

## Molecular Hydrogen in *a*-Si:H

P. A. Fedders,<sup>1</sup> D. J. Leopold,<sup>1,2</sup> P. H. Chan,<sup>1</sup> R. Borzi,<sup>1</sup> and R. E. Norberg<sup>1</sup>

<sup>1</sup>*Department of Physics, Washington University, St. Louis, Missouri 63130*

<sup>2</sup>*Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, Missouri 63121*

(Received 11 November 1999)

It is demonstrated that in high quality hydrogenated amorphous silicon films nearly 40% of the contained hydrogen is in the form of hydrogen molecules individually trapped in the amorphous equivalent of tetragonal *T* sites. The majority of these molecular hydrogens are in the less-clustered component of the contained hydrogen. These results could have major implications for the understanding of light-induced defects and hydrogen mobility.

PACS numbers: 72.80.Ng, 73.61.Jc, 76.60.-k

It is generally believed that the only important hydrogen in *a*-Si:H is the bonded H that passivates dangling bonds. Further, it has been believed that the bonded hydrogen makes up the overwhelming fraction of hydrogen in good *a*-Si:H films although there sometimes is a small fraction of electrically and structurally unimportant molecular hydrogen that forms bubbles of highly concentrated material in microvoids. Thus it is believed that Si-bonded H atoms are the mobile species of hydrogen in *a*-Si:H and that many interesting properties of the material, such as light-induced defects and hydrogen mobility, are intimately connected with this species of hydrogen. In this Letter, we shall present substantial evidence that the above picture is incorrect and that isolated molecular hydrogen in tetragonal *T*-like sites makes up a fraction of nearly 40% of the hydrogen in good *a*-Si:H.

In earlier nuclear magnetic resonance (NMR) work on deuterated *a*-Si, we have shown that of order 40% of the deuterium occurs as relatively unclustered molecules [1–4]. However, many of these films were deposited from starting gas mixtures containing molecular D<sub>2</sub>, and it has been a concern that this is the reason for the high molecular content. The principal *a*-Si:H sample reported in the present study has been made from SiH<sub>4</sub> with no molecular hydrogen in the starting gas. We have used proton NMR to examine the distribution of hydrogen in high quality hydrogenated amorphous silicon films made by plasma-enhanced chemical vapor deposition (PECVD). In these films the microvoid-contained population of molecular hydrogen is negligible. However, we shall show that spin echo double resonance (SEDOR) experiments using <sup>1</sup>H and <sup>29</sup>Si nuclides reveal a very appreciable (of order 40%) population of molecular hydrogen in *T*-like sites. Thus we believe that the electrical, structural, and mobility consequences should be thoroughly examined.

Proton NMR studies performed on hydrogen in numerous *a*-Si:H thin film samples over many years have established [5] that there are primarily two lines: a broad Gaussian (25 kHz FWHM) component that is dipolar broadened by interactions with other nearby protons and a narrow Lorentzian (4 kHz FWHM) that also is broadened by dipolar interactions and, in some cases,

by a distribution of chemical shifts. Both of these configurations have been thought by many to be silicon-bonded hydrogen in more and less clustered hydrogen configurations, respectively [5]. All protons interact with other protons via the dipolar interaction which falls off as  $1/r^3$ , and the width of an NMR line is largely determined by the closeness and number of proton neighbors and not by whether those hydrogen neighbors are bonded or molecular. Thus linewidths alone are not a clean way to distinguish molecular hydrogen from bonded H. In some cases, the narrow and/or broad lines may be made up of a number of components which have comparable widths and the same center. However, since any line or component can consist of both bonded and molecular hydrogen, any assumption that a line or component consists entirely of bonded H or of molecular H is somewhat rash.

