Multiple-Quantum NMR Study of Clustering in Hydrogenated Amorphous Silicon

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(Received 6 November 1985)

Multiple-quantum nuclear-magnetic-resonance techniques are used to study the distribution of hydrogen in hydrogenated amorphous silicon. Using the fact that multiple-quantum excitation is limited by the size of the dipolar-coupled spin system, we show that the predominant bonding environment for hydrogen is a cluster of four to seven atoms. For device-quality films, the concentration of these cluster defects increases with increasing hydrogen content. At very high hydrogen content, the clusters are replaced with a continuous network of silicon-hydrogen bonds.

Hydrogen incorporation into amorphous silicon thin films has improved their electrical and optical properties to a point where they now play a significant role in the electronics industry. In addition to passivating "dangling bond" defects, the hydrogen modifies the electronic structure of these materials. Films containing between 8 and 20 at.% hydrogen are "device quality" and have roughly 10^{15} defects/cm^{13}; films with higher hydrogen content can also be prepared but usually have higher defect densities than device films. In recent years, a number of researchers have characterized amorphous hydrogenated silicon (a-Si:H) by numerous techniques and have furnished information on the relationship between the structure of a-Si:H and its properties.[1]

Structural information gained from electron microscopy indicates that device films can differ from one another to the extent that some show no features down to 10 Å while others show structures on the order of 100 Å. In contrast, nondevice and polymeric films (>50 at.% ^{1}H) show columnar growth islands and other structural features. Information on the different types of silicon-hydrogen bonds have been obtained by infrared spectroscopy; predominantly monohydride (Si-H) silicon-hydrogen bonds are observed in device films, whereas dihydride (Si-H$_2$), trihydride (Si-H$_3$), and polymeric [(Si-H$_2$)$_n$] species are observed in the higher hydrogen-containing films. From proton nuclear magnetic resonance it has been ascertained that the hydrogen is inhomogeneously distributed in device materials.[2,3] Approximately 4 at.% hydrogen is present as spatially isolated monohydrides and molecular H$_2$, and gives rise to a narrow (3–4-kHz) resonance line. The remaining hydrogen results in a broad (25-kHz) resonance line indicating clusters of monohydrides. While the magnetic resonance linewidths and magnitude of the narrow component remain constant, the magnitude of the broad component grows with increasing hydrogen content. Heating of the material to 600 K causes the hydrogen associated with the broad component to evolve, leaving only a narrow resonance line in the NMR spectrum.

Many questions concerning the distribution of hy-

drogen in a-Si:H films still remain unanswered. A drawing of local hydrogen structure shown in Fig. 1 serves to illustrate the issues raised in this Letter: What is the nature of the hydrogen distribution responsible for the broad resonance line? How does the dense hydrogen coexist with the dilute hydrogen? On the atomic level, what are the differences between device- and nondevice-quality films? By using multiple-quantum NMR, a technique inherently sensitive to spatial arrangements of atoms, we present the first study in which the size and extent of hydrogen clustering, in selected a-Si:H thin films, has been determined.

To overcome the Zeeman selection rule $\Delta M = 1$ and thereby to create multiple-quantum coherence among a group of spins, appropriate sequences of radiofrequency pulses must be applied to the system to force the spins to interact collectively via their dipolar couplings.[4] Subjected to a multiple quantum pulse sequence designed for solids,[5,6] a system of N spins $\frac{1}{2}$ undergoes a dynamical evolution under a nonsecular Hamiltonian of the form

$$H = -\frac{1}{2}\sum_{i<j}D_{ij}(I_{i+}I_{j+} + I_{i-}I_{j-}),$$
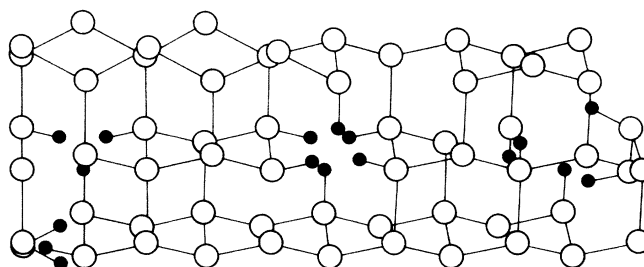

FIG. 1. Schematic three-dimensional drawing of clustered monohydrides in hydrogenated amorphous silicon, with all silicon atoms in a tetrahedral bonding configuration. Silicon atoms, hydrogen atoms, and covalent bonds are represented by open circles, filled circles, and solid lines, respectively. The drawing is intended to motivate questions concerning the distribution of hydrogen in a-Si:H thin films; it is not a proposed structure.

