

Radial distribution functions of amorphous silicon

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Substantial changes in the radial distribution function of amorphous Si films have been observed in neutron-diffraction studies. The spectra indicate changes in short-range order associated with an $\sim 11\%$ modification in the bond-angle distribution width. The results allow the first direct comparison of structural and vibrational Raman probes of variations in local order in thin-film amorphous solids. Good agreement is obtained between the measured bond-angle variation and that based on Raman estimates.

A basic constraint on structural models of noncrystalline systems and their calculated physical properties is an accurate description of the experimental radial distribution function (RDF). This is particularly important in amorphous semiconducting systems as the short-range order (SRO) sensitively influences the basic electronic and vibrational states.¹ In addition to structurally relaxed, conventional ball-and-stick models,^{2,3} recent first-principles, self-consistent electronic-state calculations⁴ have predicted models for amorphous (*a*-) Si. This system is of special current interest given the large property variations that may exist depending on conditions of formation for pure *a*-Si or its alloyed forms with hydrogen. Although extensive vibrational- and optical-property studies of *a*-Si have suggested changes in SRO, an accurate measure of such changes based on a direct radial-distribution-function analysis has not been performed to date. In this work we present RDF measurements on two diverse forms of *a*-Si films which more accurately determine changes in SRO than previously obtained for other noncrystalline systems. The results yield information on the range of bond-angle disorder that may be achieved in this system. A comparison with Raman scattering measurements in these same materials provides the first comparison of disorder parameters obtained from the "direct" diffraction method and an "indirect" vibrational probe. The results further allow estimates of structural order in other forms of *a*-Si, including its hydrogen alloys, that are not currently feasible by direct methods.

Accurate studies of changes in the structural order of amorphous semiconductors have been difficult to obtain and are confined to detailed studies of *a*-Ge films.⁵ Here x-ray-diffraction studies on two forms of *a*-Ge indicated small changes in the bond-angle distribution of $\sim 7\%$, as well as $\sim 2\%$ changes in the coordination number. The estimated errors in the RDF's made accurate estimates of SRO changes difficult. RDF studies in *a*-Si films, in contrast, have been confined to studies of very thin evaporated films ~ 100 Å thick. Annealing studies at 400°C which emphasized void effects, indicated very little change in the RDF.⁶ While it has been proposed that *a*-Ge and *a*-Si exhibit intermediate-range order (IRO) in their dihedral angle distributions, an analysis of RDF and modeling studies¹ in *a*-Ge suggest that variations in this distribution are small. The present results confirm this analysis

for *a*-Si films of variable SRO.

In order to emphasize variations in SRO, *a*-Si films of $\sim 30 \pm 10$ - μm thickness were prepared by rf sputtering at low Ar pressure (10 m Torr) and substrate temperature ($\sim 100^\circ\text{C}$). Neutron-diffraction measurements were performed on the SEPD instrument of the Argonne National Laboratory Intense Pulsed Neutron Source. The films were subsequently annealed at 600°C for 1 h and remeasured to determine changes in the RDF that result from structural relaxation processes that modify SRO. The structure factor $S(Q)$ was obtained by employing standard background and inelastic Placzek corrections.⁷ For the as-deposited sample, the presence of a small quantity ($\sim 0.3\%$) of hydrogen contributed a slowly varying incoherent background to the $S(Q)$ obtained from detectors at 15° , 30° , 60° , and 90° . Corrections for the angular dependence of the scattering, which result in $S(Q)$ oscillating about unity at high scattered wave vectors Q , were performed using cross sections for water.⁸ Values of Q up to 22 \AA^{-1} were employed to determine the function $F(Q) = Q[S(Q) - 1]$ whose Fourier transform yields $G(R)$. The latter is related to the RDF $J(r)$ by the equation $J(r) = rG(r) + 4\pi r^2 \rho_0$, where ρ_0 is the average density. Given the presence of voids in these films, the density was determined by the condition that the average value of $J(r) = 0$ at low r values. This yielded densities of $\sim 11\%$ and $\sim 4.5\%$ below that of crystalline (*c*-) Si for as-deposited and annealed samples, respectively. A Lorch termination function of the form $(\sin x)/x$, where $x = \pi Q/Q_{\text{max}}$ was employed to reduce noise in the RDF. Electron-spin-resonance measurements indicate similar paramagnetic spin concentrations of $\sim 10^{19}/\text{cm}^3$. Neutron-activation analysis found ~ 5 at.% Ar present in the as-deposited film associated with the sputtering process.

