Absence of an Abrupt Phase Change from Polycrystalline to Amorphous in Silicon with Deposition Temperature

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Using fluctuation electron microscopy, we have observed an increase in the mesoscopic spatial fluctuations in the diffracted intensity from vapor-deposited silicon thin films as a function of substrate temperature from the amorphous to polycrystalline regimes. We interpret this increase as an increase in paracrystalline medium-range order in the sample. A paracrystal consists of topologically crystalline grains in a disordered matrix; in this model the increase in ordering is caused by an increase in the grain size or density. Our observations are counter to the previous belief that the amorphous to polycrystalline transition is a discontinuous disorder-order phase transition.

Since the measurements of Veprěk *et al.* [1–4], it has been believed that a sharp order-disorder phase transition exists between the polycrystalline and amorphous phases of silicon. They studied plasma-deposited hydrogenated silicon thin films deposited at varying substrate temperature [3], plasma current [3], and substrate bias voltage [4] using x-ray diffraction as their primary structural investigation method. They observed peaks in the structure factor, $S(k)$, of the polycrystalline films corresponding to the crystalline Si (*c*-Si) $\langle 111 \rangle$, $\langle 220 \rangle$, and $\langle 311 \rangle$ reflections. In $S(k)$ of the amorphous films, they observed a peak at the $\langle 111 \rangle$ position broadened by disorder, but the second peak fell between the *c*-Si $\langle 220 \rangle$ and $\langle 311 \rangle$ peaks. They reported that this change in the second peak was abrupt as a function of the deposition conditions and took it as a signature of a first-order, order-disorder phase transition, requiring a symmetry-breaking change in the bonding topology [3]. Other properties with less direct structural connections including the electrical conductivity, the sign of the Hall coefficient, and the Raman spectra were also reported to change abruptly.

Veprěk *et al.* observed a minimum polycrystalline grain size of ~ 30 Å by applying the Scherrer formula to their x-ray data [1]. The difficulty with this method, which they noted [1], is that the Scherrer formula assumes the material is a compact of small perfect crystals acting as coherent scatterers. Atomistic simulations have suggested that, except in special low energy tilt configurations, ~ 10 Å of disordered material can form at the grain boundaries [5], and the grains themselves can be distorted by strain [6]. When the grain diameter is comparable to the width of the intergranular and strained material, i.e., near the 30 Å minimum size Veprěk observed, the Scherrer analysis no longer gives information about the structure of the majority of the sample.

The pair (or radial) distribution function (PDF), which is the Fourier transform of $S(k)$, provides another way to analyze the x-ray data; however, the PDF is not directly sensitive to order at a length scale of $10-30$ Å in the presence of disorder such as strain. For amorphous silicon, the best experimental PDF contains no information beyond the average density for $r > 8$ Å [7]. Moreover, it has been shown that atomistic models which have different structure at a ~ 10 Å length scale can have indistinguishable PDFs [8].

Between the regimes of short-range order measurable by the PDF and long-range order measurable as Scherrer broadening of the crystalline $S(k)$, lies the possibility of medium-range order (MRO). The disappearance of 30 Å grains in silicon and the possibility of even smaller grains is essentially a question of MRO. Experiments using fluctuation microscopy have shown that such grains do exist [9], which fundamentally changes our understanding of the amorphous state in silicon and its phase transformations. In this Letter, we investigate the amorphous to polycrystalline transition in silicon deposition.

Fluctuation electron microscopy is a transmission electron microscopy (TEM) technique which is sensitive to medium-range structure in the presence of disorder. In fluctuation microscopy, we compute the normalized variance of low-resolution hollow-cone dark-field (HCDF) electron micrographs, defined as

$$V(k, Q) = \frac{\langle I^2(k, Q) \rangle}{\langle I(k, Q) \rangle^2} - 1, \qquad (1)$$

where $I(k, Q)$ is the image intensity and $\langle \rangle$ indicates averaging over the image. k is the magnitude of the dark-field scattering vector, and Q is the objective aperture collection radius. We employ a deliberately low image resolution of $0.61/Q \simeq 15$ Å so that $V(k)$ measures the magnitude

of the fluctuations in the diffracted intensity from mesoscopic volumes of the sample which extend 15 Å laterally and through the ~200 Å sample thickness.