where I_+, I_- are raising and lowering spin angular momentum operators and where the coupling constant D_{ij} is inversely proportional to the cube of the distance between two spins i and j. This results in a coherent superposition of states with differences in magnetic quantum number ΔM equal to $0, \pm 2, \pm 4, \ldots, \pm N$. When $\Delta M = N$, roughly speaking, N spins have "flipped" collectively from the ground state to the highest excited state. By capitalizing on this notion, multiple-quantum experiments have been used to determine the structure of small molecules adsorbed on metal surfaces.[7] In order for spins to become correlated in this manner, the Hamiltonian must act for a time τ proportional to the inverse of the pairwise dipolar interactions. As a result, the preparation time τ can be short if spins are near one another, and must be longer if spins further apart are to communicate with one another. If a solid contains isolated clusters, then the dipolar couplings of spins between groups can essentially be neglected on the experimental time scale, and there will then be an upper bound to the number of interacting spins. One can imagine clusters as independent subgroups containing a maximum number of spins. Consequently, after an initial induction period, the number of correlated spins will remain roughly constant over time and will reflect the size of the isolated cluster. Clearly, if the distribution of spins
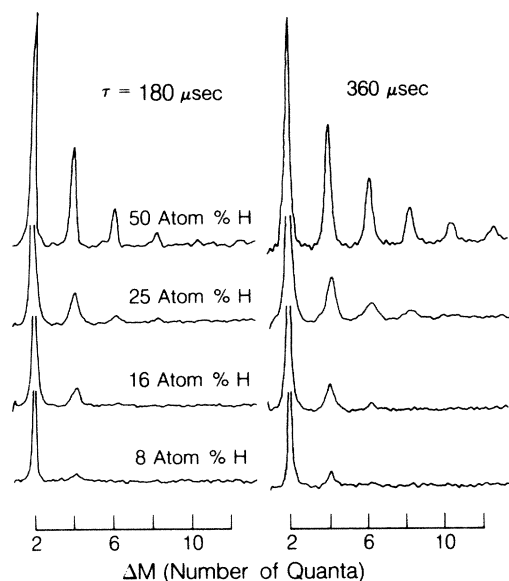

FIG. 2. 180-MHz ^{1}H multiple-quantum spectra of a polymeric, a nondevice, and two device-quality a-Si:H samples for two different preparation times, $\tau = 180$ and 360 μs. From top to bottom, these samples contain 50, 25, 16, and 8 at.% ^{1}H, respectively. Over time, the distribution of intensity across the multiple-quantum orders (ΔM) does not change in the 8-at.% sample, suggesting a bounded spin system. As the hydrogen concentration increases, the spectra begin to change more from one preparation time to another.

is uniform or if clusters exist very near one another, then the number of interacting spins will no longer be limited, and over time, more and more spins will become correlated and higher multiple-quantum orders (ΔM) will be observed in the spectra. Thus, a time-dependent multiple-quantum experiment, which measures the number of correlated spins, can be used to determine whether atoms are clustered or uniformly distributed.[6, 8]

Five different a-Si:H samples, prepared by plasma deposition, are considered: two device-quality films with different hydrogen concentrations, one non-device-quality film, one polymeric, and one annealed sample. Sample preparation procedures, i.e., the reactant gas composition, the substrate temperature, the power of the rf electrode, and the final atomic percentage of ^{1}H, are listed in Table I. Details of the solid-state multiple-quantum experiments have been summarized elsewhere.[5b,6,8] As usual, the two-dimensional multiple-quantum experiments are divided into four distinct periods: preparation (τ), evolution (t_1), mixing (τ), and detection (t_2). The basic radio-frequency pulse cycle of the preparation and mixing periods is composed of eight $\pi/2$ pulses of length t_p separated by delays Δ and $\Delta' = 2\Delta + t_p$. The total preparation/mixing time τ is formed by repetition of the 60-μs basic cycle m times.

