

Hydrogen-silicon nuclear spin correlations in α -Si:H: A two-dimensional NMR study

N. Zumbulyadis

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

(Received 21 October 1985)

The two-dimensional Fourier-transform technique described in this report demonstrates that there is a strong dipolar coupling between the protons that give rise to the narrow line and neighboring ^{29}Si nuclei. Other applications of the technique in understanding the structure of amorphous semiconductors are discussed.

The ^1H and ^{29}Si solid-state NMR spectra of amorphous hydrogenated silicon, α -Si:H, have been the subject of intensive research in recent years.¹⁻⁵ The interpretation of the composite line shape in the proton spectrum and its variation with deposition conditions is of particular interest since hydrogen plays a crucial role in determining device properties. The proton spectrum consists of the superposition of a "broad" (25 kHz) and a "narrow" (3.0–4.5 kHz) component, the latter commonly attributed to isolated monohydride (Si-H) groups experiencing only weak homonuclear dipolar broadening. Recently, Lamotte⁶ has suggested that gaseous molecular hydrogen trapped in microvoids might also account for the narrow component of the NMR signal. This alternative interpretation has met with some criticism.⁷ More recently, additional NMR evidence was presented in support of the view that gaseous hydrogen contributes a negligible fraction of the narrow line for unannealed samples.⁸ In this Brief Report we present a two-dimensional (2D) Fourier-transform (FT) NMR method which supports the conclusions in Ref. 8. We demonstrate that for at least one typical sample of α -Si:H the narrow component originates with hydrogen bonded to silicon in the lattice and dipolarly coupled to adjacent silicon(s). The method we describe can be used as a diagnostic tool for the mode of hydrogen binding in α -Si:H and its alloys. Furthermore, it does not require experiments at cryogenic temperatures.

The 2D solid-state NMR technique described below involves cross polarization and magic-angle spinning (CP-MAS) and is similar in some respects to the heteronuclear chemical shift correlation spectroscopy of Caravatti, Bodenhausen, Ernst, and Braunschweiler.^{9,10} The pulse sequence is shown in Fig. 1. A variable delay is inserted

between the proton 90° pulse and the polarization transfer step to ^{29}Si . Successive increments of this delay define the t_1 time domain. The ^{29}Si free induction decay (FID) defines as usual the t_2 domain. Fourier transformation along t_2 yields the ordinary ^{29}Si CP-MAS spectrum. If the spinning frequency is less than the proton homonuclear dipolar coupling, a Fourier transform along t_1 yields the broad-line NMR spectrum of the proton pool from which cross polarization to ^{29}Si occurs.

Thirty-two data blocks were acquired, and the transposed FID was zero filled to 256 points prior to the second Fourier transform. The imaginary part of the transposed FID was set to zero, to symmetrize the spectra. Symmetrization leads to a phased spectrum without the line-shape distortions inherent in the absolute-value representation characteristic of other 2D experiments. This procedure is allowed, since the proton spectra of solids have typically vanishing odd moments. The α -Si:H sample used in this study was prepared on an aluminum substrate in a hot-wall, rf (13.56 MHz) plasma-enhanced chemical vapor deposition system. The material was device quality with a Fermi-level density of states of about $5.4 \times 10^{15} \text{ cm}^{-3}$ and contained ~ 11 at.% H. The film was removed from the aluminum substrate by thermally shocking the substrate with dry ice. ^1H and ^{29}Si spectra were obtained at 200.00 and 39.74 MHz, respectively, on a multinuclear solid-state NMR system described elsewhere.¹¹

The 200-MHz ^1H NMR spectrum of the sample is shown in Fig. 2. It consists of two components of roughly equal

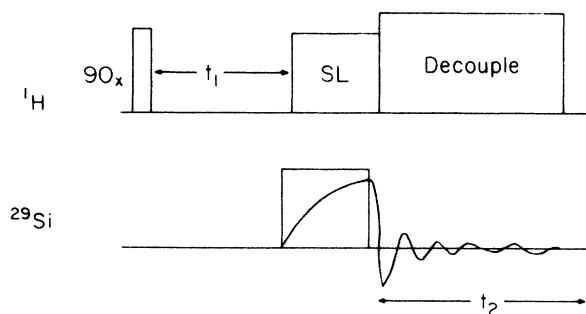


FIG. 1. Pulse sequence used for the two-dimensional NMR experiment. Experimental parameters: proton 90° pulse width 4.5 μsec ; t_1 increment, 10 μsec ; spin locking (SL) and cross polarization time, 10 msec.

