

Weakly bound deuterium in *a*-Si:D,H

V. P. Bork, P. A. Fedders, D. J. Leopold,\* and R. E. Norberg  
 Washington University, St. Louis, Missouri 63130

J. B. Boyce and J. C. Knights  
 Xerox Palo Alto Research Center, Palo Alto, California 94304  
 (Received 19 June 1987)

The existence of a weakly bound deuterium component in deuterated amorphous silicon is demonstrated by changes in deutron magnetic resonance spectra upon annealing. Quantitative determinations of the amounts of weakly bound, tightly bound, and molecular deuterium are presented for a sequence of progressive anneals between 250 and 600 °C.

Direct confirmation of the existence of weakly bound deuterium (WBD) in plasma-deposited *a*-Si:D,H is provided by deutron magnetic resonance (DMR) spectral changes which accompany a series of sample anneals. The presence of weakly bound hydrogen or deuterium has been proposed on the basis of reported gas evolution studies by Mackenzie *et al.*<sup>1</sup> and from previous DMR measurements.<sup>2</sup> In the present experiments the DMR signal arising from weakly bound deuterium disappears after a 30-min anneal at 350 °C while signal components from tightly bound deuterium and molecular deuterium (D<sub>2</sub> and a small amount of HD) remain detectable after subsequent anneals to 600 °C.

Many of the DMR data were taken on an amorphous film prepared at the Xerox Palo Alto Research Center by lower-power rf plasma deposition from 5% SiH<sub>4</sub>/95% D<sub>2</sub> at 0.1 W/cm<sup>2</sup> onto a 25 °C Al substrate which subsequently was removed with dilute HCl. The DMR line shapes are Fourier transforms of 30-MHz quadrupole echoes. Figure 1 shows six 11-K spectra which exhibit some of the results of a progressive series of 30-min heli-

um atmosphere anneals at 250, 350, 450, 500, 550, and 600 °C (samples A through F). Very similar changes in DMR line shapes also were observed upon annealing of a high-quality *a*-Si:D sample produced from perdeuterated silane. In this case the rf plasma deposition was carried out in 5% SiD<sub>4</sub>/95% Ar at 0.75 W/cm<sup>2</sup> onto a 230 ° substrate. The unannealed sample<sup>2</sup> contained 10 at.% deuterium.

In Fig. 1 there are at least three distinct DMR spectral components. First there is a well-resolved small asymmetry parameter 66-kHz quadrupolar doublet that is independent of temperature between 4 and 300 K. The doublet arises from tightly bound deuterium and is characterized by a single electric field gradient (EFG) along a bond axis defined by a Si atom and a D atom. The doublet splitting corresponds very well<sup>2,3</sup> with the 1460 cm<sup>-1</sup> ir stretching mode frequencies observed for SiD and SiD<sub>2</sub> configurations in *a*-Si. The doublet signal intensity does not change upon annealing at 250 °C. It then diminishes with increased annealing, but still remains detectable after the 550 °C anneal (and after a subsequent 600 °C

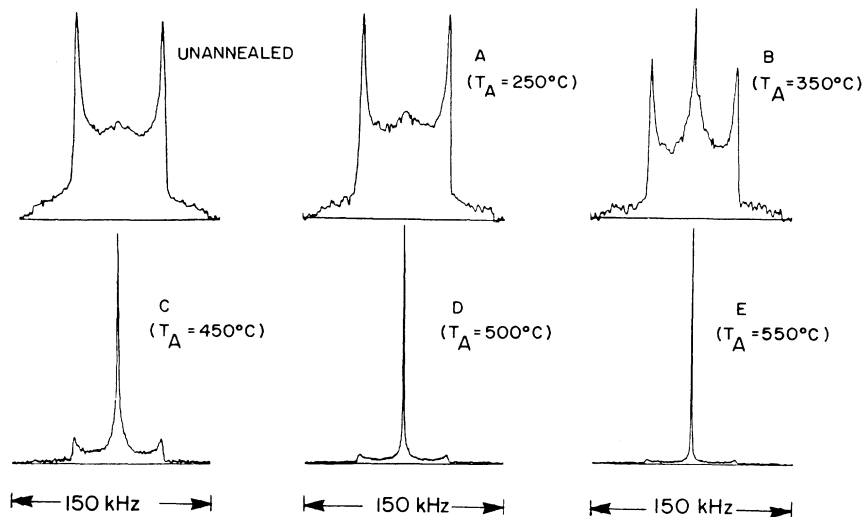


FIG. 1. 30-MHz DMR spectra at 11 K in an *a*-Si:D,H sample before and after anneals at temperatures  $T_A$ .

