charge distribution of the a-Si matrix with the o-H_2 quadrupole moment. Both contribute to the crystal-field splitting, Δ, which determines the ordering temperature T_c and which, for an axially symmetric field gradient, is the splitting between the $m_J=0$ ground state and the doubly degenerate $m_J=\pm 1$ states. In a-Si, one expects a distribution of local environments, so that Δ, in this case, represents a mean value. For $T \ll T_c$, the probability that the $m_J=0$ state is occupied is 1 and the H_2 molecules are *locally* ordered in their respective crystal fields. For this low-temperature case and an axially symmetric crystal field, the NMR spectrum[12] consists of a Pake doublet with a splitting that depends on the dipolar coupling constant, $d=57.67$ kHz, between the two H atoms in the molecule and the angle of the molecular axis relative to the applied magnetic field. For a-Si, one has a distribution of such angles, giving the well-known powder pattern which has singularities, broadened by intermolecular dipole-dipole interactions, at $\nu-\nu_0=\pm 3d/2$. The predicted splitting between these singularities is $\delta\nu=3d=173$ kHz, in good agreement with that observed in Fig. 1.

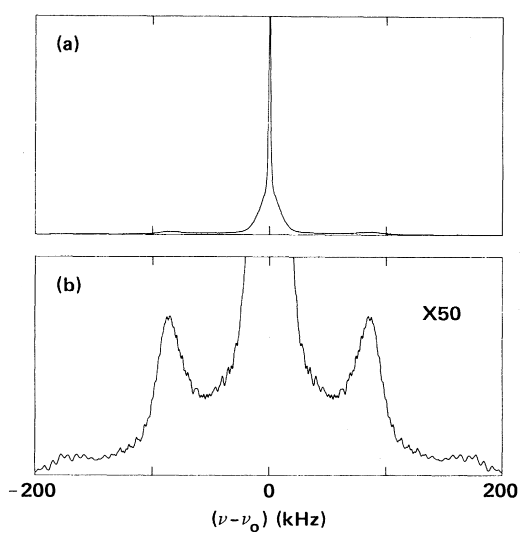

FIG. 1. H NMR spectrum for a Fourier transform of the free induction decay at 92 MHz and 1.43 K in the annealed sample, showing (a) the broad and narrow central lines and (b) the molecular H_2 powder pattern with broadened singularities at $\pm(88\pm5)$ kHz.

For $T \gg T_c$, all three m_J levels are equally occupied and the H_2 molecules are orientationally disordered with respect to the local fields. In this case, $\delta\nu=0$, i.e., the Pake doublet has collapsed into a central, unsplit line. This is seen in Fig. 2 where the fraction, α, of the total signal in the various lines—Pake doublet (α_P); broad, unsplit line (α_B); and narrow, unsplit line (α_N)—is plotted against temperature. Well below T_c, α_P is constant as observed in solid H_2, which indicates that all the H_2 molecules are orientationally ordered and are contributing to the Pake doublet. As $T \to T_c$, the value of α_P drops to zero, with a corresponding increase in α_B. In addition to this drop in α_P, there is also an increase in the Gaussian broadening of this powder pattern as T_c is approached. This may be due to the distribution in the crystal-field splittings, giving rise to a distribution in T_c's. We now consider the three major differences between samples A and U.

First, $n(H_2)$ is larger in sample A than in U since the hydrogen diffusion and bond reconstruction at

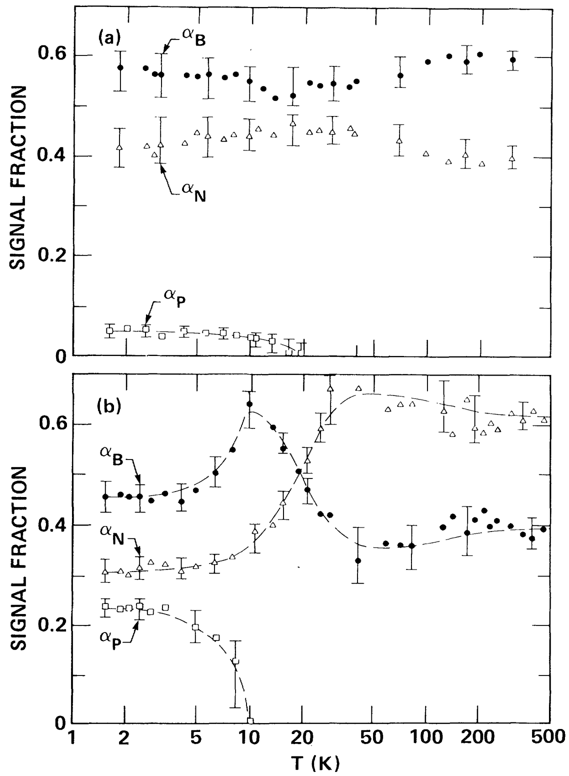

FIG. 2. Fraction, α, of the total H NMR signal in the three components of the line vs temperature for (a) the unannealed sample and (b) the annealed sample.