The structure factors for the as-deposited and annealed *a*-Si samples are shown together in Fig. 1. The spectra indicate substantial variations in $S(Q)$ with formation conditions. A comparison of the changes in $F(Q)$ relative to that of *a*-Ge studies of Tempkin, Paul, and Connell⁵ indicate approximately three times larger magnitude variations in the present data. The Fourier-transformed RDF spectra employing Lorch termination are shown in Fig. 2. For purposes of discussion it is useful to discuss the RDF in terms of three spatial ranges: (A) the first peak and the minimum region between the first two peaks, (B) the

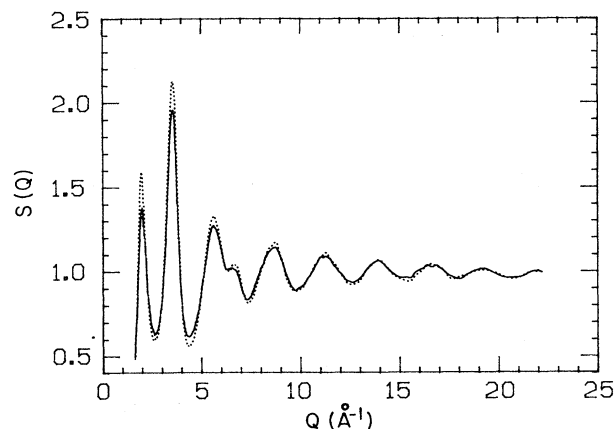


FIG. 1. Comparison of $S(Q)$ of a -Si as-deposited (solid) and annealed at 600° (dotted).

lower portion of the second peak, and (C) the region beyond the second peak. The major changes of interest occur in regions A and B corresponding to SRO variations. In region C, aside from increased density contribution in the annealed film, small differences are observed in the RDF. This indicates that were IRO present, its changes are small. As discussed below, the RDF spectra suggest that evidence for IRO is weak and as such, changes in regions A and B are of primary interest.

The form of the second RDF peak in region B indicates substantial changes in width that reflect SRO variations in the bond-angle distribution. The peak position indicates most probable values of $108.4^\circ \pm 0.2^\circ$ and $108.6^\circ \pm 0.2^\circ$ for the tetrahedral angle for as-deposited and annealed films, respectively, versus 109.5° in c -Si. An evaluation of the approximate width of the bond-angle distribution may be obtained from either a Gaussian fit to $J(r)$ or the function $T(r) = J(r)/r$. The resulting values contain thermal smearing due to phonons which may be subtracted utilizing the c -Si second peak width, assuming the independent static and thermal contributions add in quadrature. This yields static disorder widths of 9.9°

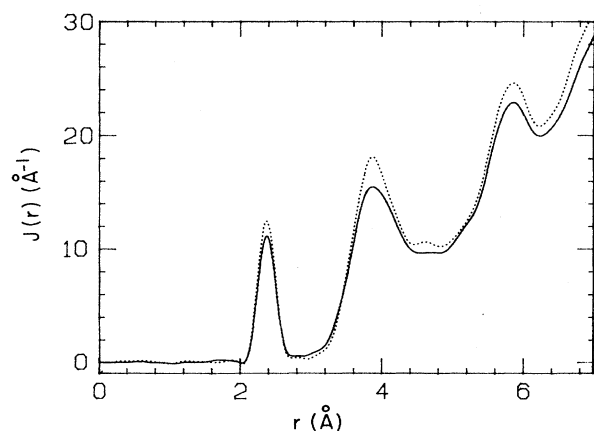


FIG. 2. Radial distribution functions of as-deposited (solid) and annealed (dotted) a -Si.