anneal). This doublet arises from deuterium bound to Si atoms where any distortion of the bond angles from tetrahedral symmetry is very small (less than one degree).

Second, there is a broad central 27-kHz full width at half maximum (FWHM) line that is independent of temperature between 4 and 70 K and then narrows by a factor of 5 between 70 and 300 K. This DMR feature vanishes after the 350°C anneal and so arises from weakly bound deuterium which rearranges and may be associated with the gas evolution observed<sup>1</sup> near 350°C. It reflects the existence of a broad distribution of magnitude and/or asymmetry parameter for the EFG's. These D may be bound with strained bonds and/or bond angle distortion arising from constraints by neighbors.

Third there is a narrow central DMR line, which in Fig. 1 appears after the 350°C anneal and which is associated with molecular D<sub>2</sub> and HD in microvoids or bubbles. In most cases the narrow central line itself is compound with two components (Fig. 2) which we believe reflect dense bulk molecular deuterium and microvoid surface-dominated molecular deuterium. The EFG's here are partially averaged by the molecular motion and can be small if the molecules are contained in large voids. Some of the molecules are physisorbed on the void surfaces and their relaxation times differ from those characteristic of the rest of the dense molecular fluid. The spin-lattice relaxation for the microvoid-contained molecular deuterium shows compound  $T_1$  relaxations with minima near 1 sec and 30 K. The  $T_1$  minima are sharp because the magnetization transport to effectively dilute<sup>4</sup> relaxation center  $p$ -D<sub>2</sub> occurs via rapid mass diffusion in the dense fluid D<sub>2</sub>.

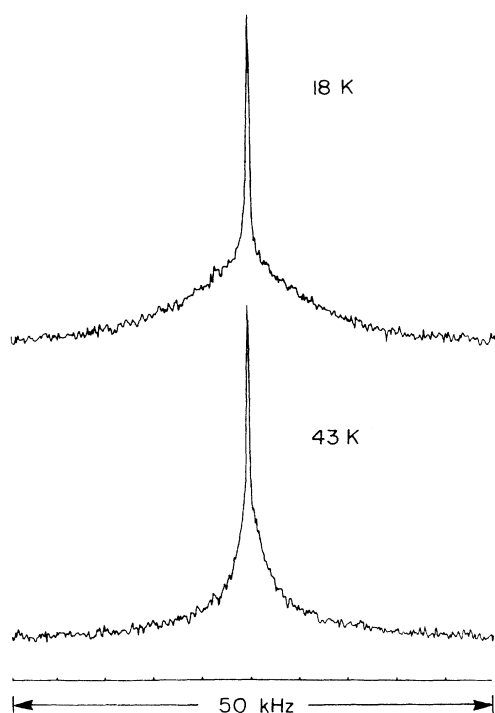


FIG. 2. Narrow central DMR spectra in sample B, after a 350°C anneal.

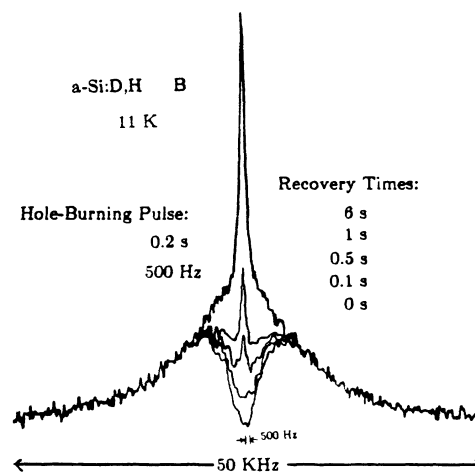


FIG. 3. A series of 11-K hole-burning line shapes for sample B, after a 350°C anneal. Recovery times were varied between 0 and 6 sec. The intensity  $\gamma H_1/2\pi$  for the hole-burning pulse was 500 Hz, as indicated.