Deuteron magnetic resonance (DMR) established long ago [6,7] that a substantial fraction (about 40%) of the hydrogen (deuterium) population was a weakly bonded species, very different from the silicon bonded hydrogen typically seen in infrared measurements. DMR can easily distinguish bond strength because deuterons have spin 1, an electric quadrupole moment, and are sensitive to electric field gradients (EFG). The much weaker (compared to protons) dipolar coupling results in deuteron NMR line shapes and widths that are determined by distributions of electric field gradients and angular averages about the applied magnetic field direction  $H_0$ . As shown in Fig. 1, the primary features of the deuteron DMR line shape in high quality *a*-Si:H,D are a sharp powder-pattern Pake doublet with an approximately 66 kHz splitting attributed to the tightly silicon-bonded species and a faster relaxing broad central approximately 33 kHz FWHM Gaussian component originally interpreted as a weakly bound component, but now recognized as *T*-site trapped molecular D<sub>2</sub> and HD [3]. The electric field gradient calculated from the SiD doublet splitting agrees, when corrected for mass, with the infrared absorption band observed for bonded Si-H [6]. The fact that we have attributed the 33 kHz Gaussian DMR line component (Fig. 1) to molecular D<sub>2</sub> and HD in *T*-like sites might lead one to believe that the EFG felt by a molecule at a *T*-like site is almost the same as the one felt by a

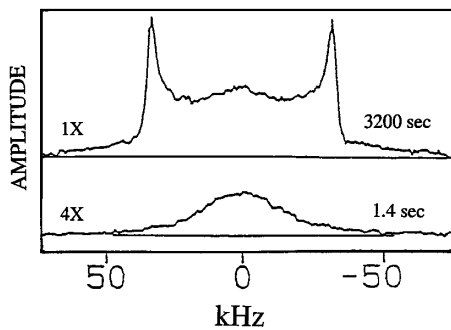


FIG. 1. DMR line shapes at 20 K and at long and short magnetization recovery times in a high quality  $a$ -Si:H,D film. A broad central feature arises from  $D_2$  and HD trapped in  $T$ -like sites.

Si-bonded D. This is not the case. The electric field gradient felt by the nucleus of a  $D_2$  or HD molecule is magnified by the electronic shell of the molecule by an amount often called the anti-shielding factor. The calculation of this factor is particularly simple for hydrogen molecules, and our calculations, in progress, show that the effective EFG at the center of an HD molecule is increased by a factor of 39.5 and the factor is 26.5 for a  $D_2$  molecule. These calculations are a straightforward (albeit tedious) application of second order perturbation theory. The electric field gradient perturbs the molecular  $J$  state and mixes it with higher  $J$  states. Using this wave function for the molecule, the effect on the nucleus is easily calculated with the dipolar and quadrupolar Hamiltonians between the nucleus and fields from the molecule as described in Ramsey's book [8]. Thus the 33 kHz broad central and 66 kHz SiD doublet DMR linewidths (Fig. 1) indicate that the EFG at a molecular site is about 2 orders of magnitude smaller than that at the site of a Si-bonded D. This is consistent with our contention that the molecules reside at slightly distorted  $T$ -like sites.

In general, it is very difficult or impossible to determine the fraction of H that is molecular in  $a$ -Si:H using NMR on protons only. The one exception is very low temperature experiments (of order millikelvin) where virtually all of the molecular proton NMR signal will be in a Pake doublet. However, no such experiment has been reported. Some recent NMR studies have reported isolated  $H_2$  in  $a$ -Si:H samples but the fractions are too low because the temperatures were too warm [2,9,10]. Previous proton NMR studies performed near 4 K revealed a freeze-out of a small fractional signal into a 175 kHz doublet, which is uniquely characteristic of orthohydrogen molecules [11]. The resulting signal, shown in Fig. 2, confirms the presence of a few percent fraction of molecular hydrogen in  $a$ -Si:H, beyond that already known to exist at the ppm level in small microvoids from spin-lattice relaxation time measurements [12–14]. From our earlier work [15], we find that the condition necessary to get a Pake-like doublet from molecular  $H_2$  is that the quadrupolar splitting of the molecular  $m_j$