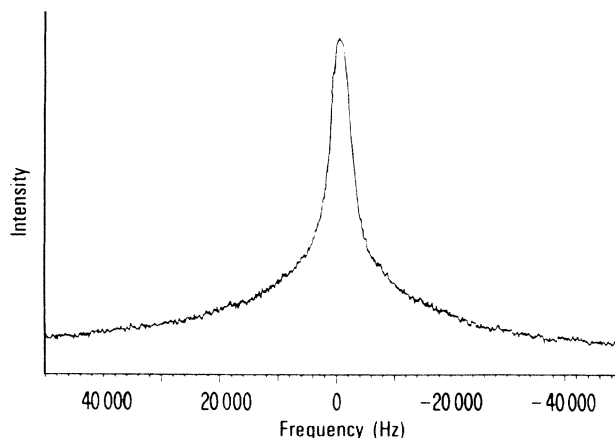


FIG. 2. ^1H NMR spectrum of the sample used in this study; average of 1000 transients.

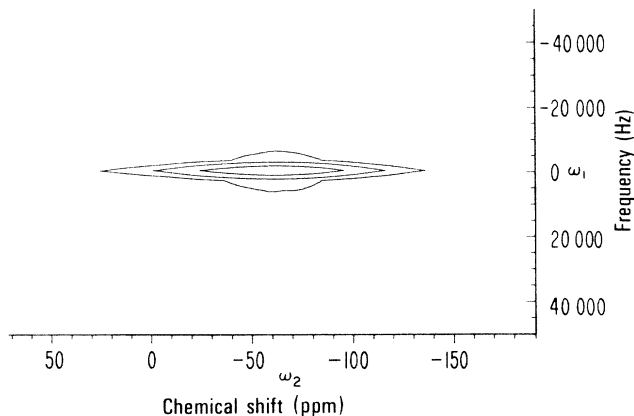


FIG. 3. Contour plot of the 2D spectrum; each data block is the average of 248 transients; the ω_2 frequency scale is in ppm relative to tetramethylsilane.

intensity with linewidths of 22.8 and 4.6 kHz. The corresponding 2D spectra are shown in Figs. 3 and 4. The contour plot representation (Fig. 3) gives an indication of the composite line shape along the ω_1 dimension. Figure 4 shows a cross section through the middle of the spectrum, parallel to the ω_1 dimension. This spectrum can be regarded as a proton spectrum obtained indirectly by monitoring the ^{29}Si FID. The spectrum of Fig. 4 agrees remarkably well with that of Fig. 2 in terms of line shape, linewidths, and relative proportions of the two components.

The agreement between the proton spectra obtained directly and indirectly has several implications concerning the nature of the narrow line. First, it demonstrates that both proton pools are coupled to ^{29}Si through dipolar interactions, since both pools contribute to proton-silicon cross polarization. Second, the proton-silicon dipolar coupling must be comparable in both pools. Otherwise the relative proportions of the broad and narrow components would be different in the directly and indirectly obtained spectra. Entrapped hydrogen gas in the extreme narrowing limit would have no static dipolar coupling to silicon and could

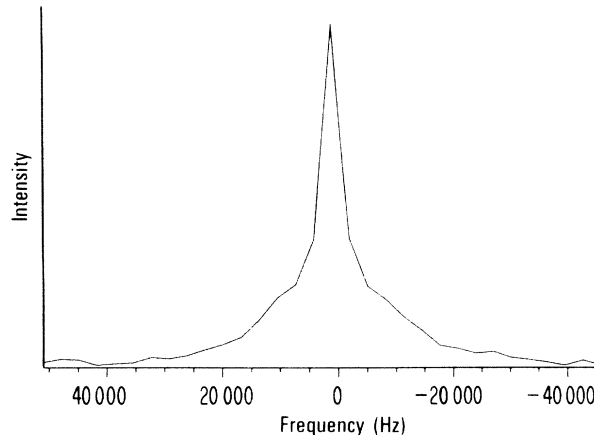


FIG. 4. Cross section parallel to the ω_1 dimension showing the indirectly obtained proton broad-line spectrum.

not function as a magnetization reservoir for cross polarization. Finally, the fidelity of the reproduction of the proton spectrum by indirect detection is evidence for the spatial separation of clustered and dilute monohydride groups with little spin diffusion in the proton rotating frame during the duration of the cross polarization, i.e., 10 msec. More detailed studies of proton-spin diffusion are in progress using Goldman-Shen-type pulse sequences.

A more general application of the experiment described here would be in the characterization of amorphous semiconductor alloys such as $\alpha\text{-Si}_x\text{Ge}_{1-x}\text{:H}$ and $\alpha\text{-Si}_x\text{C}_{1-x}\text{:H}$. The 1D proton spectrum displays a two-component line shape. A $^{29}\text{Si}\text{-}^1\text{H}$ 2D spectrum could resolve the fraction of broad and narrow components associated with Si. In the case of $\alpha\text{-Si}_x\text{C}_{1-x}\text{:H}$, analogous $^{13}\text{C}\text{-}^1\text{H}$ 2D experiments could further help characterize the distribution of protons associated with carbon. Combined $^{29}\text{Si}\text{-}^1\text{H}$ and $^{13}\text{C}\text{-}^1\text{H}$ 2D experiments are currently underway in our laboratory.

I thank Mr. T. Barge and the late Dr. L. C. Isett for the sample and many stimulating discussions.

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