

High Resolution Radial Distribution Function of Pure Amorphous Silicon

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The structure factor $S(Q)$ of high purity amorphous Si membranes prepared by ion implantation was measured over an extended Q range (0.03–55 Å⁻¹). Calculation of the first neighbor shell coordination (C_1) as a function of maximum Q indicates that measurement of $S(Q)$ out to at least 40 Å⁻¹ is required to reliably determine the radial distribution function (RDF). A 2% change in C_1 and subtle changes in the rest of the RDF were observed upon annealing, consistent with point defect removal. After annealing at 600 °C, $C_1 = 3.88$, which would explain why amorphous Si is less dense than crystalline Si. [S0031-9007(99)09040-7]

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The atomic structure of pure amorphous silicon (a -Si) is believed to be that of a roughly fourfold coordinated continuous random network [1–3], where the local order is similar to that of crystalline silicon (c -Si). Because of the isotropic nature of amorphous materials, the most that can be determined from a diffraction measurement is the radial distribution function (RDF) which contains only one-dimensional information. In order to discern the three-dimensional atomic structure, one must construct models and compare them with experiment. Successful agreement with experiment is therefore extremely difficult to achieve, even when other data such as density and the vibrational spectrum are considered. Hence, radial distribution functions with the highest spatial resolution are needed. The study of a a -Si is of particular interest because it is the canonical system for the study of all covalently bonded amorphous materials and has long served as a test material for comparing theoretical and model calculations involving the role of order and disorder in continuous random networks. In spite of all the work that has been done to date, many aspects of the structure of a -Si are not well understood. For example, it is still not clear why a -Si is 1.7% less dense than c -Si [4].

Currently, there are two main reasons for the lack of reliable RDF's of a -Si. First, most earlier experiments were done using amorphous Si or Ge produced by deposition techniques such as vacuum evaporation or sputtering [5–10]. Both methods can be optimized to yield a -Si layers of sufficient thickness for x-ray diffraction measurements. But such samples usually suffer from large numbers of voids or impurities in the films [8,11], resulting in a majority of the Si atoms actually having an impurity or void as one of its "neighbors." These problems can be overcome if the a -Si is prepared by self-ion implantation of c -Si, which has been shown to reproducibly yield high purity, dense a -Si without any detectable voids [12]. The second reason for the lack of reliable RDF's is that ex-

periments that were carried out on high quality samples do not extend out to sufficiently high Q ($= 4\pi\lambda^{-1}\sin\theta$). The spatial resolution of the RDF is inversely proportional to the Q range (extent in reciprocal space) of the experimental data. For example, a resolution of 0.1 Å would require data out to 30 Å⁻¹, yet few experiments have explored the range beyond 25 Å⁻¹. In addition, there is the related problem that the atomic scattering factor for silicon is not well determined beyond 20 Å⁻¹. An RDF from a measurement over a restricted Q range typically shows severe termination ripples. Such ripples can be reduced by applying damping functions to the data; however, these treatments severely degrade the resolution of the RDF.

In order to overcome these difficulties and obtain a more reliable RDF, two a -Si membranes suitable for x-ray diffraction experiments were prepared and their chemical purity verified [13] by ion implantation of silicon ions into c -Si substrates at 77 K. Thirteen different ion energies were used, varying from 0.5 to 27 MeV, with doses ranging from 5×10^{15} to 9×10^{15} cm⁻². A 5 mm diameter area on the backside of the sample was exposed to a wet chemical etch (20% KOH at 80 °C) in order to remove the crystalline substrate. No etch stop was used other than a -Si itself. This procedure resulted in pure edge-supported a -Si membranes of 10 and 11 μm thickness. One of the two samples was annealed (before the wet etch) under vacuum at a temperature of 600 °C for 1 hour, in order to induce structural relaxation. Both membranes were slightly buckled.

X-ray diffraction measurements were carried out using a Huber six-circle diffractometer at the Cornell High Energy Synchrotron Source (CHESS) A2-wiggler beam line. In order to cover an extended region in Q space from 0.5 to 55 Å⁻¹ at equidistant ΔQ of 0.025 Å⁻¹, four x-ray energies (13, 21, 43, and 60 keV) were used in either transmission, for the low- Q region from 0.5 to 6 Å⁻¹, or reflection geometry. Angular scans at the different

energies were chosen in such a way as to have significant overlap between scans in reciprocal space. Multiple scans were recorded in order to average out artifacts associated with the stability of the source. A displacive cryostat was mounted on the diffractometer to cool the samples to 10 K so as to minimize thermal effects on the diffraction pattern as well as air scattering. The absorption coefficient of Si was measured for each x-ray energy. A *c*-Si powder sample was also measured and analyzed under the same conditions, but only in the range from 1.5 to 35 \AA^{-1} .