The compound nature of the quadrupole-broadened narrow central line shape is shown in Fig. 2 for sample B (after the 350°C anneal). There is a narrow 300-Hz line which we believe to be associated with mobile dense fluid molecular deuterium in the microvoids. The linewidth for this narrower component narrows with sequential annealing and reflects the corresponding increase of typical microvoid sizes manifested via decreasing average interior electric field gradients within microvoids. There is also a broader line-shape component probably arising from molecular deuterium adsorbed on microvoid surfaces and which motionally narrows with increasing temperature from 13 kHz at 18 K to 1 kHz near 300 K.

Spectral hole-burning experiments provide additional information on the transport of magnetization. Figure 3 shows a sequence of spectra for the central portion of the DMR line during recovery from an on-resonance hole burning in sample B at 11 K. A hole-burning pulse of intensity  $\gamma H_1/2\pi = 500$  Hz was applied for 0.2 sec. The spectra were taken with a quadrupole echo sequence applied after the delays indicated in the figure. The hole burning saturated the narrower spectral component and burned a 3.4-kHz hole in the broader components. The deuteron-deuteron homonuclear flip-flop rate is no more than 500 Hz, so the observed wider hole burned in the broader line arises from translation of the molecular deuterium during the hole-burning pulse. After the hole burning the two spectral components recover at similar rates, but maintain their separate spectral identities, without further appreciable spectral diffusion. We conclude that the broader component of the narrow central lines arises from D<sub>2</sub> that are physisorbed on void surfaces or trapped in voids with an appreciable average electric field gradient. The narrower part of the narrow central line arises from voids with an average electric field gradient that is nearly zero. This is consistent with the assumption that these voids are larger but not necessarily

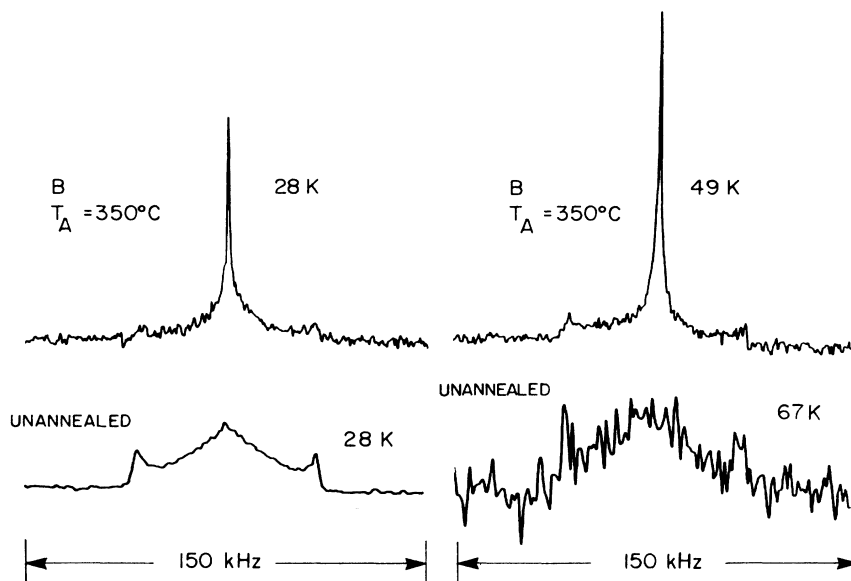


FIG. 4. DMR spectra at 28 K and near 60 K in samples before and after a 350°C anneal.

large in all dimensions.

