Proton Magnetic Resonance Spectra of Plasma-Deposited Amorphous Si:H Films

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Proton magnetic resonance data are presented for a series of plasma-deposited a-Si:H films with hydrogen contents ranging from 32 to 8 at.%. Line-shape and line-width analysis leads to the conclusion that the spatial distribution of hydrogen is inhomogeneous in all samples.

Recent reports of structural inhomogeneity in hydrogenated amorphous silicon[1-3] have led to the suggestion that there may be compositional inhomogeneity on the same scale as the microstructure, i.e., ~60–100 Å. Specifically, microscopic phase separation involving polysilane $[(\mathrm{SiH}_2)_n]$ as one of the phases has been inferred from the interpretation of Si-H vibrational spectra.[4,5] There are, however, limitations to the information that can be extracted from hydrogen vibrational spectroscopy in this system. The presence of local bonding configurations such as SiH, SiH_2, and SiH_3 can be determined with relative ease, but only in the case of $(\mathrm{SiH}_2)_n$ has any longer range structure been inferred and that inference is not universally accepted.[6] No information has been forthcoming about the relative degrees of clustering or intermingling of these local bonding configurations that might be expected to occur on the internal surfaces now presumed to exist. It is the purpose of the Letter to report the observation of dipole-broadened two-component resonance lines in high-resolution proton magnetic resonance that provide direct evidence for the existence of a two-phase compositional inhomogeneity in hydrogenated amorphous silicon. This inhomogeneity is such that spin diffusion between the two components is negligible at room temperature, implying average separations of protons in the two phases of greater than ~7 Å. Analysis of the data further indicates (1) that one phase is solely monohydride, that is itself clustered; and (2) that the inhomogeneity persists in material that shows no polysilane vibrational spectra.

The samples were prepared in an rf-diode deposition system, details of which have been published elsewhere.[7] Proton magnetic resonance spectra were taken with a solid state spectrometer described previously[8] with proton resonance at 56.4 MHz. The spectra were obtained either by Fourier transformation of the free-induction decay (FID) following a 90° pulse or by Fourier transformation of the stroboscopically observed magnetization while an eight-pulse sequence[9] suppressed homonuclear dipole-dipole interactions. The cycle time in the eight-pulse experiments was 50 μsec. In all experiments approximately 100 averages were accumulated, with care being

TABLE I. Details of sample composition and structure.

Sample	Conditions[a]	Hydrogen content[b] (at.%)	Microstructure[c] (TEM/SEM)
A	5%; 18 W; 25°C (A)	32.3	Columnar
B	5%; 18 W; 25°C (K)	6.3	Weak columnar
C	5%; 1 W; 25°C (K)	2.6	None visible
D	100%; 2 W; 230°C (A)	7.8	None visible

[a] The conditions refer to percentage silane in gas (diluent argon), rf power (net into matching network), and substrate temperature. (A) and (K) distinguish between deposition on grounded electrode (anode) or hot rf electrode (cathode).

[b] Determined from integrated proton spin density and sample weight.

[c] See Ref. 1 for details.

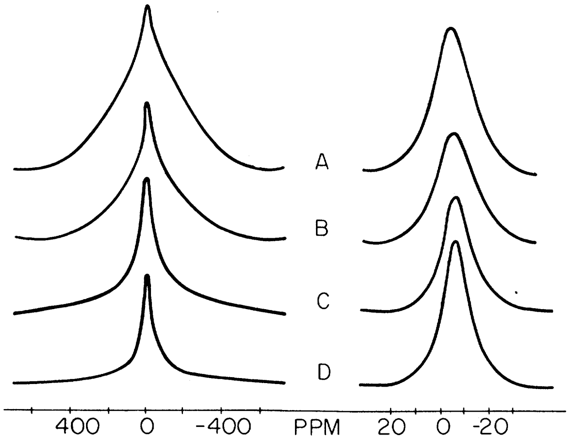

FIG. 1. Proton FID spectra (left) and eight-pulse spectra (right) for plasma-deposited silicon hydrogen alloy samples *A–D* (see text for deposition conditions). Shifts are relative to tetramethyl silane where 1 ppm equals 56.4 Hz.

taken to allow full spin-lattice relaxation to occur between acquisitions.