The Compton incoherent scattering could be resolved from the elastic coherent scattering, except for the lowest Q region, by fitting the energy spectrum of the scattered beam using theoretical Compton profiles. The method we developed to extract the coherent scattering is described elsewhere [14]. The extracted elastic scattering intensity $I(Q)$ underwent a series of corrections for dead time, background, absorption, polarization, and the detector efficiency factor. No multiple scattering correction was required for such thin samples. The agreement among different scans in the overlapping Q regions was good to within 1%. We used an iterative procedure to extend the atomic scattering factor for Si, f , to 55 \AA^{-1} . Details of this procedure and the complete data analysis will be published elsewhere [15]. Once f was known, the elastic scattering intensities were normalized to electron units (I_{eu}) [16]. Results from earlier small-angle x-ray scattering (SAXS) measurements [12] were added to the actual data to achieve a total Q range from 0.03 to 55 \AA^{-1} .

The structure factor $S(Q)$ ($= I_{\text{eu}}/f^2$) was then determined for both annealed and as-implanted *a*-Si as shown in Fig. 1. The inset shows the corresponding interference function ($F(Q) = Q[S(Q) - 1]$). Oscillations in the structure factors persist far into Q space (up to 40 \AA^{-1}); beyond this value, statistical noise drowns out the damped oscillations. A small difference can be seen between the

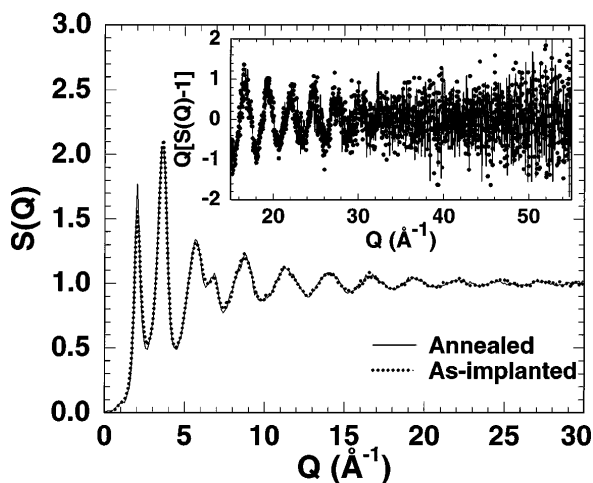


FIG. 1. The structure factor $S(Q)$ of as-implanted (\cdots) and annealed ($—$) *a*-Si. The inset plot represents the corresponding interference functions $F(Q)$ of the two samples in the high- Q region.

two structure factors, indicative of a change in the structure during the annealing process. The Fourier transform of the structure factor $S(Q)$ yields the RDF $J(r)$ with

$$J(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ. \quad (1)$$

Our data may extend to 55 \AA^{-1} , but that is still not the infinite value required for a proper Fourier transform. In order to avoid interference effects caused by statistical noise in the last data point, we used only interference functions which terminate with a value of 0 at the upper integration limit. In other words, we calculated the RDF only for r values which satisfy

$$r = n \frac{\pi}{Q_{\text{max}}} \quad \text{or} \quad r = (2n + 1) \frac{2\pi}{Q_{\text{max}}}$$

where $n = 1, 2, 3, \dots$

This is known as the sampling method [17]. The resulting RDF of annealed *a*-Si is shown in Fig. 2. Every point in the graph is the result of an unbiased Fourier transform of the $S(Q)$ data; no damping function was used. The number of points is limited because of the restriction imposed by the sampling method, but in fact this reflects the true spatial resolution.

