

On the nanostructure of pure amorphous silicon

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New features of the nanoscale structure of amorphous (*a*)-Si produced by ion-implantation-induced amorphization of crystalline (*c*)-Si have been determined by the technique of small-angle x-ray scattering (SAXS). Si ion energies up to 17 MeV were used to generate a thick amorphous layer (8 μm) on a *c*-Si wafer to enable the SAXS measurements. As-implanted and thermally annealed (up to 540 °C) *a*-Si were studied. No nanovoids were detected within a sensitivity of 0.1 vol %, but the atomic-scale structure produced a measurable diffuse scattering signal that decreased with increasing anneal temperatures. These measurements show that the known density deficit of 1.8% in *a*-Si relative to *c*-Si cannot be due to voids and that *a*-Si is homogeneous on nm length scale. © 1995 American Institute of Physics.

The intrinsic morphology of pure amorphous silicon (*a*-Si) on a nm length scale has been an elusive issue for more than two decades. This is mainly due to the fact that the actual morphology depends on the method of preparation and the thermal history of a particular sample of *a*-Si, as do many other structural properties.¹ As an example, *a*-Si prepared by physical vapor deposition (by either vacuum evaporation or sputtering) at high deposition rates on cold substrates almost inevitably shows the formation of nm-sized voids, that may or may not be connected. The existence of such structures has been shown directly by electron microscopy² and electron diffraction,³ and has been inferred from the clustering of dangling bonds and from the rapid indiffusion of oxygen and water vapor. Such structure is often accompanied by a density deficit relative to crystalline Si (*c*-Si) of more than 10%.

The void structure is widely believed to be an artifact of the preparation method since thermal annealing densifies the film and reduces void scattering observed in electron diffraction³ and prevents the indiffusion of gases.⁴⁻⁶ With *a*-Si prepared by ion implantation, no indiffusion has been observed even without thermal annealing.²⁻⁴ However, the absence of a small density of nm- and sub-nm-sized voids is hard to prove directly, and it cannot be excluded that some (unconnected) voids remain. Two different observations show that a void-containing structure could be intrinsic to pure *a*-Si. The first is the observation that in hydrogenated *a*-Si (*a*-Si:H), the void structure may be the thermodynamically preferred state.^{7,8} It remains to be seen whether this can be translated to pure *a*-Si since it is likely that the internal surfaces of the voids are decorated with hydrogen,^{9,10} which generally reduces their energy. The second observation cast-

ing doubt on the void-free nature of pure *a*-Si is the fact that, experimentally, it *always* shows a density deficit relative to *c*-Si, even in pure *a*-Si prepared by ion implantation.¹¹⁻¹³ The atomic density of *a*-Si according to model building is higher than that of *c*-Si,¹⁴ although it has been found to depend on the simulation conditions.¹⁵

Early measurements showed the density of *a*-Si to be much less than that of *c*-Si, and to be variable, depending on the thermal history.^{16,17} Moreover, the density of dangling bonds was found to be reduced in relatively dense *a*-Si, and an extrapolation of the density to a structure without dangling bonds suggested that such a structure could be more dense than *c*-Si. Two recent results from *a*-Si prepared by ion implantation inferred from the (separate) measurements of atomic density¹² and dangling bond density¹⁸ before and after thermal annealing are not consistent with the earlier extrapolation and show that *a*-Si cannot be made more dense than *c*-Si; its intrinsic atomic density is 1.76% less than that of *c*-Si. More recent wafer curvature measurements of Si wafers before, during, and after ion implantation have shown that during structural relaxation *a*-Si does in fact expand even further (by 0.15% to a 1.9% deficit) whereafter it re-densifies (by 0.1%).¹⁹

The two most obvious possible explanations for the density deficit in *a*-Si are (1) a small increase in average bond length (0.6% would be enough) and (2) the presence of a small density of nm-sized voids. In this letter, we present small-angle x-ray scattering (SAXS) measurements providing direct evidence that the nanovoid density in pure *a*-Si, prepared by ion implantation, is well below the above value. SAXS is a well established technique for the detection of void distributions and it has been applied with success to both *a*-Si²⁰ and *a*-Si:H.^{10,21-23} The early SAXS work on *a*-Si²⁰ was done on evaporated films with density deficits of about 10% and maximum void radii of 4 nm were reported.²⁰

Ion implantation is an ideal method to *reproducibly* prepare high-purity *a*-Si but it yields normally films of only 2

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μm maximum thickness. Here, in order to improve x-ray counting statistics, we have increased the implantation energy considerably and prepared an *a*-Si film of 8.1 μm thickness. Our results show that *a*-Si has an intrinsically homogeneous morphology and that the density deficit of 1.8% relative to *c*-Si is native to its atomic structure rather than due to its nanostructure.