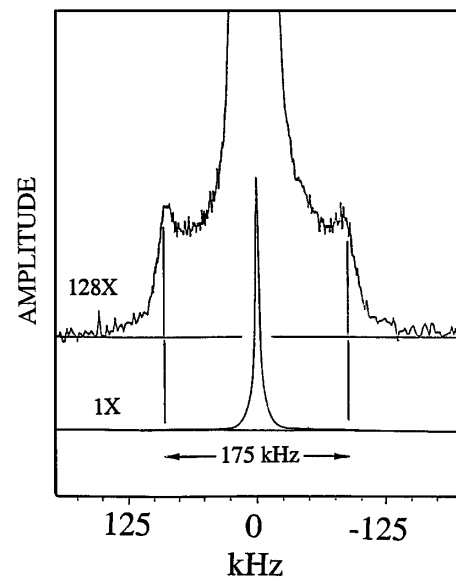


FIG. 2. A proton NMR spectrum in a high quality  $a$ -Si:H,D film at 4.2 K includes a small population in a 175 kHz Pake doublet arising from molecular orthohydrogen.

states in the  $H_2$  molecule must be greater than  $kT$ . From the numbers above, the ratio of this energy splitting to  $kT$  at one degree K is about 0.28 using the 33 kHz width of the broad central DMR line. Since the inverse of 0.28 appears as an exponent, we find that one needs low temperatures of order 0.01 K in order to observe most of the  $H_2$  as a Pake-like doublet. Experiments detecting a Pake-like doublet at higher temperatures (Fig. 2) include only that very small fraction of the total  $H_2$  population that is in the wings of the EFG distribution [11,16]. Our calculations show that the freeze-out of the hydrogen molecules into a 175 kHz doublet is not even close to completion unless the temperature is reduced to the millikelvin range. Thus doublet measurements performed at 4 K and above drastically underestimate the molecular  $H_2$  population.

Another possibility for confirming the existence of  $H_2$  in  $a$ -Si:H is with ortho ( $I = 1$ ) to para ( $I = 0$ ) conversion experiments, where signal intensity is lost as molecules convert to the ground state. Ortho-to-para conversion of  $H_2$  molecules can depend on whether the process is one phonon, two phonon, etc., but the rates for all processes decrease drastically with increasing intermolecular separation. For example, the one phonon process goes as the tenth power of the distance. Note that two to the power of ten is 3 orders of magnitude. Thus any attempts to quantify total molecular hydrogen concentrations by observing signal loss from  $I = 1$  ortho to  $I = 0$  para ground state conversion experiments at low temperature could take a very long time.

Finally, temperature dependences are complex. Aside from microvoids, which are negligible in good films, actual global motion of hydrogen can take place only with activation energies of the order of 1.0 to 1.5 eV. However,

temperature dependent changing of lines is seen with far smaller activation energies or as power laws of temperature. These poorly understood phenomena could easily arise from local motion and/or nonmotional changing of the H<sub>2</sub> line shapes. The proton line shape for a translationally immobile H<sub>2</sub> molecule will start to broaden when  $kT$  becomes comparable to the energy between the  $m_j$  states. This splitting in energy is the EFG times the (molecular) quadrupole moment. At this point, a narrow H<sub>2</sub> line broadens and starts to get peaks at the Pake doublet positions. The Pake doublet splitting does not increase and thus is not temperature dependent for relatively isolated molecules residing in the presence of substantial crystal fields. Further, the narrowing upon warming has nothing to do with motion although it is very easy to misinterpret it as motional narrowing. The narrowing rather has to do with the phonon-driven transitions among the molecular  $m_j$  states [13].

