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^{29}Si NMR spectra for reactively sputtered amorphous silicon

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High-resolution nuclear magnetic resonance using magic-angle spinning has been applied to reactively sputtered amorphous Si-H. The line broadening expected from dispersion in the paramagnetic shielding due to charge-density variations is calculated and compared to experiment. A substantial upfield shift from amorphous Si-H produced by glow discharge is noted.

At present there is great interest in determining the local environment of hydrogen bonded in amorphous Si-H (*a*-Si-H). Infrared studies in the past have grouped bonding structure into two classes: SiH and SiH_2 configurations.[1,2] These classifications helped explain the differences between material produced by glow discharge and reactive sputtering when all reactively sputtered samples contained some SiH_2. It has now been shown that reactive sputtering can produce films with only SiH bonding which still have characteristics different from exclusively SiH films prepared by glow discharge.[3] Detailed infrared work also has shown that oscillator strengths for vibrational modes vary between samples, showing variations in the local fields of SiH configurations.[4] Reimer *et al.*[5] have suggested, based on proton nuclear magnetic resonance (NMR) results, that there is clustering of SiH in glow-discharge-produced *a*-Si-H. Observed differences might be caused by variations in this clustering. Variations similar to the columnar structure shown to exist by Knights[6] in films containing SiH_2 might also occur. A better understanding of these possible differences must be gained in order to improve control over the film characteristics.

Narrow line ^{29}Si NMR using magic-angle spinning was recently applied to glow-discharge-produced samples in hopes of obtaining information on local bonding configurations.[7] The intention was to identify local chemical environments by shielding. The observed linewidth, however, was broadened to the point where small differences in shifts were not distinguishable. Only generalizations about the presence of SiH and SiH_2 were possible.

We report the first application of the narrow line NMR method to reactively sputtered *a*-Si-H. One of the purposes is to identify differences between reactively sputtered and glow-discharge-produced material. A sizable chemical shift between the two material types is observed. In addition, a calculation of broadening due to variations in diamagnetic shielding is presented. The calculation is based on the charge-density variations derived from a recent model by Guttman, Ching, and Rath.[8]

Samples for this study were prepared by rf reactive sputtering of Si in an Ar-H atmosphere. Details of the preparation system are given elsewhere.[9] The substrates were Al foil bonded to a Pyrex plate. After deposition the foil was peeled off the plate and the Al was dissolved in dilute HCl. The resultant flakes of *a*-Si-H were filtered, washed in distilled H_2O, and dried at 120 °C. Deposition conditions for one sample were: partial pressure (pp) of $Ar = 30$ mTorr, pp of $H_2 = 3$ mTorr, rf power = 570 W, target voltage = 2 kV, substrate–target separation = 2.5 cm. Conditions for a second sample were: pp of $Ar = 60$ mTorr, pp of $H_2 = 3$ mTorr, rf power = 350 W, target voltage = 1.4 kV, substrate–target separation = 5 cm. In both cases the substrates were grounded and were not externally heated. Infrared measurements on similarly produced samples showed no SiH_2 present in sample 1 while 70% of the H in sample 2 was in the SiH_2 configuration.

The NMR spectrometer used in these measurements has been previously described.[10,11] Resonance frequencies were 56.03 MHz for ^{1}H and 11.13 MHz for ^{29}Si. The Hartman-Hahn condition[12] ~~for~~ ~~cross~~ for cross polarization was matched with rotating-frame fields: H_1 (proton) = 8 G and H_1 (^{29}Si) = 40 G with 8-G proton irradiation also used for decoupling. The contact time for cross polarization was 4 msec with the rotation rate for the magic-angle spinning being 2 kHz. The data for each sample were the accumulation of 8000 scans.

Figure 1 shows the ^{29}Si Fourier transform for two samples of reactively sputtered *a*-Si. The solid curve is for the exclusively SiH-bonded sample 1 while the dashed curve is for sample 2 containing both SiH and SiH_2. Full width at half maximum for samples 1 and