Figure 2 shows the RDF of annealed *a*-Si as calculated with the sampling method (\square). Significant noise remains in $J(r)$ due to the statistical noise in $S(Q)$ at high Q . Noting that the $S(Q)$ data beyond 20 \AA^{-1} is almost exclusively due to first neighbors, we have adopted the following procedure to suppress the noise: The first neighbor peak in the RDF was isolated and its contribution to the interference function evaluated through a reverse Fourier transform. This contribution was subtracted

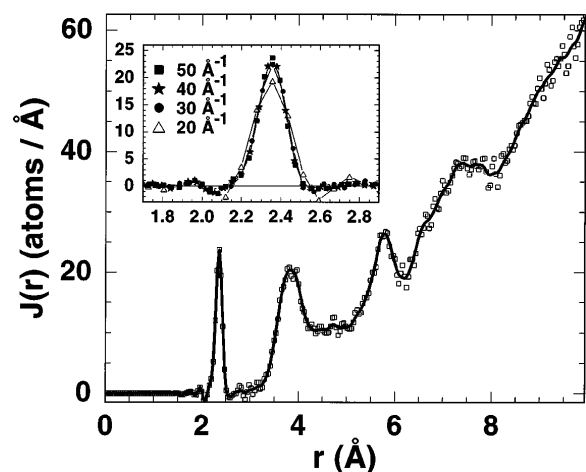


FIG. 2. The RDF of annealed *a*-Si calculated before (\square) and after filtering the noise from $S(Q)$ at large Q as described in the text. The inset shows the first neighbor peak of $J(r)$ calculated using various values of Q_{max} for the upper limit in Eq. (1).

from the total interference function, and the remaining signal (which, beyond $Q = 20 \text{ \AA}^{-1}$, is essentially statistical noise only) is damped through multiplication by a factor $\exp[-\alpha(Q/Q_{\max})^2]$, where $Q_{\max} = 55 \text{ \AA}^{-1}$, and the constant α is chosen so that a satisfactory reduction of the noise is achieved, typically $6 < \alpha < 9$. The unfiltered first neighbor contribution is then added to the filtered data, and the resulting interference function is Fourier transformed to yield the solid line shown in Fig. 2.

A full interpretation of the RDF shown in Fig. 2 requires extensive modeling of the atomic structure, but a few initial observations are already secure. The absence of features for $r < 2 \text{ \AA}$ confirms that the corrections and the atomic scattering factor have been dealt with properly. The inset of Fig. 2 shows an expanded view of the region around the first peak calculated using different values of Q_{\max} , for the upper integration limit in Eq. (1). Here it can be seen that the subsidiary satellites around the first peak become less important above 40 \AA^{-1} . The coordination number, peak position, and width of the first neighbor peak of each RDF were determined for both annealed and as-implanted amorphous membranes as well as the *c*-Si powder using various values for Q_{\max} . For this purpose, the peaks were fit to Gaussian distributions. In Fig. 3, the variation of the coordination number of the first peak (C_1) of the RDF versus Q_{\max} is shown. The coordination number of each sample initially decreases with Q_{\max} then approaches a constant value around 40 \AA^{-1} . Although the data on the *c*-Si powder extend only to a Q_{\max} of 35 \AA^{-1} , it is clear that C_1 approaches a value of 4. For low values of Q_{\max} , the fit overestimates C_1 because of the contribution from termination ripples (see the inset plot of Fig. 2). For large Q the peak shape becomes independent of Q_{\max} with a mean value C_1 of 3.79 ± 0.01 for the as-implanted sample, and 3.88 ± 0.01 for the annealed sample. We believe that the undercoordination, even in annealed *a*-Si, is due to vacancy-type defects (hence the density deficit) rather

than to isolated dangling bonds, as will be discussed in detail in a forthcoming publication [15]. There is a $\sim 2\%$ increase in C_1 as a result of the annealing process. For all three samples the peak was centered at $\sim 2.35 \text{ \AA}$. The width of the first peak, due to static disorder and thermal motion, corresponds within the errors to 0.065 \AA for *a*-Si, compared to 0.057 \AA in *c*-Si measured with a Q_{\max} of 35 \AA^{-1} . This leads to an rms static disorder of 0.031 \AA for *a*-Si. Beyond $Q_{\max} > 40 \text{ \AA}^{-1}$, we believe that the intrinsic value for the position, coordination number, and width has been reached. This would indicate that, even for a simple single-atom system such as *a*-Si, reliable RDF's require scattering intensity data that extend to at least 40 \AA^{-1} .