Four samples were chosen that represent a proton content ranging from 33 to 8 at.% produced by varying of the deposition parameters. Table I details the preparation conditions, the hydrogen content measured from the FID area, and the microstructure determined by transmission and scanning electron microscopy on similar samples. The samples were deposited onto ~2-in.-diam aluminum foil substrates in thicknesses ranging from 20 to 110 μ resulting in sample masses in the range ~0.1–0.25 g after removal of the substrates with a dilute hydrochloric acid etch.

Figure 1 shows the proton FID and eight-pulse spectra at room temperature for the samples described in Table I. The FID spectra show overlapping lines with at least one broad component superimposed on a narrow component. The multiple-pulse spectra, in contrast, show that when the homonuclear dipolar interaction is suppressed only a single narrow line remains whose width is consistent with that expected from chemical shift interactions. These measurements were repeated at 120 °K. No substantial changes in linewidth were observed indicating that motional narrowing is not a major factor in linewidth determination at 300 °K and suggesting that a temperature-independent spin-spin relaxation process is operative. It is therefore concluded that the FID spectral linewidths are dominated by homonuclear dipolar interactions. Combining this result with the two-component spectrum implies directly that the two components must be spatially isolated (average separation ≥ 7 Å) with no possibility of spin diffusion. Both this conclusion and the spectra themselves are very similar to the results of similar experiments on partially crystalline polyethylene[10] in which there is microscopic amorphous/crystalline phase separation coupled with motional narrowing in the amorphous phase. Since nearest neighbors provide the major contribution to the dipolar broadening it is also clear in the *a*-Si:H that there are different nearest neighbor configurations within the two components.

To permit comparison of the data with models of proton distributions it is necessary to separate the two components. As will be shown later, neither of the two components corresponds to a homogeneous distribution of spins, i.e., there is clustering within each component. Given this clustering and the amorphous matrix in which the spins are embedded, it is assumed as a first approximation that the line shapes are Gaussian. With this assumption and the further assumption that there are only two components, these data have been least-squares fitted. Excellent fits were obtained. The full linewidths at half maximum and areas obtained from these fits are shown in Table II. For comparison these data have also been fitted with two Lorentzians; χ^2 was found to be an order of magnitude larger.

The dipolar linewidth full width at half maximum (FWHM) for a Gaussian line is equal to $3.36\sqrt{M_2}$ where M_2 is the second moment of the line given by[11]

$$M_2 = \tfrac{3}{5}\gamma^4\hbar^2 I(I+1)\textstyle\sum_{ij} 1/r_{ij}^{\,6}, \qquad (1)$$

where I is the nuclear spin, $\frac{1}{2}$ for protons, γ is the nuclear gyromagnetic ratio, and r_{ij} is the spacing between spins i and j. In the limit where the spin density is less than 0.01 of the available site density the system is termed dilute[8] and an exact linewidth (Lorentzian) can be calculated for a random distribution; however, none of the proton densities measured here corresponds to this limit. We have therefore considered two types of proton configuration to which Eq. (1) can be simply applied. In the first, the spins are distributed uniformly on a cubic lattice whose spacing is equal to the inverse cube root of the spin density. The results of linewidth calculations for this configuration using the densities obtained for the narrow component are shown in Table II. The second is the situation of local clustering into

TABLE II. Proton resonance linewidths and distributions.

	Linewidth (FWHM, kHz)			Hydrogen distribution				Homogeneous width (kHz)[b]	Center of Mass[c]
				Broad[a]		Narrow[a]			
Sample	Broad[a]	Narrow[a]	8-pulse	(%)	(at. %)	(%)	(at. %)	Narrow	(ppm)
A	26	4.7	1.07	92	29.7	8	2.6	0.71	-17.8
B	22	3.9	1.00	87	14.2	13	2.1	0.65	-16.8
C	26	4.7	0.79	72	9.1	28	3.5	1.04	-18.3
D	27	3.8	0.74	56	4.4	44	3.4	0.87	-18.0

[a] Values obtained from fitting two Gaussian lines to the data shown in Fig. 1.

[b] Calculated with use of Eq. (1).

[c] Shift of resonant frequency relative to tetramethylsilane: 1 ppm = 56.4 Hz.

configurations such as SiH_3, $(SiH_2)_n$ and a hydrogenated [111] *c*-Si surface. The results of these calculations and an estimate[12] of the linewidth for isolated SiH_2 are as follows: SiH_2, 13.6 kHz; SiH_3, 19.2 kHz; $(SiH_2)_n$, 17.1 kHz; and Si[111], 23.5 kHz.