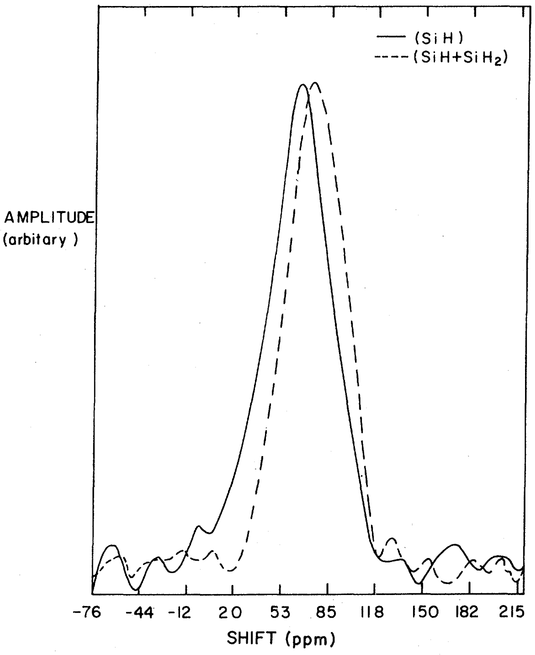

FIG. 1. Narrow line ^{29}Si NMR spectra for a pure SiH and a mixed phase ($SiH+SiH_2$) sample of amorphous Si-H.

2 are 52 and 50 ppm, respectively. This broadening is slightly larger than that for the glow-discharge samples. In determining the first moments, the base lines were first carefully corrected to eliminate any zero-order or first-order terms. Such artifacts have been shown to cause uncertainties of up to ± 10 ppm at the resolution levels employed in these experiments. The free-induction decay of both samples has been multiplied by a Gaussian exponential before being transformed. This procedure increases the signal-to-noise ratio to improve the first-moment calculation, but also broadens the line by about 4 ppm. The first moment of the SiH sample is shifted 62 ± 5 ppm upfield from tetramethyl silane (TMS) while that of the mixed-phase sample is shifted slightly farther to 75 ± 5 ppm. This is significantly greater than the 41- and 50-ppm shifts reported on glow-discharge-produced samples.[7]

In the absence of the broadening, one would expect a series of peaks showing chemical shifts due to shielding changes in different bonding configurations. The relative shift between the SiH and SiH_2 bonding configurations should be in the range of 15 ppm based on the shifts in liquid NMR of Ph_3SiH and Ph_2SiH_2.[13] Shifts due to substitutions of H for Si in the next-nearest-neighbor positions would be still smaller. The broadening clearly makes such shifts difficult or impossible to identify. The broadening is also too large to be explained by a distribution of bonding configurations.

The model of Guttman, Ching, and Rath[8] shows a considerable charge transfer in *a*-Si due to disorder. Their calculations show a rms deviation of 0.2 electron units from neutral on the Si atoms of the amorphous network. The diamagnetic shielding of the nucleus of an isolated atom due to the atom's electrons is given by [14] $\Delta B = (0.319 \times 10^{-4} Z^{4/3}) B_{\text{ext}}$ where Z is the number of electrons and B_{ext} is the applied field. By substituting the electron number (14) modified by the charge distribution calculated by Guttman *et al.* for Z, one gets a histrogram of the expected distribution of diamagnetic shifts. This has been calculated and is shown in Fig. 2. The result is a line broadening just slightly less than that experimentally observed broadening in Fig. 1.

With present understanding and data, the explanation of the upfield shift of the reactively sputtered samples relative to the glow-discharge samples is not clear. Electron-spin-resonance measurements have shown glow-discharge material to have few spins, eliminating the possibility of a paramagnetic shift from free radicals. It is also apparent that the whole peak is shifted without much change in distribution, showing that the change is uniform throughout the bulk and not due to local variations. One possible explanation would be a varied paramagnetic shift due to conduction electrons. As this effect is proportional to the square of the extended wave-function intensity at the nucleus, variations in the integrity of the wave function could cause a shift. If this were the case, however, one might expect shifts between the material containing SiH and SiH_2.

In summary, narrow line NMR data have been presented for reactively sputtered *a*-Si which shows

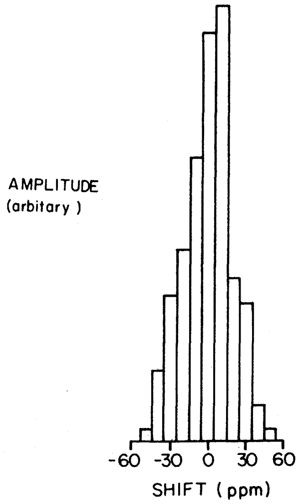

FIG. 2. Histogram showing dispersion in the paramagnetic shift calculated using the charge-density variation of Guttman *et al.* (Ref. 8).

considerable broadening and a upfield shift from glow-discharge-produced *a*-Si. It has been shown that the broadening can be explained by variations in diamagnetic shielding due to charge transfer in the distorted *a*-Si network. The upfield shift is intriguing, but will require more work to be adequately explained.

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