The basic idea of a proton-<sup>29</sup>Si SEDOR experiment [17] is to perturb the <sup>29</sup>Si nuclei while performing an NMR experiment on the protons. The resultant change in the proton spectrum then allows investigation of the Si-H interactions. We now present SEDOR proton NMR evidence that approximately 40% of the contained hydrogen in high photoelectronic quality PECVD hydrogenated amorphous silicon films is in fact molecular hydrogen trapped in the amorphous equivalent of  $T$  sites. Assuming that SiH<sub>2</sub> and SiH<sub>3</sub> populations are negligible in high quality  $\alpha$ -Si:H, the anticipated <sup>29</sup>Si-<sup>1</sup>H SEDOR signal fraction for Si-bonded H should reflect the 4.7% isotopic abundance of <sup>29</sup>Si.

The proton NMR signal responses differ for the two radio frequency pulse sequences which we have employed. For  $\theta = \pi/2$  proton nutations, the two-pulse solid echo  $90_x-\tau-\theta_y$  sequence yields  $\sin\theta = 1$  for proton-proton-like spin interactions and  $\sin\theta/2 = 0.707$  for proton-unlike spin interactions (those with different gyromagnetic ratios), while the three-pulse  $90_x-\tau-\theta_y-\tau_1-90_y$  sequence yields  $\sin\theta = 1$  for unlike spins and  $\sin 2\theta = 0$  for like spins. In each case the SEDOR sequence is achieved by immediately following the last proton pulse with a <sup>29</sup>Si nutation pulse. For pulse spacings greater than 200  $\mu$ s, the two-pulse proton solid echo signal is found to experimentally be larger than the three-pulse stimulated echo by a factor of 1.9. This is not a  $T_1$  effect, but rather reflects the spin selectivity of the two different pulse sequences described above. From comparison of these anticipated and experimentally observed two- and three-pulse signal fractions, we can infer like ( $L$ ) and unlike ( $U$ ) proton spin interaction populations:  $L + 0.707U = 1.9U$ , or a  $U$  fraction of 0.45.

For Si-bonded H the probability that an H atom is coupled to a <sup>29</sup>Si is given by the isotopic abundance 0.047. An SiH bond length is about 1.5 Å. However, at a  $T$  site in crystalline Si there are four nearest Si neighbors forming a tetrahedron, but six more at a distance only 14% larger. So, effectively, there are ten nearest neighbors, with four at a distance of 2.35 Å and six at a distance of 2.73 Å.

These numbers are slightly different when a molecular hydrogen occupies the  $T$  site. The <sup>1</sup>H-<sup>29</sup>Si dipolar couplings at these two radii could differ by a factor near 3/2 in a perfect crystalline lattice but they average to a more uniform distribution in the amorphous material. Bond angle distortion alone yields several tenths Å variations in H<sub>2</sub>-Si separations. The probability that a hydrogen molecule trapped in a  $T$  site in crystalline Si has no <sup>29</sup>Si neighbors is  $(1-0.047)^{10} = 0.62$ . Thus the probability that at least one of the neighbors is <sup>29</sup>Si is 0.38. The situation will be similar for  $\alpha$ -Si:H.

Figure 3 shows our SEDOR results for a high quality  $\alpha$ -Si:H film plasma deposited from SiH<sub>4</sub>. The figure shows the observed fraction of <sup>29</sup>Si-coupled <sup>1</sup>H nuclei at 80 K. The fractional signal is the difference between the proton signals without and with the <sup>29</sup>Si pulse in a  $90_x^H-\tau-90_y^H-\tau_1-90_y^H-\theta^{Si}$  stimulated echo sequence with  $\tau_1 = 2$  ms and with  $\tau$  varied from 40 to 300  $\mu$ s. The proton spin-lattice relaxation time is about 550 ms. For  $\tau$  in the range 100 to 200  $\mu$ s and <sup>29</sup>Si rotation angles of 150° and 180°, a plateau is reached near an observed signal fraction of 0.35. At longer  $\tau$  the <sup>29</sup>Si-<sup>1</sup>H fraction increases slowly, presumably because of spin diffusion. The observed 35% fraction strongly suggests an origin from  $T$ -like site H<sub>2</sub> rather than Si-bonded H. Using the observed plateau value of 0.35 in Fig. 3 and the anticipated coupling to <sup>29</sup>Si of protons from Si-bonded H and from H<sub>2</sub> in  $T$ -like sites, we can calculate the fractional concentrations of each species. The fraction  $x$  of protons in  $T$ -like site H<sub>2</sub> molecules then is given by the equation