In Fig. 4, we compare the RDF of both annealed (\cdots) and as-implanted ($—$) *a*-Si in the range of 1 to 5 \AA , to examine closely the difference between the relaxed and nonrelaxed material. The first neighbor peaks of both samples are nearly indistinguishable, the only significant difference being the 2% increase, as described above, in C_1 upon annealing. Note that the height of the second neighbor peak increases upon thermal annealing. Surprisingly, the widths of the second neighbor peaks are almost identical, even though one would expect a significant sharpening of the second peak as a result of the structural relaxation, reflecting a narrowing of the bond angle distribution. In order to verify that the annealing process indeed altered the structure, we performed Raman spectroscopy on the pieces of *a*-Si which had been exposed to the x rays [13], and indeed there was a characteristic shift in position of the TO-like band in the Raman spectra. In the region between the second and third peak, at about 4.7 \AA , a small enhancement in the annealed RDF, over the as-implanted RDF, suggests the existence of a peak (seen earlier by Moss and Graczyk [5]) indicative of dihedral bond ordering [6]. We do not believe that this peak is spurious, since it appears at the same position in all of the RDF's calculated using

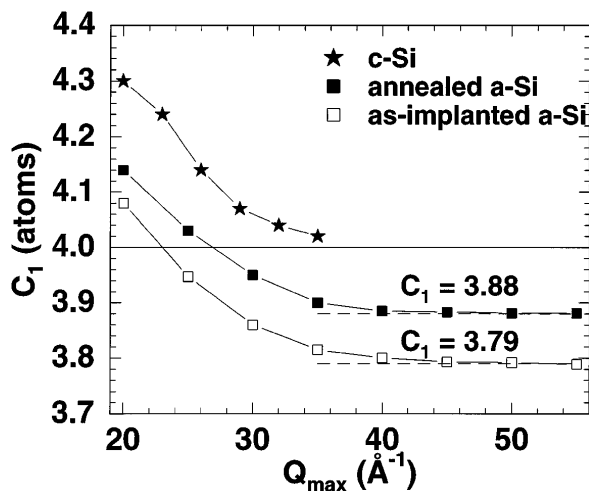


FIG. 3. Coordination number of the first neighbor peak for the as-implanted (\square) and annealed (\blacksquare) *a*-Si, and that for the *c*-Si powder (\star) as a function of Q_{\max} .

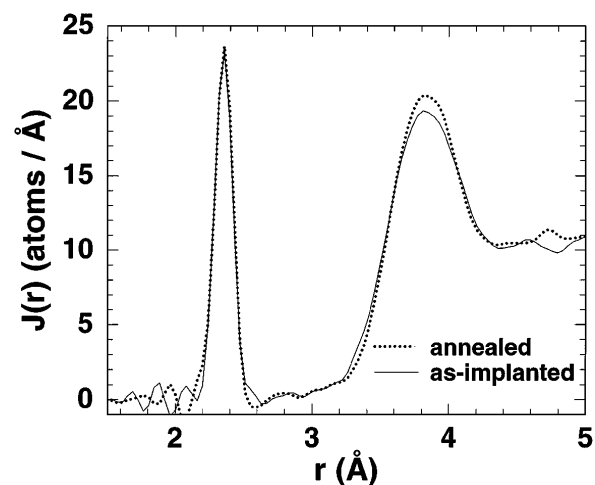


FIG. 4. Radial distribution function $J(r)$ of annealed (\cdots) and as-implanted ($—$) *a*-Si.

different values of Q_{\max} . It, in a sense, represents the loss of the distinct (12) third neighbor peak that appears in the crystal [5].

The 2% change in C_1 upon thermal annealing is consistent with other experimental work, which has shown that the positron spectra [18], Pd solubility and diffusivity [19], and hydrogen trapping [20] all change upon thermal annealing according to a decrease of 2 at. % of trapping sites, i.e., defects. The increase in the first neighbor coordination number by the same amount leads us to believe that the change in the second and third peak of the RDF can be discussed in terms of point defects, instead of average medium range order [21]. Upon thermal annealing, 2% of the vacancylike defects are removed, effectively changing the first shell coordination. Before removal, each of these defects induced a distortion in its surrounding, breaking the local tetrahedral symmetry, because neighboring atoms of the defect will tend to rearrange in order to eliminate broken bonds. The extent of the local rearrangements can be estimated from the calculations of defect structures in *c*-Si. Several studies have shown that, in *c*-Si, a single vacancy defect influences the immediate atomic environment by altering the interatomic distances, so that the distance which separates silicon atoms on either side of a relaxed vacancy is about 3.4 to 3.5 Å [22]. In Fig. 4, these distances correspond to the region (3.2 to 3.6 Å) where a shoulder or broadening of the second neighbor peak of as-implanted *a*-Si appears. Moreover, in a fully coordinated random network, the second neighbor coordination C_2 would be equal to $C_1(C_1 - 1)$. An increase in C_1 due to defect removal by thermal annealing would lead to a significant increase in C_2 , as is observed. Comparison with computer models is required to quantify the increase in C_1 and the shoulder or broadening of the second neighbor peak. We thus conclude that all visible changes in the first and second neighbor peaks induced by thermal annealing are consistent with the annihilation of 2 at. % point defects, which is in excellent and quantitative agreement with a range of other experiments characterizing structural relaxation [18–21].

