PHYSICAL REVIEW B VOLUME 41, NUMBER 13 1 MAY 1990

Magic-angle spinning ^{29}Si NMR study of short-range order in *a*-Si

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(Received 11 January 1990)

The magic-angle spinning ^{29}Si nuclear magnetic resonance (NMR) of annealed rf-sputter-deposited amorphous silicon was measured as a function of annealing temperature up to crystallization. The NMR peak width is observed to narrow significantly with little change in peak position. A comparison with Raman-scattering and neutron-diffraction results indicates that the distribution of NMR chemical shifts is modified by variations of the electronic density of states with bond-angle distribution.

It is well established that short-range order (SRO) influences the physical properties of noncrystalline systems.[1-5] Variations in the SRO of tetrahedral amorphous semiconductors such as *a*-Si and *a*-Ge with formation conditions indicate, for example, strong evidence for changes in the vibrational properties.[3,6-9] Inelastic neutron scattering[7-10] and detailed Raman-scattering[9] measurements have established that changes in the bond-angle distribution are primarily responsible for variations in the phonon density of states. There is also considerable evidence linking SRO to the electronic properties.[11] Since the transverse-optic (TO) bandwidth Δ_{TO} has been shown to be linearly related to the bond-angle distribution width $\Delta\theta$,[3,8,9] correlations observed between the optical gap E_g and Δ_{TO} suggest sensitivity of the electronic density of states to $\Delta\theta$. This is also supported by theoretical calculations of valence-band-tail variations with bond-angle distributions.[12]

An additional means of studying the role of SRO on the electronic states of noncrystalline solids is through nuclear magnetic resonance (NMR).[13] Solid-state magic-angle spinning (MAS) NMR,[14,15] in which dipolar and anisotropic chemical shift interactions weaker than the spinning frequency are eliminated, is very sensitive to the local environment. In particular, the distribution of isotropic chemical shifts is expected to provide a measure of the distribution of ground- and excited-state wave functions. As the conduction-band edge states are believed to undergo minor changes with annealing or hydrogen alloying relative to the valence-band edge states,[16] the MAS NMR width changes are an indication of variations in the valence-band edge states. This paper describes such MAS NMR measurements on *a*-Si samples in which the SRO was continuously varied by isochronal annealing from an initially highly disordered amorphous state. Correlations observed between the width of the NMR line and the radial distribution function (RDF) and Raman-scattering measurements of the SRO provide strong evidence for the role of changing (mostly valence) electronic states with annealing. While selected solid-state NMR studies of noncrystalline solids have been employed to study local order,[15] this work represents the first direct correlation between NMR spectra and independent structural and vibrational probes of SRO. Thus, the linewidth is apparently dominated by the distribution of isotropic chemical shifts due to the distribution of bond angles. The correlation between the evolution of this linewidth and that of the TO Raman mode following similar annealing procedures of the same samples demonstrates the applicability of MAS NMR to the study of SRO, quantified by the bond-angle distribution width, in distorted tetrahedral networks. In addition, it provides important input to check the validity of simulations of band-edge electronic states in such systems.

The behavior of the ^{29}Si MAS NMR line center in *a*-Si is unrelated to the paramagnetic centers but significantly shifted from the value in *c*-Si. The observation of comparable shifts in various silicates[17] suggests that it is partially due to intermediate-range-order (IRO) effects. As the electronic wave function at the Si nucleus is obviously different in the two phases (the amorphous phase contains a very considerable density of localized tail states), this also is likely to contribute to the MAS NMR shift.

Two samples were prepared by Ar rf-diode-sputtering deposition from a Si target onto nominally unheated substrates. The effective temperature during deposition was estimated to be $\sim 125\,^{\circ}\mathrm{C}$.[18] The samples contained ~ 0.2 at.% H, as determined from secondary-ion-mass spectrometry (SIMS) measurements on some of the samples. This small residual content is expected to have little effect on either the Raman or the MAS NMR results. The oxygen content was also determined to be negligible, i.e., not above the background levels in the SIMS system. The samples were isochronally annealed for 1 h in evacuated sealed quartz tubes at 30 °C steps at $400 \leq T \leq 640\,^{\circ}\mathrm{C}$, and cooled to room temperature (RT) within 10 min following each annealing step. RT x-ray diffraction and electron spin resonance (ESR) spectra were obtained following each annealing step. RT ^{29}Si MAS NMR spectra were obtained from a homebuilt superconducting solenoid spectrometer operating at 43.72 MHz (51.69 kG for ^{29}Si). The MAS frequency was 5.0–5.2 kHz, and the 90° pulse repeat time was longer than $5T_1$, where T_1 is the ^{29}Si spin-lattice relaxation time. Additional details of the