$$F = \frac{0.35}{1.9} = 0.38x + 0.047(1 - x). \quad (1)$$

The solution to this equation is  $x = 0.41$ . Thus 41% of the <sup>1</sup>H are in  $T$ -site molecular H<sub>2</sub>. Here the plateau value

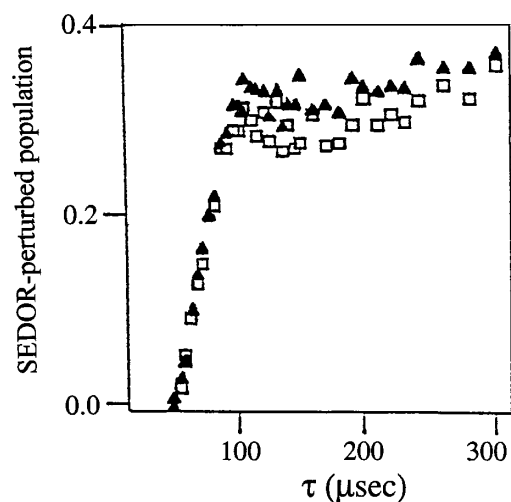


FIG. 3. Stimulated echo-determined fraction of protons dipolar-coupled to <sup>29</sup>Si in high quality  $\alpha$ -Si:H made from SiH<sub>4</sub>. The 35% plateau is consistent with  $T$ -site molecular H<sub>2</sub>, but not with Si-bonded H.

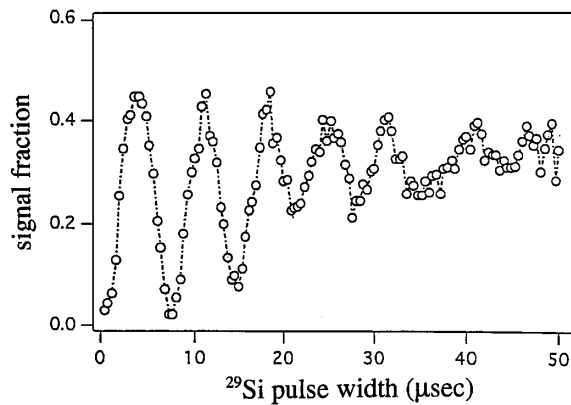


FIG. 4. Signal fraction of the  $^{29}\text{Si}^1\text{H}$  SEDOR proton signals at 80 K for a three pulse stimulated echo sequence with various  $^{29}\text{Si}$  pulse widths and  $\tau = 400 \mu\text{s}$ .

of 0.35 has been normalized to the 1.9 total two-pulse proton signal strength factor discussed above. We note the reasonable agreement of the independently determined fractions 0.41 and 0.45.