In view of the sensitivity of the calculation to small changes in interatomic spacings and the errors and assumptions involved in the fitting procedure, we conclude that any of the local clusters could give rise to the broad line although the fact that the model structures yield values consistently lower than those observed suggests that further clustering may be present. In contrast, comparison of these linewidths with those of the narrow component indicates directly that the narrow component must originate primarily from monohydride species, the multiply bonded SiH_x species all yielding much larger linewidths than those observed. It then follows that the observed linewidths in the narrow component (~ 3–4 kHz) must be due to clustering of the monohydride species, the average proton density required to account for the broadening being ~ 4–6 times that of the homogeneous distribution. In addition we emphasize that all of the films have at least some of the monohydride species spatially isolated from all other protons in the sample.

Although the NMR data by themselves do not provide unique structural information about the broad component, comparison with previous infrared and Raman studies[5] produces an interesting result. Samples similar to *A*, *B*, and *C* all exhibit hydrogen vibrational modes characteristic of SiH_2, $(SiH_2)_n$, and SiH_3. No detailed quantitative studies have been performed on exactly the same samples, but the results on similar samples suggest that the broad component might be explained wholly by SiH_x species. Sample *D*, however, is prepared under conditions where monohydride vibrational modes dominate and only a vestigial SiH_2 bending mode at 875 cm^{-1} can be observed. Unless it is argued that the oscillator strength for SiH_2 is strongly suppressed, the finding that ~ 60% of the hydrogen is contained in the broad line suggests that dense monohydride clustering does indeed occur. In view of the fitting inaccuracies, however, we believe that confirmation of this suggestion must await further more detailed experiments.

There are several implications of these results for models of both microstructure and defects in *a*-Si:H. The first stems from the universal observation of proton inhomogeneity. The sample preparation conditions described span a large fraction of the available range, as do the defect densities[7] (electron spin densities from 10^{19} to 3×10^{15} cm^{-3}) and microstructures.[1] The implication is that the observed changes in microstructure and defect properties are correlated primarily with quantitative rather than qualitative changes in proton distribution, a possible exception being changes in the origin of the broad line. The previous study of microstructure led to the conclusion that film growth occurred via nucleation and coalescence of islands followed by columnar growth with an $(SiH_2)_n$ phase being formed in the boundary regions under favorable conditions. If we identify the broad line with protons in this interstitial phase, then their association solely with $(SiH_2)_n$ is clearly an oversimplification since sample *D* exhibits no vibrational modes of that type.

A second implication stems from the clustering implicit in the width of the narrow line and the magnitude of the proton concentration observed in that line. Even with the errors and assumptions used in the fitting and deconvolution, it is clear that the magnitude of the proton content of this line is approximately independent of sample preparation condition and is ~3%. Since the two-component nature requires that the protons in the narrow component are separate from those located in the interstitial regions (separations ~7 Å), we propose that they are located within the columns. The clustering can then be explained on the basis of hydrogenated internal surfaces of small voids or multivacancy complexes whose concentration does not depend strongly on preparation conditions. This proposal is consistent with the observation in the study of microstructure[1] that the major changes with preparation conditions occurred in the area and resolution of the interstitial regions, while the columnar dimensions did not change substantially.

Lastly, there is information to be derived from the absence of any narrower line that would be associated with a random distribution of monohydride. With use of a third Gaussian to approximate a dilute distribution it is found that in sample D, if 10% of the protons are in a line with a 600 Hz width, the distortion of the experimental line shape would be detectable. This places an upper bound of ~0.8 at.% of protons in this configuration, a feature to be borne in mind when considering models for point defects.

In conclusion, we have shown that the hydrogen in a series of a-Si:H films prepared by plasma deposition is spatially inhomogeneous on two levels in that (1) some of the monohydride species are spatially isolated from $\mathrm{SiH}_x (x=2,3)$, and (2) that clustering of monohydride (SiH) species occurs even in a sample that has a low density of electronically active defects. We further observe that both levels of inhomogeneity are present even in the absence of visible microstructure. These results indicate that in addition to the multiplicity of local hydrogen bonding configurations, longer-range spatial fluctuations in composition may also be important in determining the relationship between hydrogen and defect structures.

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[12] SiH_2 will give rise to a Pake doublet with a 13.6-kHz splitting. In the amorphous matrix the doublet components will be expected to broaden and merge, in which case the splitting will give an approximate measure of the linewidth.