Multiple-quantum spectra of the a-Si:H samples for two different preparation times are shown in Fig. 2. A comparison of the spectra at $\tau = 180$ and 360 μs was made to see whether the intensity distribution of the multiple-quantum orders changes with time or remains constant. Two extremes can be observed; the 50-at.% spectra clearly show higher orders at longer times, whereas the 8-at.% spectra remain very similar, suggesting a bounded spin system. Although not shown in Fig. 2, spectra were also obtained to assess the contribution of the isolated monohydrides and molecular H_2 to the multiple-quantum experiment. After annealing of the 8-at.% ^{1}H device sample, the remaining hydrogen (<4 at.%) yields a spectrum with a narrow ^{1}H resonance line (4 kHz). No multiple-quantum coherences are created for short preparation times and only at times greater than 360 μs can small accounts of two-quantum coherence be observed. Therefore, on

TABLE I. Sample preparation conditions.

Sample	Gas composition	Temperature (°C)	Power (W)	At.% ^{1}H
Annealed[a]	100% SiH$_4$	275	1	4
Device A	100% SiH$_4$	275	1	8
Device B	5% SiH$_4$/He	230	18	16
Nondevice	100% SiH$_4$	75	1	25
Polymeric	100% Si$_2$H$_6$	25	1	50

[a]Annealed 600 °C, 90 min.

the experimental time scale, the dominant contributions to the multiple-quantum spectra result from spins responsible for the broad resonance line.

For a finite cluster of size N, the integrated intensity of a multiple-quantum order can be related to the number of multiple-quantum transitions within that order. These can be calculated directly from combinatorial arguments which can then be approximated by a Gaussian distribution for $N > 6$.[4] As a result, a time-dependent effective system size $N(\tau)$ is found from $I(\Delta M, \tau) = \exp[-\Delta M^2/N(\tau)]$ by fitting of the multiple-quantum intensity envelope to a Gaussian and then associating of its variance with $N(\tau)/2$.[6] In this way, the number of correlated spins at different preparation times is quantified by the parameter $N(\tau)$. For clusters, where there is an upper bound to the number of interacting spins, $N(\tau)$ will remain essentially constant over long times. A growth of $N(\tau)$ may be accounted for in either of two ways: On the one hand, the spins may be distributed uniformly throughout the sample, while on the other hand, groups of spins may exist but with intergroup separations too small to produce a discernible plateau in the plot of $N(\tau)$ vs τ. These two cases can be distinguished from one another with an analysis based on a two-Gaussian model where the intensity distribution is now approximated by the sum of two Gaussians. One, with variance N_c, represents correlations occurring within a cluster, while the other represents interactions occurring between clusters.[8] Therefore, two time-dependent effective sizes can be extracted from the multiple-quantum data: a cluster size $N_c(\tau)$, and a system size $N(\tau)$ that may encompass many interacting groups. Absence of change in $N_c(\tau)$ over time, in conjunction with an increase in $N(\tau)$, is evidence that higher concentrations of clusters exist. When $N_c(\tau)$ grows with time as well, then the distinction between clustered and uniform distributions becomes blurred.

The effective system size, $N(\tau)$, is plotted versus preparation time for the a-Si:H samples in Fig. 3; the dashed lines are used for the aid of the eye to indicate the growth of N versus time. Reflecting the trends seen in the multiple-quantum spectra, $N(\tau)$ remains roughly constant over time for the 8-at.% device quality sample, confirming the hypothesis that the spin system is limited to isolated clusters of atoms. By contrast, $N(\tau)$ grows with time for the 16-at.%, the nondevice 25-at.%, and the polymeric 50-at.% ^{1}H samples. On the basis of the above analysis, the increase in $N(\tau)$ for the polymeric sample is attributed to a uniform distribution of spins, whereas the increase in $N(\tau)$ for the 16- and 25-at.% samples is attributed to the existence of clusters near one another. For these two materials, the size of the clusters and the behavior of $N_c(\tau)$ is indicated by the solid line in Fig. 3. Their effective cluster size values, now very similar to those
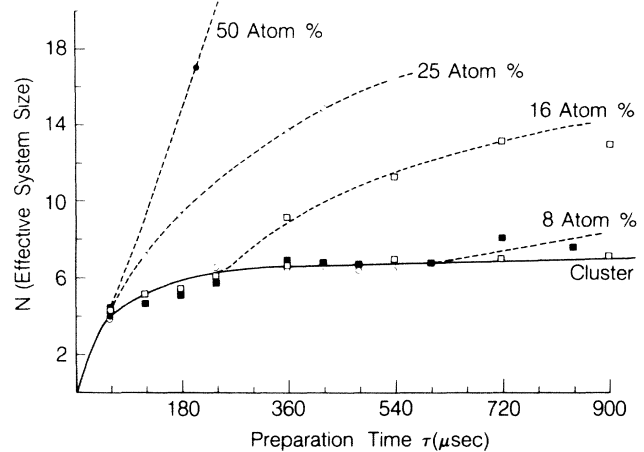