Figure 4 shows the variation of the  $^{29}\text{Si}^1\text{H}$  stimulated echo proton signal at 80 K and as a function of the width of the  $^{29}\text{Si}$  modulation pulse in the three-pulse sequence. Here  $\tau$  is  $400 \mu\text{s}$ ,  $\tau_1$  is 2 ms, and  $t_w$  is the width of the  $^{29}\text{Si}$  pulse. Here again the  $^{29}\text{Si}^1\text{H}$  signals are obtained by subtracting the proton signals with the  $^{29}\text{Si}$  pulse from those without the  $^{29}\text{Si}$  pulse. The first three maxima of the  $^{29}\text{Si}^1\text{H}$  signal occur at  $\theta^{\text{Si}} = \pi, 3\pi,$  and  $5\pi$  and correspond to a 45% fractional proton population. The fraction is somewhat larger than that in Fig. 3 because more spin diffusion has occurred at a  $400 \mu\text{s} \tau$ . Further  $^{29}\text{Si}^1\text{H}$  SEDOR experiments on the same sample at 80 K, this time with a two-pulse solid echo sequence, give rise to a  $T$ -site  $\text{H}_2$  difference spectrum primarily in the narrow less clustered 4 kHz proton population, which we now identify with  $T$ -site trapped molecular hydrogen. The large number (ten) of Si neighbors at almost the same distance from a  $T$  site is vital for the existence of the plateau in Fig. 3 and crucial to the interpretation of these results. No such configuration of Si neighbors exists for the Si-bonded H. Since molecular hydrogen makes up a substantial fraction of the total hydrogen content and since the molecular hydrogen  $T$ -site to  $T$ -site activation energy is of the order of 1 eV, the pos-

sibility that the observed transport of hydrogen in  $a$ -Si:H arises primarily from the motion of molecules should be considered [18].

The PECVD amorphous silicon films were provided by William Paul's laboratory at Harvard. Support was provided, in part by the NSF under DMR 93-05344 and by the Lillian Sirovich Fund.

- 
- [1] R. Borzi, F. Mascarenhas, P.A. Fedders, D.J. Leopold, R.E. Norberg, P. Wickboldt, and W. Paul, Mater. Res. Soc. Symp. Proc. **557**, 287 (1999).
  - [2] R.E. Norberg, D.J. Leopold, and P.A. Fedders, J. Non-Cryst. Solids **227**, 124 (1998).
  - [3] T.S. Cull, M.J. Kernan, P.H. Chan, P.A. Fedders, D.J. Leopold, R.E. Norberg, P. Wickboldt, and W. Paul, Mater. Res. Soc. Symp. Proc. **467**, 123 (1997).
  - [4] R.E. Norberg, P.A. Fedders, and D.J. Leopold, Mater. Res. Soc. Symp. Proc. **420**, 475 (1996).
  - [5] M.A. Petrich, Magn. Reson. Rev. **16**, 183 (1993).
  - [6] D.J. Leopold, J.B. Boyce, P.A. Fedders, and R.E. Norberg, Phys. Rev. B **26**, 6053 (1982).
  - [7] D.J. Leopold, P.A. Fedders, R.E. Norberg, J.B. Boyce, and J.C. Knights, Phys. Rev. B **31**, 5642 (1985).
  - [8] Norman F. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, 1963), Chap. VIII.
  - [9] T. Su, P.C. Taylor, S. Chen, R.S. Crandall, and A.H. Mahan, Mater. Res. Soc. Symp. Proc. **557**, 293 (1999).
  - [10] J. Baugh, D. Han, Qi Wang, and Yue Wu, Mater. Res. Soc. Symp. Proc. **557**, 383 (1999).
  - [11] J.B. Boyce and M. Stutzmann, Phys. Rev. Lett. **54**, 562 (1985).
  - [12] M.S. Conradi and R.E. Norberg, Phys. Rev. B **24**, 2285 (1981).
  - [13] P.A. Fedders, Phys. Rev. B **20**, 2588 (1979).
  - [14] W.E. Carlos and P.C. Taylor, Phys. Rev. B **25**, 1435 (1982).
  - [15] P.A. Fedders, Phys. Rev. B **34**, 7489 (1986).
  - [16] R.E. Norberg, Y.W. Kim, P.H. Chan, J.R. Bodart, M.J. Kernan, D.J. Leopold, P.A. Fedders, W.A. Turner, and W. Paul, Mater. Res. Soc. Symp. Proc. **377**, 179 (1995).
  - [17] C.P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1990).
  - [18] C.G. Van de Walle and B. Tuttle, Mater. Res. Soc. Symp. Proc. **557**, 275 (1999).