

PULSED NMR STUDIES OF HYDROGENATED AMORPHOUS
SILICON (a-Si:H)

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Pulsed ^1H NMR experiments (at temperatures between 4.2 and 500K and at frequencies between 10 and 42 MHz) demonstrate the existence of at least two different hydrogen sites which do not correlate well with infrared vibrational measurements. These NMR results also indicate the presence of disorder modes associated with hydrogen in a-Si:H. As a function of temperature, the NMR spin lattice relaxation rates of ^1H in a-Si:H films exhibit an asymmetric maximum near 40K of ~ 3 Hz.

I. Introduction

A number of experimental measurements have suggested that films of hydrogenated amorphous silicon (a-Si:H) are inhomogeneous on a scale of ~ 100 Å [1], and recent NMR investigations [2,3] have confirmed the spatial inhomogeneity of the hydrogen atoms in a wide variety of samples. In this paper we briefly describe the structural information which one can infer from the observed ^1H NMR lineshapes and discuss the relationship of these results to inferences drawn from other experimental techniques. In addition, we report measurements of the ^1H spin lattice relaxation rates, T_1^{-1} , which indicate the presence of disorder modes associated with hydrogen in a-Si:H. A model which explains both the magnitude and the temperature and frequency dependences of T_1 is summarized.

II. Experimental Background

Samples of a-Si:H were obtained from several sources and contained between 7 and 15 at.% H. All samples were deposited on heated substrates (250-330°C) at relatively slow rates. The present paper will concentrate on samples made by rf decomposition of silane and obtained from the Naval Research Laboratory (NRL), the RCA Laboratories (RCA), Brookhaven National Laboratory (BNL), and the University of Chicago (CHI).

The ^1H pulsed NMR data were taken using a standard set-up. Spin lattice relaxation time (T_1) measurements were taken on the free induction decay (FID) signal using a repetition rate technique [4]. NMR samples were made as described in an earlier publication [3].

III. Structural Implications

The free induction decay (FID) signals observed at 4.2K in two representative samples are shown in Fig. (1). There are two components to the lineshapes exhibited in Fig. (1), a broad Gaussian

line represented by the curved portion of the FID at short times superimposed on a narrow Lorentzian line represented by the exponential decay of the FID at long times. In both samples the intensities of the broad and narrow lines correspond to ~ 9 at.% and ~ 3 at.% H, respectively. For the broad Gaussian line the full widths at half maximum are 25.7 and 31.2 kHz for the RCA and NRL samples, respectively. The narrow Lorentzian linewidths are 3.8 and 2.9 kHz for the RCA and NRL samples, respectively. Linewidths obtained on the other samples were within 10% of these values.

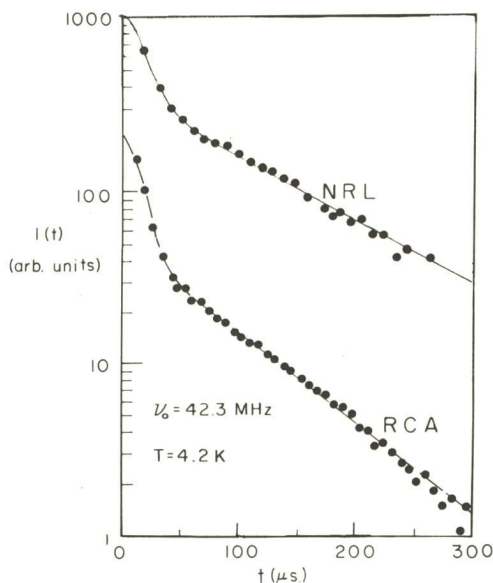


Figure 1 ^1H NMR free induction decay in two samples of $\alpha\text{-Si:H}$

In all our samples the broad line is Gaussian and the narrow line has a Lorentzian shape; whereas in some cases [2] both lines have been observed to be Gaussian. "Solid echo" experiments indicate that there is little spectral diffusion between the two hydrogen sites and that the linewidths are dominated by homonuclear dipolar interactions as previously reported by Reimer, et al. [2]. The magnitudes of the two linewidths indicate that the hydrogen atoms on both types of sites are clustered [2,3]. Dipolar effects are expected to yield a Gaussian lineshape except in dilute systems ($\lesssim 1$ at.%) where a Lorentzian lineshape is predicted [5]. It is possible that the Lorentzian lineshape of the narrow line can be explained by the dilute nature of the spins (~ 3 at.% H) in this component. In short, there exist two distinctly different local hydrogen environments in which (a) the individual H atoms are clustered and (b) there is sufficient physical separation between the two types of clusters to insure that significant spin diffusion via the dipole-dipole interaction does not occur.

The structural implications of these results are still a matter of some debate. By comparison with infrared studies, Reimer et al. [2] suggested that the narrow NMR component originated only from a monohydride species (SiH) while the broad NMR line was attributed to SiH_x ($x=1, 2$ and 3) species. This assignment seems improbable for two reasons. Firstly, the assignments of specific infrared vibrational features to SiH , SiH_2 , SiH_3 , etc., are still controversial [6,7,8]. Secondly, for a given hydrogen concentration the infrared vibrational

features vary considerably with film preparation conditions while the two NMR lines are relatively insensitive to preparation conditions. At the present time there is little evidence to suggest any direct correlation between the infrared and the NMR results.