Any MRO that changes the samples' local diffraction will change the magnitude of $V(k)$. For example, a small crystal-like cluster will diffract more strongly (or more weakly, depending on the diffracting condition) than the same volume randomly filled with atoms. Many measures of MRO have been proposed, including the topological ring statistics [10], the Raman I_{TA}/I_{TO} ratio [11], and correlations between connected dihedral angles [12]. Fluctuation microscopy does not measure any of these quantities directly, but we have shown correlations between structure in $V(k)$ and all of these measures in simulated atomistic model structures [13,14]. Quantitatively, $V(k)$ depends on the three- and four-body atom distribution functions [15], which retain information well past 10 Å [16]. Qualitatively, $V(k)$ gives information about the degree of "diffracting" MRO from the height of the peaks, and the internal structure of any ordered regions from the peak positions. Connecting features in $V(k)$ with particular aspects of the sample structure currently requires some model for that structure.

To probe the amorphous to polycrystalline transition in Si, we have examined a series of thin films deposited by dc magnetron sputtering on single-crystal NaCl substrates at a growth rate of 0.9–1.0 Å/s and varying substrate temperatures T_s. The films were grown in immediate succession but not sequentially to avoid uncontrolled variation in the deposition parameters. TEM samples were prepared by floating the films off the substrate in deionized water and catching them on 1000 mesh TEM sample grids. Fluctuation microscopy and transmission electron diffraction (TED) experiments were performed in a Hitachi H9000NAR TEM operated at 200 kV accelerating voltage and 15 Å image resolution and equipped with a Gatan cooled CCD camera. Each $V(k)$ trace is the average of ten areas of the film for a total sampled volume of ~0.005 μm^3 and has been corrected for the effects of incoherent variance and varying sample thickness [17]. The error bars are one standard deviation of the mean. The higher T_s samples show a degree of Si agglomeration at a length scale of ~350 Å, much larger than the 15 Å length scale we probe for MRO. The only effect on our measurements is that the incoherent variance subtraction scheme produces a fictitious negative variance for some samples; those data have been vertically offset so the smallest reported variance is zero. This does not effect our conclusions, which are based on comparisons of the relative size of features in $V(k)$.

Figure 1 shows the electron $S(k)$ of the samples measured by TED. $S(k) = I(k)/f^2(k)$, where $I(k)$ is the TED intensity and $f(k)$ is the electron atomic scattering factor for Si. From this data we can determine the "phase" of the samples by the Vepřek second peak criteria. The $T_s = 440\,°C$ sample shows the c-Si $\langle 220 \rangle$ and $\langle 311 \rangle$
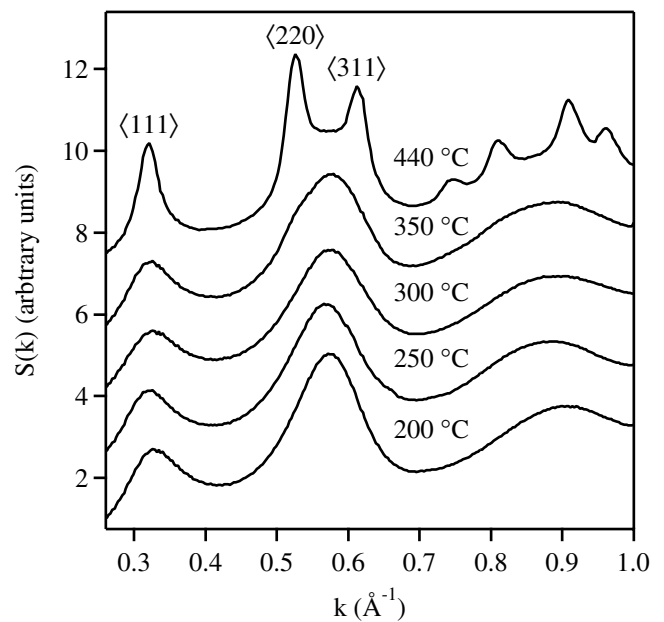

FIG. 1.   Electron structure factors as a function of T_s.

reflections, as well as other higher-index peaks, indicating it is polycrystalline. The typical grain size is ~150 Å, measured by conventional TEM. The $T_s = 200–300\,°C$ samples are diffraction amorphous. The $T_s = 350\,°C$ sample shows a small shoulder on the $\langle 220 \rangle$ side of the amorphous second peak, caused by the introduction of crystals ~100 Å in diameter, which is large enough to be clearly visible in HCDF TEM images. We estimate from such images that the 350 °C sample has a ~0.1% crystalline volume fraction.

Figure 2 shows fluctuation microscopy data $V(k)$ for the samples. The $T_s = 200–300\,°C$ samples show the characteristic pattern of diffraction amorphous silicon [18], with peaks at $k = 0.30$ Å^{-1} and $k = 0.55$ Å^{-1}, which are also the positions of the first two peaks in the structure factor of a-Si [7]. The height of both peaks increases with increasing T_s from 200 to 300 °C. There is a reversal in the relative peak heights between 200 and 250 °C. All the $T_s \leq 350\,°C$ data are well fit by a sum of two Gaussians, indicated by the solid lines in the figure. The error bars of the 200 °C data fall within the data markers.