FIG. 3. For each preparation time τ, the number of correlated spins are characterized by two time-dependent parameters: an effective system size $N(\tau)$ and an effective cluster size $N_c(\tau)$. The growth patterns of $N(\tau)$ for the 8-, 16-, 25-, and 50-at.% a-Si:H samples are indicated by the dashed lines to aid the eye. After an initial induction period, $N(\tau)$ is essentially constant for the 8-at.% sample (filled square), remains nearly level up to 250 μs for the 16-at.% sample (open squares), grows continuously for the 25-at.% sample (open circles), and increases very rapidly for the 50-at.% sample (filled circles). The solid line, again drawn to aid the eye, represents values of $N_c(\tau)$ for the 16- and 25-at.% samples only (open squares and open circles, respectively). The values of $N(\tau)$ for the 8-at.% sample are very similar to the values of $N_c(\tau)$ for the other two samples. These data indicate that the two device samples (8 and 16 at.%) and the nondevice sample (25 at.%) all contain clusters of approximately six atoms; as the hydrogen concentration is increased, the clusters become closer to one another. In contrast, the polymeric 50-at.% sample is composed of a uniform distribution of spins.

obtained for the 8-at.% sample, indicate that the 25-, 16-, and 8-at.% samples all contain small clusters of four to seven atoms. The uniform distribution of atoms in the polymeric sample is consistent with the fact that it was prepared differently from the others and contains $[(Si-H_2)_n]$ species.

Having established that the two device samples and the nondevice sample all contain clusters of roughly six atoms, we can now distinguish features between them from the pattern of growth of the effective system size, $N(\tau)$, versus time. Depending on how close the clusters are to one another, the increase in $N(\tau)$ will be more or less dramatic. For the 8-at.% device sample, $N(\tau)$ is essentially constant for all times; for the 16-at.% device sample, $N(\tau)$ is nearly level for times up to about 250 μs, after which it begins to increase; and for the nondevice sample the growth in $N(\tau)$ is continuous. Therefore, what distinguishes one sample from another is that the concentration of clusters increases as the hydrogen concentration is

raised. The above results are corroborated by a set of experiments performed on model compounds with known concentrations of six spin clusters.[8] Solid solutions of 1,8-dimethylnaphthalene-d_6 (ring positions deuterated) in perdeuterated dimethylnaphthalene were prepared and the multiple-quantum experiments, done for comparable ^1H concentrations, result in plots of $N(\tau)$ and $N_c(\tau)$ that are very similar to those obtained for the a-Si:H samples. In addition, the mean square error for the values of $N(\tau)$ or $N_c(\tau)$ is always less than 1%, indicating a reasonably well-defined cluster size at each preparation time. Therefore, if distributions of cluster sizes exist, they occur in very low concentrations.

In conclusion, by use of a time-resolved solid-state multiple-quantum experiment, the extent of ^1H clustering in selected a-Si:H films has been determined. It is found that two device-quality films with 8 and 16 at.% ^1H and one nondevice quality film of 25 at.% ^1H all contain clusters of approximately six atoms. As the ^1H concentration is increased from 8 to 25 at.%, the multiple-quantum experiments indicate that these clusters become physically closer to one another. In contrast, a polymeric sample with 50 at.% ^1H was also investigated and found to consist of a uniform distribution of spins. The geometrical implications of modeling the hydrogen microstructure of a-Si:H with six-spin clusters are worth considering. For samples containing 8, 16, and 25 at.% ^1H, the concentration of cluster defects would be approximately 0.7, 2, and 3.3 "atomic" percent, respectively. If clusters were distributed randomly over a silicon lattice, their average distance from one another would be 14, 10, and 8 Å, respectively. This is superimposed on a "random" lattice of isolated monohydride groups with an average spacing of approximately 8 Å. Thus the transition from device-quality a-Si:H to nondevice quality (which occurs at roughly 20 at.% ^1H) is seen as increasing the concentration of clusters until their separation roughly equals the separation of dilute monohydride groups. This "lattice saturation" phenomenon may be relevant to electronic structure models based on disorder[9] and quantum well localization.[10]

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