Amorphous Si was prepared by Si ion implantation into a 76- μm thick monocrystalline Si wafer. During the implantation the sample was heat sunk to a liquid-nitrogen-cooled copper block. The ion energy was varied in 10 steps from 0.5 to 17 MeV, keeping the beam power on the target at or below 4 W. The total fluence exceeded the amorphization threshold by about a factor of 5. The ion beams were scanned electrostatically over an area of approximately 0.5 cm \times 2 cm, an appropriate dimension for the line-focus SAXS measurements. The implantation sequence resulted in a continuous *a*-Si surface layer, with a thickness of 8.1 μm as confirmed by infrared interferometry.

The SAXS system consists of a Kratky compact small-angle system²⁴ attached to a Rigaku rotating anode (Cu) x-ray generator, a crystal monochromator to select the Cu $K\alpha$ radiation, and a proportional counter operated with an Ar–Xe gas mixture. The observed SAXS signals were only about two to three times the background rate so rather long signal averaging was used in collecting the data. A step-scanning mode was used to count the scattered x rays as a function of the momentum transfer $q=(4\pi/\lambda)\sin\theta$ (λ =x-ray wavelength =0.154 nm, 2θ =scattering angle) over a range from about 0.1 to 6 nm⁻¹. Scans were repeated two or three times and averaged. For each SAXS scan of the sample a reference scan was made by passing the beam through the *c*-Si wafer adjacent to the amorphized layer. Since the x-ray absorption by the *a*-Si+*c*-Si sample and the *c*-Si reference was then identical, a simple subtraction of the reference scan data from the sample scan data yielded the *explicit* extra SAXS from the *a*-Si. This difference was then normalized by the thickness of the *a*-Si and the incident intensity, corrected for the absorption by the entire thickness of the wafer. This normalized intensity was then converted into electron units (electrons/atom=e/a) using the appropriate geometry factors in the SAXS system and the scattering cross section of the electron. This conversion has been checked by measuring the diffuse SAXS intensity from H₂O with the same system and comparing with known values.²⁵

Anneals of the sample were made under high-purity, flowing He. Each anneal was for 1 h and was done in approximately 50 °C increments up to 540 °C. Note that this procedure produced the same anneal for the reference sample since it is part of the same piece of *c*-Si wafer containing the *a*-Si layer. The final anneal at 540 °C was expected to induce a small amount of epitaxial regrowth, about 0.3 μm ,²⁶ which is less than 4% of the total *a*-Si layer thickness.

Figure 1 compares measured and theoretical SAXS intensities (in e/a) as a function of the momentum transfer. Data from the as-implanted *a*-Si are compared to those after the 150 and 400 °C anneals and with those from a *c*-Si reference (the latter obtained by subtracting absorption-corrected scan data with no sample in the beam). The dashed

lines represent the SAXS intensities expected from a random distribution of 0.1 vol. % voids of radii 0.5 or 1.0 nm. Note that a 0.1% volume fraction of voids is much less than would be required for the experimentally observed 1.8% density deficit.^{11–13} The theoretical curves were obtained using the known structure factor for spheres and applying the slit-smearing correction appropriate for our line-focus geometry.²⁴ Before smearing, the intensity $I(q)$ (in e/a) was adjusted to yield the expected value of the integral $\int I(q)q^2dq=2\pi^2\Omega_{\text{Si}}n^2V(1-V)$,²⁴ where V is the volume fraction of voids (0.001 assumed for present calculation) and n is the electron density in the *a*-Si matrix. The effect of the smearing is to reduce the absolute intensities by about 10% for the $R=0.5$ nm spheres and about 35% for the $R=1$ nm spheres. A constant baseline intensity (6.7 e/a) was added to these curves to account for the observed diffuse scattering and to allow a clear comparison to the experimental data.

Upon examination of Fig. 1, a number of observations can be made: (i) all experimental data points in the lower q region fall well below the expected intensities for 0.1% void fractions for the two sizes shown (larger sizes would produce even higher intensities, but at smaller q); (ii) all experimental data are nearly independent of q (implying diffuse scattering only), and if there is a slope it is positive, not negative as characteristic of void scattering shown by the dashed curves; (iii) the diffuse scattering is much stronger from the *a*-Si than from the *c*-Si, but is reduced somewhat by thermal annealing. For an explanation of this third observation, a detailed analysis of all contributions to diffuse scattering of x rays, including those from point defects, is required and this will be done in a forthcoming paper. Here, we want to emphasize the first two observations: *Both* show that the volume fraction of nanovoids in *a*-Si is well below 0.1% and we therefore conclude that *a*-Si prepared by self-ion implantation is homogeneous on a nm length scale. We also conclude that voids do not spontaneously appear in pure *a*-Si, even after prolonged annealing at temperatures up to 540 °C. Nanometer-sized voids are not intrinsic to the structure of pure *a*-Si and, therefore, void structures observed earlier were indeed artifacts of the preparation methods.