MAS NMR procedure may be found elsewhere.[19,20]

The MAS NMR spectra, plotted vs ppm from the ^{29}Si resonance frequency in tetramethylsilane (TMS), are shown in Fig. 1. Although the changes in the spectra from 460 to 550 °C are not obvious from this figure, the full width at half maximum, $\Delta\omega_{1/2}$, does decrease from 81 ppm in the unannealed sample to 73.3 ppm following annealing at 460 °C to 67.6 ppm after annealing at 580 °C. The peak due to crystalline Si (*c*-Si) domains at -79.9 ppm from TMS, observable as a weak shoulder following annealing at 580 °C, is very clear after annealing at 610 °C, and the *a*-Si phase is no longer detectable after annealing at 640 °C. The x-ray-diffraction spectra were consistent with the MAS NMR.

The *c*-Si peak at -79.9 ppm seen following recrystallization after annealing at 640 °C is 5.7 ppm wide. While this width is far smaller than the widths of the *a*-Si phase, it is still far larger than the established value of 0.3 ppm in *c*-Si.[19,20] This indicates considerable residual disorder in the *c*-Si phase obtained in this manner. Indeed, the dangling-bond ESR spin density N_{DB}, measured relative to the unannealed value N_{DB0}, yielded $N_{\mathrm{DB}}/N_{\mathrm{DB0}} \sim 0.1$ following this annealing, far greater than in single-crystal Si or even *a*-Si:H.

$\Delta\omega_{1/2}$ and the line-center position of the *a*-Si resonance relative to TMS, $\Delta\omega_0$, are plotted versus annealing temperature in Fig. 2. As clearly seen, $\Delta\omega_0$ only changes from -38.3 ppm in the unannealed sample to -42.9 ppm following annealing at 580 °C, and then drops to the crystalline value of -79.9 ppm after annealing at 640 °C. On the other hand, the dangling-bond spin density N_{DB} at $g = 2.0055$, between 10^{19} and 10^{20} cm^{-3} in the unan-

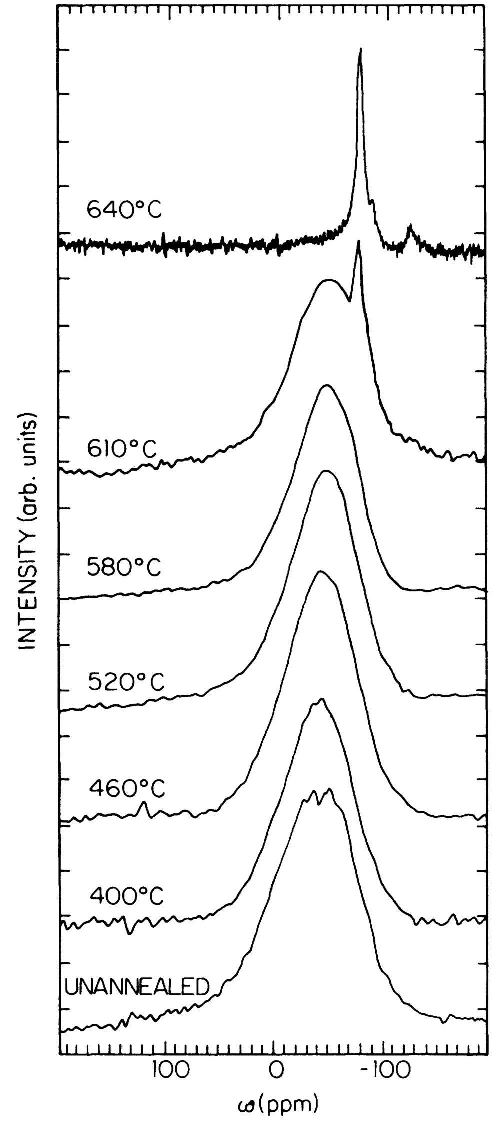

FIG. 1. ^{29}Si MAS NMR spectra of *a*-Si isochronally annealed for 1 h at the denoted temperatures, plotted vs the frequency relative to the ^{29}Si resonance frequency in TMS, in a magnetic field of $H_0 = 51.69$ kG. Note the shoulder at ~ -80 ppm following annealing at 580 °C, due to the formation of some *c*-Si domains, the emergence of a clear peak at this frequency following annealing at 610 °C, and the disappearance of the *a*-Si peak following annealing at 640 °C. Note also the considerable width of the *c*-Si line (~ 5.7 ppm) as compared to that of single-crystal Si (0.3 ppm) (Ref. 19).