elevated temperatures[17] increases the amount of trapped H_2. From the spectral area under the Pake doublet, we obtain the $n(H_2)$ given in Table I. We see that $n(H_2) = 1$ at.% for sample A, consistent with the value of 0.5 at.% obtained from calorimetry experiments[6] on the similarly prepared sample.

This value of $n(H_2)$ is also larger than that inferred from T_1 measurements. An analysis[18] of T_1 for sample U yields $n(H_2) \simeq 0.1$ at.%. For sample A, the minimum T_1 is about two times smaller[19] than that for U, so that $n(H_2)$ is approximately two times larger, i.e., ~ 0.2 at.%. These values are smaller than $n(H_2)$ calculated from the spectral area of the Pake doublet, all listed in Table I. But the T_1 is determined by molecules that serve as relaxation centers for the H bonded to the Si. This is predominately the H_2 on the surface of a void, not that in the void interior since they have a weaker coupling to the H in the bulk and a much longer T_1.[13] Thus the different determinations of $n(H_2)$ can give an estimate of the mean surface to volume ratio of the void, given the assumption that they are completely filled with H_2. This is about 0.4 for U and 0.2 for A. A rough estimate of the mean void radius in the unannealed sample, with the assumption of solid H_2 density and spherical shape, is of order 20 Å, with the void size about twice as large in the annealed sample.

Secondly, the value of T_c for sample A is ≈ 10 K, whereas for sample U it is ≈ 20 K. This difference can be understood as follows. For solid n-H_2, $T_c \simeq 1.6$ K and Δ is due to the electrostatic quadrupole-quadrupole interaction.[16] For large voids in a-Si filled with H_2, this same interaction is operative, but there is also the added a-Si matrix EFG, which increases the average value of Δ. As a result, sample A has a larger T_c of about 10 K. For sample U, the amount of H_2 in the voids is smaller and the void size itself is smaller. Thus most H_2 experience the larger EFG from the a-Si and T_c is increased to about 20 K.

Thirdly, above T_c, the line shape for sample U is about the same as that at room temperature. This is due to the fact that the H_2 is only 4% of the total H signal and its contribution to the line-shape parameters is within the uncertainties, except when split off as a doublet below T_c. For sample A, this is not the case since the H_2 molecules contribute 25% of the total signal. For this sample, the line-shape parameters are seen to change with temperature, as shown in Fig. 2(b). Above T_c, the doublet has collapsed onto the unsplit central line because of the averaging of the spectral splitting by the rapid tumbling of the molecules; all the m_J states are equally occupied. This component contributes to the broad line since the intermolecular dipole interaction is not averaged out by the tumbling. This causes an increase in α_B, corresponding to the decrease in α_P. When the H_2 molecules begin to diffuse, with a hopping rate comparable to their linewidth, this intermolecular interaction will be averaged out and the line will narrow. This happens between 15 and 40 K, above which the H_2 molecules contribute only to the narrow line. Their width has been motionally narrowed, resulting in an increase in α_N with a corresponding decrease in α_B. This happens in solid n-H_2 where above $T_c = 1.6$ K only a broad line exists, which narrows as the melting temperature of 14 K is approached. It is fully narrowed within a few degrees of the melting temperature, T_m. As the pressure is increased, both transition temperatures increase.[20] If we assume that the T_m versus pressure curve for pure H_2 applies,[14] our value of $T_m \approx 15$–40 K can be interpreted as if $p \sim 0$–2 kbar. This result is comparable to the 2-kbar value obtained from infrared measurements,[8] but also indicates that there is a rather broad range of pressures.

The results of Fig. 2(a) also show that H_2 contributes a negligible fraction to the narrow line for the unannealed sample. This differs from the conclusion of Lamotte[9] that molecular H_2 is the main component of the narrow line in sputtered material. There is thus no need to revise the original interpretation[10] of the narrow line. When molecular H_2 makes a significant contribution to the narrow line, as in the annealed sample, then the line-shape parameters are modified, as shown in Table I.

In conclusion, we have directly observed the Pake doublet due to orientationally ordered H_2 molecules in *a*-Si:H. This spectrum has the splitting expected for solid H_2, thereby unambiguously identifying the molecular H_2 and allowing a determination of many of its properties.

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