To further examine the latter point, we have measured SAXS from several *a*-Si films prepared by magnetron sputtering of a pure Si target and *always* see large intensities with a q , dependence characteristic of nanometer-sized voids. These intensities rise to values of 10^3 – 10^4 e/a at low q and approach the intensities shown in Fig. 1 at high q . Systematic variation of the sputter deposition conditions (rf power, Ar pressure, substrate temperature) does lead to reductions in the SAXS (and to density deficits of only $\sim 2\%$) but the weak, diffuse signal observed from the implantation-produced *a*-Si shown in Fig. 1 has not been achievable for sputter-deposited *a*-Si.

Having ruled out voids as a possible cause for the density deficit in pure *a*-Si prepared by the self-implantation technique, there are two remaining possibilities to consider: an increase in the average Si–Si bond length from 0.2352 to 0.2366 nm (i.e., a 0.6% increase) or an imbalance in density change due to vacancy-type and interstitial-type defects.

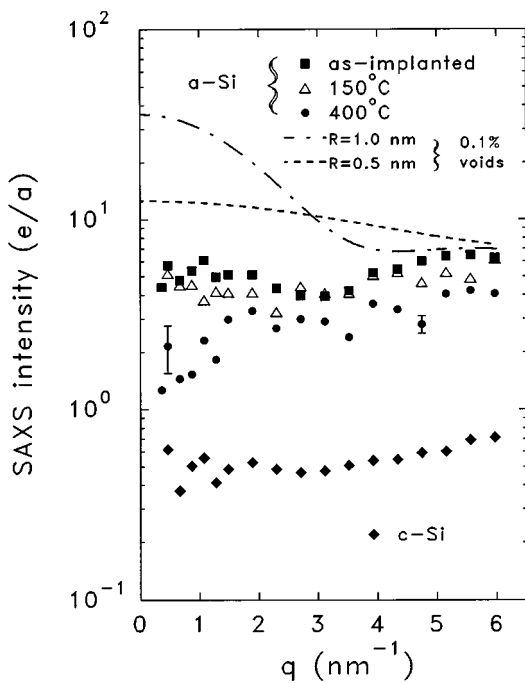


FIG. 1. SAXS intensities from *a*-Si prepared by ion implantation in the as-implanted state and after annealing for 1 h at 150 and 400 °C. Also shown are data from the *c*-Si reference wafer and theoretical curves based on spherical nanovoids of two radii and volume fractions of 0.1%. Typical error bars at low and high q are shown.

Measurements of the bond length by x-ray or electron diffraction or by extended x-ray absorption fine structure (EXAFS) are inconclusive, as values smaller than,²⁷ equal to,³ and larger than^{28–31} 0.235 nm have been reported, and *none* of these measurements were made on *a*-Si prepared by the ion implantation method. It is noteworthy that the latest EXAFS results from a sputtered *a*-Si sample yielded average bond lengths 0.6% to 0.9% longer than *c*-Si,³¹ depending on the substrate temperature. However, sputtered *a*-Si is quite likely to contain significant void fractions as noted above and the microstructures of the *a*-Si samples studied by EXAFS³¹ were not characterized by other methods. The other possibility, unbalanced strain fields around defects, at first seems likely because it is known that an equal number of vacancies and interstitials in *c*-Si leads to a net lattice expansion.³² However, at least two problems arise: the density deficit of 1.8% is simply too large to explain this way and the majority of defects in *a*-Si can be removed in *a*-Si by thermal annealing^{1,18} without a large effect on the density.^{12,19}

In conclusion, small-angle x-ray scattering measurements of an 8.1 μm thick, high-purity *a*-Si layer prepared by Si ion implantation demonstrate that the maximum volume fraction of nanovoids in this layer is well below 0.1%. Upon thermal annealing at temperatures up to 540 °C, no voids appear and the observed diffuse scattering intensity from the *a*-Si decreases. Thus, the previously observed $1.8\% \pm 0.1\%$ density deficit in *a*-Si is not related to nanovoids and *a*-Si prepared by ion implantation is homogeneous on a nm length scale.

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