$V(k)$ for the polycrystalline $T_s = 440\,°C$ sample is much larger in magnitude, so it has been divided by 5 for easy visual comparison with the other data. $V(k)$ for this sample also shows a shift in the position of the second peak from the position of the a-Si second peak in $S(k)$ toward the c-Si $\langle 220 \rangle$ position. To obtain a good fit to this data, we must introduce a third Gaussian peak at the c-Si $\langle 311 \rangle$ position. The $T_s = 350\,°C$ data is intermediate between the amorphous and polycrystalline data. It shows the same peak-to-dip height as the 300 °C data, although the trace shows a small vertical offset due to experimental error in the incoherent variance correction. However, the second peak position is shifted slightly towards lower k.
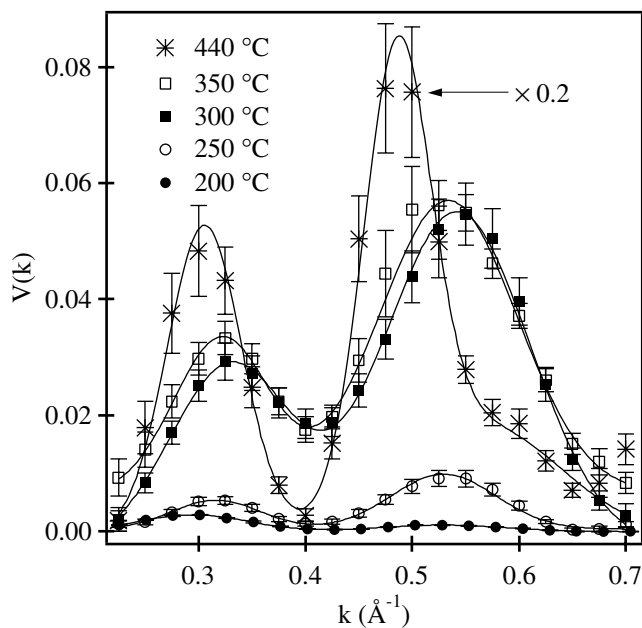
FIG. 2. $V(k)$ for the samples. The solid lines are Gaussian peaks fit to the data.

Overall, the data indicate a smooth, monotonic increase in "diffracting" MRO with T_s over the entire temperature range investigated, whether the samples are "diffraction amorphous" or not. The increase in peak heights in $V(k)$ from $T_s = 200-300\,°C$ indicates an increase in the MRO. The reversal in the peak weights indicates increased ordering because diffraction from $\langle 220 \rangle$ planes is more sensitive to MRO, such as dihedral angle ordering, than diffraction from $\langle 111 \rangle$ planes [19]. The shift in the second peak position in the 350 °C sample is also evidence of increased ordering, associated with the introduction of the 0.1% crystalline volume fraction, since this shift is also observed in the polycrystalline data. Of particular importance, we have observed a continuous increase in MRO right up to the temperature at which a small crystalline volume fraction first appears. This continuous evolution of ordering is in marked contrast to the abrupt splitting of the $S(k)$ peak reported by Veprek.

What is the character of this ordering? Based on earlier fluctuation microscopy results, we have proposed the paracrystalline (PC) structural model of amorphous semiconductors [9]. A paracrystal consists of small (<30 Å in diameter), topologically crystalline [6] grains in a more disordered matrix. The disordered matrix is likely to have a structure similar to that of a continuous random network (CRN). The strain field from the grain boundaries extends completely across the grains, so few of the atoms sit precisely on their crystalline lattice positions, rendering the grains (and the material) amorphous to diffraction experiments, even though the grains retain a crystalline topology. The grains are the source of the MRO measured with fluctuation microscopy. In terms of the three- and four-body distribution functions, we picture a PC grain as a

region 10–30 Å in diameter in which well-aligned nearest-neighbor and next-nearest-neighbor pairs produce significant three- and four-body correlations. The grains also tend to favor the c-Si dihedral angle of 60°, whereas this angle is approximately random in the matrix. $V(k)$ simulations from PC molecular dynamics model structures show the characteristic double peak pattern observed in the data [9], and the height of the peaks increases with the grain size and density [13]. Simulations from a wide variety of pure CRN atomistic models do not show the double peak shape. All of the current samples are to some degree PC, indicating that even the lowest temperature sample has more MRO than an ideal CRN.