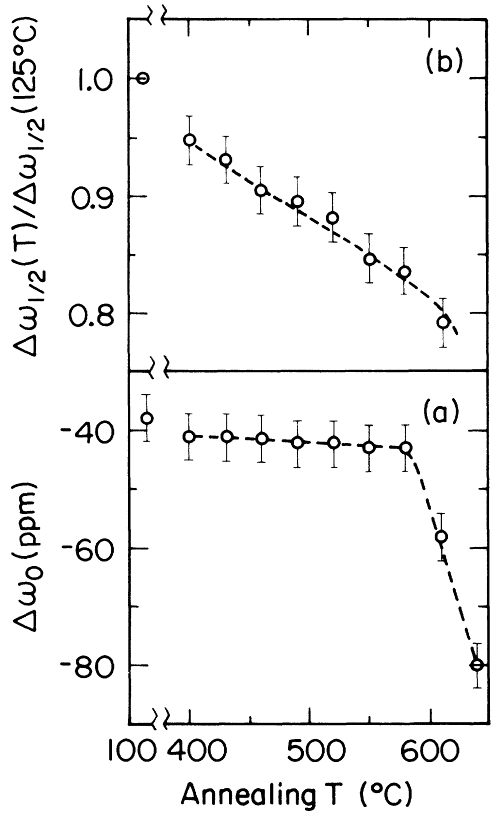

FIG. 2. (a) The position of the center of the line of the ^{29}Si MAS NMR in *a*-Si relative to TMS, as a function of annealing temperature. (b) The full width at half maximum, normalized to the value in the unannealed state, as a function of annealing temperature. The value shown following annealing at 610 °C is that of the amorphous phase. Note the break between the effective temperature during deposition, ~ 125 °C, and the first annealing temperature at 400 °C.

nealed sample, decreases to ~0.4 of its pristine value N_{DB0} after annealing at 400 °C, and decreases by another factor of ~2, to ~$0.2N_{\mathrm{DB0}}$, after annealing at 610 °C. This indicates that $\Delta\omega_0$ is not due to the paramagnetic centers. Previous MAS NMR measurements on rf-sputter-deposited hydrogenated (*a*-Si:H) containing 10 at.% H, and far fewer paramagnetic dangling bonds ($\leq 10^{17}$ cm^{-3}) also support this conclusion:[21] While $\Delta\omega_0 = -62 \pm 5$ ppm in that sample is indeed closer to that of *c*-Si, it should have been essentially equal to the *c*-Si value had $\Delta\omega_0$ been dominated by the paramagnetic susceptibility. Even more significant is the value of $\Delta\omega_0$ in samples deposited by glow discharge decomposition of silane, which is -40 to -50 ppm,[22] i.e., very close to the present values in spite of the far lower dangling-bond spin density. Since the value of $\Delta\omega_0$ is not due to the dangling-bond spins, it therefore reflects an average value of the isotropic chemical shift which is different from the crystalline phase.

Recent studies have indicated that the average bond angle is 108.5 ± 0.1° in *a*-Si, as compared to 109.5° in *c*-Si.[9] Yet this difference should only change $\Delta\omega_0$ by a few ppm, since a bond-angle distribution width of 10–11° is required to broaden $\Delta\omega_{1/2}$ from 0.3 ppm in *c*-Si (Ref. 20) to 67–81 ppm, respectively, in *a*-Si (see above and below). Thus, the differences between the wave function at the Si nucleus in *a*-Si and *c*-Si are considerably more significant than a 1° change in the bond angle. The nature of these differences is not known at present. In general, changes in the electronic states may arise from localization due to the large density of localized occupied valence-band tail states, which are far fewer in *c*-Si. NMR studies of silicates indicate that changes in IRO due to dihedral bond-angle distribution and ring statistics[17,20] relative to *c*-Si may also contribute. In any case, the present result is even more dramatic when compared to the shift in $\Delta\omega_0$ in rf-sputter-deposited *a*-Si:H containing 10 and 20 at.% H, since alloying with H and the disorder in that system only yield a difference of 18 ppm relative to *c*-Si.[21]