IV. Hydrogen-associated Disorder Modes

In many amorphous solids, atoms or groups of atoms can exist in two positions of local equilibrium. This situation gives rise to degrees of freedom called disorder modes which are a common feature of oxide and chalcogenide glasses. We describe here T_1 measurements which indicate the presence of disorder modes associated with hydrogen in a-Si:H and outline a model which explains the experimental results. The temperature dependence of the ^1H spin-lattice relaxation times T_1 is displayed in Fig. (2) for three well-characterized samples of a-Si:H obtained from RCA and BNL. For comparison we show in Fig. (3) T_1 measurements on two additional samples which exhibit the same T_1 minimum but show slightly different behavior at the lowest temperatures. The RCA samples of Fig. (2) exhibited no detectable low angle X-ray scattering while the CHI and NRL samples of Fig. (3) did exhibit observable scattering. We note that the lineshapes of the BNL and NRL samples are very similar (Fig. (1)) in spite of the differences in morphology.

For the present we ignore the differences between the T_1 behavior expressed in Figs. (2) and (3) and concentrate on an explanation of the gross features. These features are well explained by a mechanism which postulates the existence of disorder modes associated with a small fraction of the hydrogen atoms (perhaps 10^{16} – 10^{18} cm^{-3}). We assume that hopping over the potential barrier ΔE which separates the two equilibrium positions of the disorder modes (in a time $\tau \sim \tau_0 \times \exp(\Delta E/kT)$) provides both a relaxation to the lattice and a modulation of the dipolar interaction. This modulation directly relaxes those nuclei closest to the disorder mode. The relaxation then proceeds via proton-proton spin diffusion to the bulk of the ^1H sites.

If we assume for simplicity a constant distribution of barrier heights ΔE between minimum and maximum values E_m and E_M respectively, then it can be shown [3] that the average relaxation rate is given by

$$T_1^{-1} \approx \alpha [-1 - S + \sqrt{(1+6S+S^2)}] \quad , \quad (1)$$

where

$$\alpha = 2\pi aD/d^3$$

$$S = \langle R \rangle / 2\alpha$$

$$\langle R \rangle = (\gamma^2 h_O^2 / \omega_O) \{ \tan^{-1} [\omega_O \tau_O \exp(E_M/kT)] - \tan^{-1} [\omega_O \tau_O \exp(E_m/kT)] \} .$$

The parameter $D \approx 2 \times 10^{-12} \text{ cm}^2 \text{ sec}$ is the nuclear diffusion constant for ^1H in a-Si:H; $a \approx 3 \text{ \AA}$ is the average H-H separation at a disorder mode; $d \approx 40 \text{ \AA}$ is the average spacing between disorder modes; $h_O \approx 2\text{G}$ is the fluctuating magnetic field due to the hydrogen on the tunneling mode, γ is the nuclear gyromagnetic ratio for ^1H , and ω_O is the NMR operating frequency.

The solid line in Fig. (2) is the fit to the data using Eq. (1) with $E_m = 80\text{K}$, $E_M = 25\text{K}$ and $\tau \approx 10^{-9} \text{ sec}$. These parameters have also been shown to fit the frequency dependence of T_1 over the range from 10–40 MHz [3]. In Fig. (3) the solid line represents a fit to the data with $E_m \approx 10\text{K}$ and other parameters similar to those used for Fig. (2).

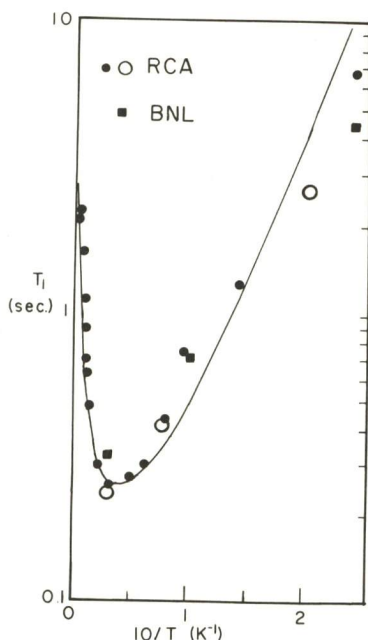


Figure 2 Temperature dependence of ^1H spin lattice relaxation time in three samples of a-Si:H at 42.3 MHz. Solid line represents a fit to the data as explained in the text.

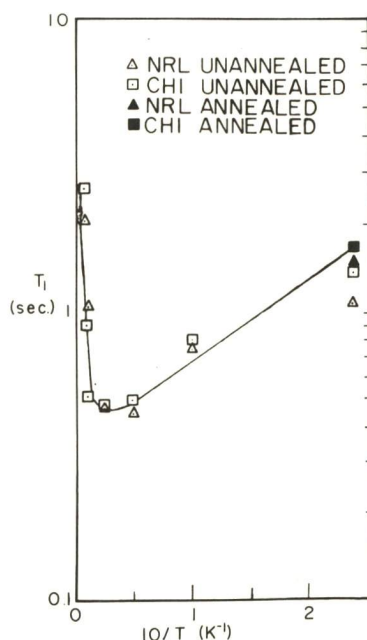


Figure 3 Temperature dependence of ^1H spin lattice relaxation time in two samples of a-Si:H at 42.3 MHz. Solid line represents a fit to the data as explained in the text.

Acknowledgements

The authors gratefully acknowledge D.E. Carlson and J. Dresner (RCA), H. Fritzsche and C.C. Tsai (Univ. of Chicago), R.W. Griffith (Brookhaven National Laboratory) and P. Reid (NRL) for supplying well characterized films of a-Si:H. This work was supported by the Department of Energy under contract No. DE-AI01-79ET23078. One of the authors (WEC) acknowledges support of the NAS/NRC Resident Research Associateship Program.

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