Many aspects of the PC grains can effect $V(k)$, including the grain size, shape, density, spatial and orientation distributions, and degree of strain. This large parameter space has yet to be fully explored, but we can make some strong but reasonable simplifying assumptions. We have proposed that the PC grains are residual, subcritical crystalline nuclei that are frozen in during deposition [20]. Therefore, we expect the primary change in the paracrystalline structure with T_s to be in the number and size of the PC grains, and the spatial and orientation distributions to be random. The compact is then characterized by a single parameter, the PC grain volume fraction f. $V(f)$ can be estimated from a simple mixing argument. In the TEM column approximation, the intensity from each column may be thought of as sampling either a distribution with width V_{dm} associated with the disordered matrix or a distribution with width V_{pc} associated with the PC grains. $V_{pc} > V_{dm}$, both depend on k, and V_{pc} is approximately linear in f [17]. This results in leading-order behavior $V \sim f^3$.

A rough estimate of f as a function of T_s based on these ideas is presented in Fig. 3. V_{pc} was measured from the polycrystalline $T_s = 440\,°C$ data, for which $f = 1$. V_{dm}/V_{pc} was estimated from computer simulations on molecular dynamics model structures. The error bars indicate the spread in f using the data for the same sample at different k. The 200 °C point is from a PC model structure
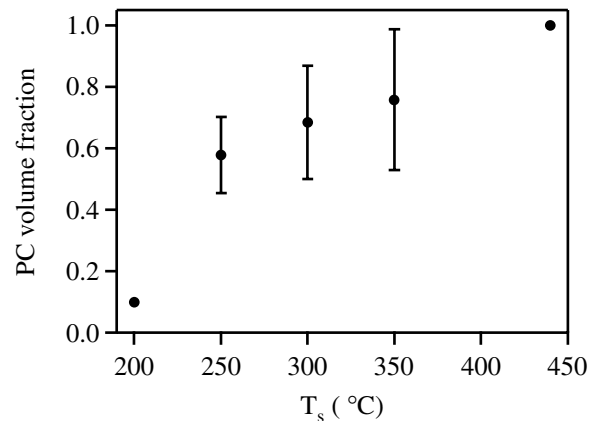

FIG. 3. PC volume fraction as a function of T_s derived from fluctuation microscopy $V(k)$ data.

that shows good agreement with the data [14]. This is a rough estimate only, since, in addition to the assumptions above, we have ignored the differences in the average diffracted intensity from the disordered matrix and the grains, which will become important at large grain sizes and low strain.

Figure 3 shows a smooth, monotonic increase in PC volume fraction with T_s. In particular, the change in f from 300 °C to 350 °C, the temperature at which identifiable grains appear, is quite small. This indicates that the appearance of crystalline grains is not a first-order phase transition. Instead, once the grains become large enough, the effects of strain are diminished, and the sample can be described as polycrystalline, with no sharp transition between "amorphous" and "crystalline." Regions with crystalline topology exist in both materials.

The amorphous to polycrystalline transition is therefore at most a continuous, second-order transition, and possibly not a phase transition at all. The paracrystalline model predicts that for small grain sizes a uniform disordered state such as a CRN is energetically favorable, with the excess energy of the PC state due to strain in the bulk and the surface energy of the grains [20]. However, under the highly nonequilibrium conditions of low substrate temperature and high growth rate that produce a diffraction amorphous sample, the structure becomes trapped in a metastable paracrystalline state. Even though there is no abrupt structural change with increasing T_s, there may be a change in the direction the system evolves on thermal annealing. Experiments on low-T_s amorphous germanium indicate it evolves toward greater disorder [21]; higher T_s samples may evolve toward greater order. If so, that would be evidence of a continuous, second-order phase transition. More experiments are necessary to investigate this possibility and the other implications of the paracrystalline model for the crystallization and relaxation of diffraction amorphous silicon.

The sharp transition previously observed by x-ray diffraction also has a natural explanation in terms of the PC model. Instead of observing a transition in the structure, Veprek *et al.* observed a transition in the *sensitivity* of x-ray diffraction to the relevant structure. The grains smaller than 30 Å did not disappear. Instead, the strain fields from the grain boundaries spread completely across the grains, rendering them diffraction amorphous, even though they retained the topology of the crystal.

In summary, we have observed using fluctuation electron microscopy a continuous evolution in the paracrystalline medium-range order of amorphous silicon thin films with increasing substrate temperature from the amorphous to polycrystalline regimes. This indicates that there is no first-order, order-disorder phase transition between amorphous and polycrystalline silicon films. This observation is naturally explained in terms of the paracrystalline structural model of amorphous semiconductors.

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