In summary, we have presented a high resolution determination of the RDF of relaxed and as-implanted high purity *a*-Si. X-ray diffraction measurements were made over a wide range of Q space (0.5 to 55 Å⁻¹), and previous SAXS data were added to extend the experimental range from 0.03 to 55 Å⁻¹. A new method for the separation of coherent and Compton scattering has been applied [14], and the atomic scattering factor of silicon has been extended beyond 20 Å⁻¹ [15]. The observed variation of the coordination number with the value of Q_{\max} indicates that data beyond 40 Å⁻¹ are required for reliable high resolution information on local atomic structure in amorphous materials. Following a thermal anneal, no major changes in peak positions and widths have been observed. Instead, subtle changes, namely, a 2% increase in the coordination number of the first neighbor peak, and accompanying changes in

the second neighbor peak are observed, which show that structural relaxation in *a*-Si is defect mediated and not a global reordering. Even after thermal annealing at 600 °C, the first peak coordination number is well below 4, while the bond length remains 2.35 Å. With the previously observed absence of nanovoids [12], this would imply that the density deficit of *a*-Si relative to *c*-Si is due to a fundamental undercoordination.

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- [1] D. E. Polk, *J. Non-Cryst. Solids* **5**, 365 (1971).
- [2] F. Wooten *et al.*, *Phys. Rev. Lett.* **54**, 1392 (1985).
- [3] R. Car and M. Parrinello, *Phys. Rev. Lett.* **60**, 204 (1988).
- [4] J. S. Custer *et al.*, *Appl. Phys. Lett.* **64**, 437 (1994); K. Laaziri *et al.*, *J. Non-Cryst. Solids* **191**, 193 (1995).
- [5] S. C. Moss and J. F. Graczyk, in *Proceedings of the Tenth International Conference on Physics of Semiconductors, Cambridge, MA*, edited by S. P. Keller, J. C. Hesnel, and F. Stern (U.S. Atomic Energy Commission, Washington, DC, 1970), p. 658.
- [6] R. J. Temkin, W. Paul, and G. A. N. Connell, *Adv. Phys.* **22**, 581 (1973).
- [7] G. Etherington *et al.*, *J. Non-Cryst. Solids* **48**, 265 (1982).
- [8] S. C. Moss and J. F. Graczyk, *Phys. Rev. Lett.* **23**, 1167 (1969).
- [9] S. Kugler *et al.*, *Phys. Rev. B* **48**, 7685 (1993).
- [10] J. Fortner and J. S. Lannin, *Phys. Rev. B* **39**, 5527 (1989).
- [11] I. Ohdomari *et al.*, *J. Appl. Phys.* **52**, 6617 (1981).
- [12] D. L. Williamson *et al.*, *Appl. Phys. Lett.* **67**, 226 (1995).
- [13] S. Roorda *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. B* **148**, 360 (1999).
- [14] K. Laaziri *et al.*, *J. Appl. Crystallogr.* **32**, 322 (1999).
- [15] K. Laaziri *et al.* (unpublished).
- [16] J. Krogh-Moe, *Acta Crystallogr.* **9**, 951 (1956); N. Norman, *ibid.* **10**, 370 (1957).
- [17] R. Lovell *et al.*, *Acta Crystallogr. Sect. A* **35**, 598 (1979).
- [18] S. Roorda *et al.*, *J. Appl. Phys.* **72**, 5145 (1992).
- [19] S. Coffa *et al.*, *Appl. Phys. Lett.* **58**, 2916 (1991).
- [20] K. F. Heidemann *et al.*, *Radiat. Eff.* **82**, 103 (1984).
- [21] S. Roorda *et al.*, *Phys. Rev. B* **44**, 3702 (1991).
- [22] A. Antonelli *et al.*, *Phys. Rev. Lett.* **81**, 2088 (1998); H. Seong and L. J. Lewis, *Phys. Rev. B* **53**, 9791 (1996).