The value of $\Delta\omega_{1/2}$ decreases from 81 ppm in the unannealed sample, to 67 ppm following annealing at 610 °C, a change of 20%. The density N_{DB} of unpaired electron spins in the unannealed sample lies between 10^{19}–10^{20} cm^{-3}, and decreases by a factor of 4 upon annealing. The linewidth of hydrogenated *a*-Si, where $N_{\mathrm{DB}} < 10^{17}$ cm^{-3}, under the same condition of NMR line-narrowing measurements, is 50–52 ppm.[21,22] It thus appears unlikely that the dominant factor in the linewidth of the samples studied in this work is the presence of unpaired electron spins. Dipolar interactions and anisotropic chemical shifts, which are weaker than the spinning frequency, also do not contribute to $\Delta\omega_{1/2}$. We therefore conclude that $\Delta\omega_{1/2}$ is due to changes in the *a*-Si network local order with annealing. Radial distribution function (RDF) studies[23] of the as-deposited and 600 °C annealed states indicate both the absence of substantial intermediate-range order, as well as more importantly, of changes in longer-range correlations. The NMR widths changes shown in Figs. 1 and 2 are thus attributed to SRO variations with annealing. The RDF spectra also demonstrate that the form of the first-neighbor peak is essentially unchanged upon annealing.[24] This implies that the changes in $\Delta\omega_{1/2}$ are primarily associated with modifications of the bond-angle distribution width $\Delta\theta$ noted in RDF measurements and in Raman-scattering studies. This is consistent with electronic-state calculations which indicate that the valence-band states are modified by variations in $\Delta\theta$.[12]

The observed decrease of $\Delta\omega_{1/2}$ from 81 to 67 ppm is attributed to a narrowing of the initially broad distribution of isotropic chemical shifts. For the as-deposited and 580 °C sequentially annealed samples, RDF and Raman-scattering spectra provide information on bond-angle disorder. Gaussian fits to the reduced radial distribution function $T(r)$ yielded $\Delta\theta = 11°$ in the unannealed sample and 9.9° following annealing. Raman-scattering data indicate that the bond-angle width in the 580 °C sequentially annealed sample is also 9.9°. Thus the structural order in the as-deposited and 580 °C sequentially annealed NMR samples is known.

The MAS NMR linewidth $\Delta\omega_{1/2}$ is much smaller in *c*-Si than in *a*-Si. As the bond-angle width $\Delta\theta$ vanishes in *c*-Si, it is reasonable to assume a simple power-law relation between $\Delta\omega_{1/2}$ and $\Delta\theta$: $\Delta\omega_{1/2} = C(\Delta\theta)^{\beta}$. If this simple form is utilized for the as-deposited and 580 °C annealed samples, this yields $\beta \simeq 0.56$. This contrasts with the reduced Raman widths Δ_{TO} which are approximately linear in $\Delta\theta$. Additional RDF measurements are required to more accurately determine the relation of $\Delta\omega_{1/2}$ to $\Delta\theta$. The stronger dependence of Δ_{TO} on short-range order may be due to a greater sensitivity of the vibrational states to larger distortions than the electronic states to which $\Delta\omega_{1/2}$ is related. Theoretical analysis of the dependence of $\Delta\omega_{1/2}$ on bond-angle variations would clearly be valuable in this regard.

Previous MAS NMR studies on glow discharge and rf-sputter-deposited *a*-Si:H also qualitatively support the above relation between $\Delta\omega_{1/2}$ and $\Delta\theta$. The addition of H to *a*-Si is found to reduce Δ_{TO},[2] which from radial distribution function studies of *a*-Si (Ref. 9) suggest $\Delta\theta \simeq 9°$.[3,8] An extrapolation of the approximate relation noted above between the MAS NMR width and $\Delta\theta$ yields a linewidth that is approximately 9 ppm larger than that observed in *a*-Si:H. This lower value in the hydrogenated alloys could easily result from H-induced wave-function modifications. Indeed, x-ray photoemission spectroscopy measurements of Ley and co-workers[16] have shown that the valence-band edge changes significantly with hydrogen alloying due to wave-function modification.

In summary, we have described ^{29}Si MAS NMR studies of *a*-Si which establish, for the first time, an approximate quantitative relation between the short-range order in amorphous tetrahedral networks and the MAS NMR linewidths. These were manifest in a set of spectra obtained from *a*-Si samples isochronally annealed up to the crystallization temperature. The MAS NMR width changes are an indication of variations in (mostly) valence-band edge states with varying disorder. In addition, the shift of the peak of the line in the amorphous phase relative to crystalline (*c*-Si) spectrum is consistent with significant changes in the average intermediate-range order relative to *c*-Si, in addition to the effects of localized states on the isotropic chemical shift of the ^{29}Si nuclei.

We thank S. Mitra and J. Fortner for preparation of the samples, and Dr. Ulrich Sternberg of Freidrich-Schiller University, Jena, Democratic Republic of Germany, for useful discussions and comments on the theory of NMR chemical shifts. Ames Laboratory is operated by Iowa State University for the U.S. Department of Energy under Contract No. W-7405-Eng-82. The work at Penn State University was supported in part by National Science Foundation Grant No. DMR8602391.

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