In Fig. 1 the presence of the compound narrow central molecular deuterium line at 11 K makes it difficult to ascertain whether the weakly bound D broad central line is disappearing significantly faster than the resolved doublet component as the annealings progress. Figure 4 clarifies the question by examining the appearance of DMR spectra which are incompletely recovered from saturation. The line shapes were obtained after  $\sim 20$  sec of recovery and show a relatively suppressed doublet signal since the doublet spin-lattice relaxation times are longer than those for weakly bound D, which thus must be located<sup>4,5</sup> nearer to effectively dilute relaxation center  $p$ -D<sub>2</sub> molecules adsorbed on void surfaces. Clearly the broad

triangular line present in the unannealed sample at 28 and 67 K is much diminished, after the 350°C anneal, in sample B where a temperature-dependent narrow central molecular deuterium line instead has appeared. The disappearance of the weakly bound D signal after the 350°C anneal corresponds well with the cooler of the two hydrogen gas evolution peaks reported<sup>1</sup> for plasma-deposited  $\alpha$ -Si:H.

Figure 5 shows the variation, with six successive annealing temperatures, of the at. % spin counts of the total D, tightly bound D, weakly bound D, and (D<sub>2</sub>+HD) spectral components. The Si-bonded D fraction remains constant through the 250°C anneal and then begins to decrease steadily, with the weakly bound D fraction virtually undetectable after the 350°C anneal. The (D<sub>2</sub>+HD) fraction increases to a maximum following the 500°C anneal and then decreases upon further annealing. After the 600°C anneal the residual amount of molecular D<sub>2</sub> is larger than the amount of Si-bonded D.

In summary, DMR spectra distinguish a weakly bound deuterium component in deuterated amorphous silicon. The weakly bound D component essentially is eliminated by a 30-min anneal at 350°C. The component may arise from disordered regions characterized by Si-bonded D with strained bond angles or it may reflect physisorbed molecular deuterium for which translational motion is restricted by confinement in very small voids. It remains to be investigated whether rearrangement of the weakly bound hydrogen fraction is related to light-induced metastable changes<sup>6</sup> in electrical conductivity.

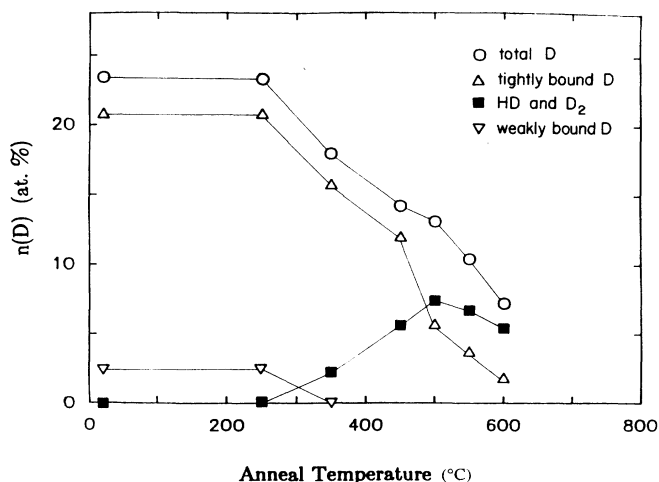


FIG. 5. Deuteron magnetization components as a function of annealing temperature.

This work was supported in part by the National Science Foundation Division of Materials Research under Grants No. DMR 85-03083 and No. 85-17198. V.P.B. thanks the Xerox Corporation for financial support.

\*Present address: McDonnell Douglas Research Laboratories, St. Louis, MO 63166.

<sup>1</sup>K. D. Mackenzie, J. H. Burnett, Y. F. Chen, J. R. Eggert, C. Hayzelden, Y. M. Li, F. Moraes, and W. Paul, *Bull. Am. Phys. Soc.* **31**, 434 (1986).

<sup>2</sup>D. J. Leopold, P. A. Fedders, R. E. Norberg, J. B. Boyce, and J. C. Knights, *Phys. Rev. B* **31**, 5642 (1985).

<sup>3</sup>D. J. Leopold, J. B. Boyce, P. A. Fedders, and R. E. Norberg, *Phys. Rev. B* **26**, 6053 (1982).

<sup>4</sup>P. A. Fedders, R. Fisch, and R. E. Norberg, *Phys. Rev. B* **31**, 6887 (1985).

<sup>5</sup>P. A. Fedders, *Phys. Rev. B* **33**, 5994 (1986).

<sup>6</sup>D. L. Staebler and C. R. Wronski, *Appl. Phys. Lett.* **31**, 292 (1977).