$\pm 0.3^\circ$ and $11.0^\circ \pm 0.3^\circ$ based on the Gaussian fits to $T(r)$ shown in Fig. 3.⁹ The $J(r)$ fit yields values that are 0.2° smaller. This change in bond-angle width of $\sim 11\%$ is substantially larger than that observed for sputtered a -Ge and is well outside experimental errors. These results thus clearly demonstrate unambiguously that SRO variations associated with bond-angle distribution widths occur in a -Si.

The first peak in the RDF's of Fig. 2 also indicates changes in SRO due to coordination number and rather small variations in the form of the nearest-neighbor distribution. Both forms of a -Si indicate a static disorder width of $\sim 1\%$ of the peak value. While the peak position is unchanged, very small changes of $\sim 0.1\%$ are observed in the width after correcting for thermal broadening. If the coordination number is estimated from the area of the first peak up to a minimum in $J(r)$ at ~ 2.73 Å, values of 3.55 and 3.90 atoms are obtained for as-deposited and annealed samples, respectively. Use of the $T(r)$ first-peak fit of Fig. 3 yields corresponding values of ~ 3.4 and 3.7 atoms. These smaller values are a consequence of non-Gaussian tails at larger r values. As Fig. 3 indicates, the region between the first and second peaks is not fit by a sum of Gaussians. The form of $J(r)$ also suggests that in

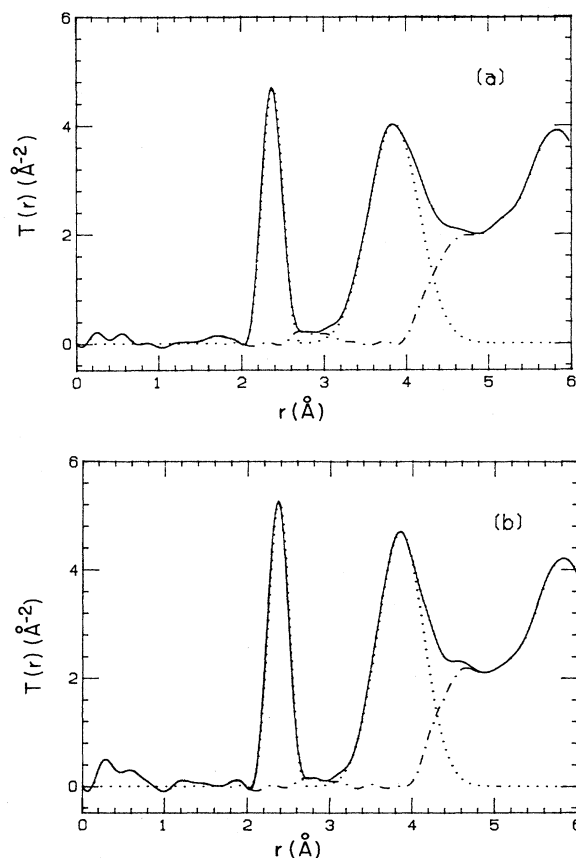


FIG. 3. Gaussian fits (dotted) of the first and lower half of the second peaks of the function $T(r) = J(r)/r$ (solid) for (a) as-deposited and (b) annealed samples of a -Si. The dot-dashed curve is the difference between total and fitted spectra.

the case of the as-deposited film additional atoms reside in this region. For the annealed film, the $J(r)$ intensity is reduced in this region indicating changes with ordering. Termination related noise in this sample make it difficult to determine the $J(r)$ intensity accurately. These results clearly indicate, as do earlier RDF studies of sputtered and evaporated a -Ge (Refs. 5 and 7) that coordination numbers that are substantially less than four are obtainable. For the as-deposited a -Si sample the increased number of atoms (~ 0.2 – 0.3) between the first two peaks imply that either longer threefold or fourfold bonded first neighbors, or second neighbors with highly distorted bond angles contribute to the RDF in this region; less probable are possibly higher bonded neighbors. In contrast, previous RDF studies of a -Ge with coordination numbers of 3.79 (low- T sputtered) and 3.68 (evaporated) indicate a small number of atoms in this region.^{5,7}

The RDF third peak occurs at 5.86 Å for both film formation conditions. Modeling studies of Tempkin for tetrahedral systems have suggested that the position of the third peak should be sensitive to the dihedral-angle distribution function¹⁰ and thus IRO. These results and those in a -Ge which indicate a constant peak position imply within this model little change in IRO associated with variations in the dihedral-angle distribution. It is useful to note that while small changes are observed beyond the second RDF peak, these are likely to have their origin in variations in SRO or in the density. The latter factor accounts for the displacement at high r of the spectra of Fig. 1. This SRO dependence is noted, for example, in relaxed random network models of Beeman.¹¹ In these models the SRO is modified by changes in the bond-angle distribution width for essentially fixed topology. The variations in the RDF's of these models of variable SRO and similar dihedral-angle distribution have a behavior comparable to that observed here. This indicates that changes in the RDF's of Fig. 2 at larger r do not require variations in IRO for their explanation. While it is possible that other models with different IRO might explain these results, the present models suggest that SRO variations are the logical origin for the observed behavior. The absence of substantial structure at ~ 4.7 Å in a -Si and in the corresponding a -Ge spectra⁷ also suggest that the dihedral-angle distribution is broad. Of importance here is that the *changes* in physical properties, such as Raman scattering, optical gap and heat of relaxation of a -Si and a -Ge are likely not to be significantly influenced by IRO, but rather are determined by SRO.

Modification of the bond-angle distribution width obtained from the RDF's imply structural relaxation effects in annealing of a -Si. These changes result in variations in the phonon density of states, its Raman scattering weight-

ed form, as well as other physical properties such as tails of the electronic density of states and enthalpy of relaxation.^{11,12} The origin of the observed variations in SRO are attributed to fluctuations in local bonding. In a -Si these fluctuations are primarily associated with higher-energy bonding p states as well as possible changes in sp^3 hybridization. Depolarized Raman scattering measurements of the high-frequency band yield reduced TO widths of 109 and 87 cm^{-1} for the as-deposited and annealed samples, respectively. These widths may be used to estimate the width of the bond-angle distribution using the theoretical variation of the depolarized spectra with the width of the bond-angle distribution. A set of relaxed Polk-Boudreaux models with variable SRO have been employed for these calculations.¹¹ This indirect estimate of the bond-angle width for the present samples yields values of 9.7° and 11.3° for as-deposited and annealed films, respectively. These results are in relatively good agreement with the values of 9.9° and 11.0° obtained from the $T(r)$ fits, given that the Raman-bond-angle width dependence is determined from fits of experimental to theoretical spectra. A comparison of the TO reduced Raman band width and the $T(r)$ derived bond-angle width allows, with the reasonable assumption of linearity, an estimate of the maximum and minimum order achievable in a -Si. As reduced depolarized Raman widths vary between 78–119 cm^{-1} , this implies a range of $\Delta\theta$ of 9.4°–11.0° between the most and least ordered materials that have been studied in our laboratory. With the addition of H to a -Si the alloy Raman spectra indicate an $\sim 5\%$ narrowing of the Raman width relative to maximally ordered chemical-vapor deposited a -Si with little or no H. This indicates that the minimum $\Delta\theta$ in these alloys is $\sim 9.25^\circ$. The result for a -Si is near to the 9.3° value estimated for maximally ordered pure a -Ge, based on Raman, RDF, and optical gap spectra.¹³

In summary, the present RDF measurements in a -Si provide basic information needed for structural models of this important material. Changes in the SRO, as suggested to a lesser extent in earlier a -Ge studies, are clearly indicated to be substantial. Variations in bond-angle disorder based on diffraction measurements in two forms of different order allow both a comparison with vibrational Raman studies, as well as establish a more accurate scale for quantifying the range of local order in this system.

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