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Comment on “The Local Structure of Amorphous Silicon”

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Treacy and Borisenko (Reports, 24 February 2012, p. 950) argue from reverse Monte Carlo modeling of electron diffraction and fluctuation electron microscopy data that amorphous silicon is paracrystalline and not described by a continuous random network. However, their models disagree with high-resolution x-ray measurements and other evidence, whereas the agreement with fluctuation electron microscopy is at best qualitative.

A Report by Treacy and Borisenko (*1*) on reverse Monte Carlo modeling of the reduced radial distribution function $G(r)$ (RDF) and fluctuation electron microscopy (FEM) of amorphous silicon (a-Si) claims that a-Si is inhomogeneous on the 1- to 2-nm length scale, consistent with a fully paracrystalline (PC) model; the authors conclude that the continuous random network (CRN) model must be dismissed and that a-Si consists of paracrystallites embedded in a medium considerably more disordered than a CRN. This would be a far-reaching conclusion. However, the simulations do not provide quantitative agreement with the FEM data and disagree with high-resolution x-ray data of pure a-Si. Further, a true CRN, with or without voids, has not been included in the modeling and therefore cannot be excluded.

The agreement between model and experimental data shown in Fig. 1B in (*1*) is qualitative only. The experimental FEM signal was multiplied by a factor $\gamma = 20$, attributed to decoherence due to inelastic scattering and insufficient knowledge of the sample thickness (*2*). However, the same authors in another paper explain that γ , which varies between 10 and 48, is not fully understood and that “results should not be interpreted in absolute terms” (*3*). Moreover, the FEM intensity measured on the same sample at different microscopes can vary by a factor of 20 (*4*). According to table 1 in (*1*), there are 94 “paracrystalline” atoms out of 1728 (i.e., about 5%). The ordering of the remaining 1634 atoms is not discussed in detail but is stated to be neither topologically crystalline nor that of a true CRN because of ring statistics. Thermal annealing is said to reduce the FEM by a factor of only 2, but other reports have observed a reduction by a factor of 5 (*5*) to 10 (*4, 6*). If one takes at face value the absolute intensities of measured and modeled FEM data, then the amount of paracrystallite matter in well-annealed a-Si may be as low as 1/20 of 1/10 of 5% (i.e., 300 parts per million).

Treacy and Borisenko (*1*) provide no evidence for excluding voids in an otherwise fully connected CRN structure giving rise to the FEM. This is a real possibility (*7*), which refutes the notion that paracrystallites are the only possible explanation of the observed FEM. The authors speculate that paracrystals nucleate at void surfaces but present no evidence and do not explain why these must be introduced when voids can account for the FEM signal (*7*). In fact, neither do they exclude the CRN model: The simulations start from random configurations that are not true CRNs (for example, the initial configuration is not tetrahedrally bonded, and the final configuration has a high proportion of three-membered rings and does not fit the RDF). The CRN model, with or without voids, has not been included in the reverse Monte Carlo modeling and therefore cannot be dismissed.

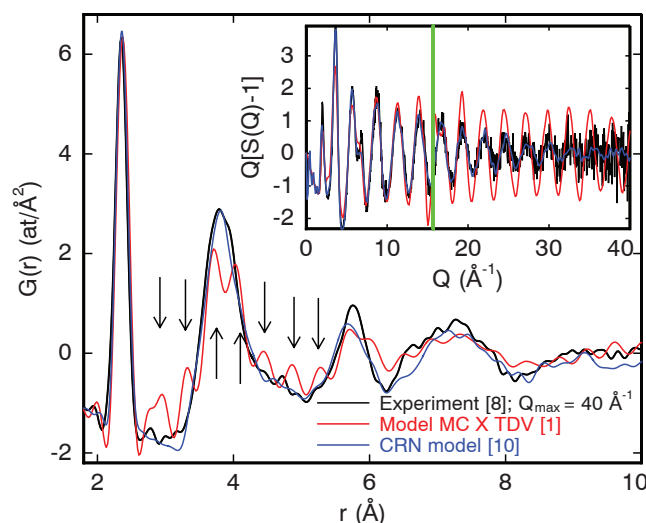
For the paracrystallite model to be valid, the RDF of pure a-Si must be accounted for. Figure 1A of (*1*) presents low-resolution data only. In Fig. 1, we compare the experimentally determined $G(r)$ at high resolution (*8*)—here, the maximum scattering vector $Q_{\max} = 40 \text{ \AA}^{-1}$ and a slight damping has been applied—with the $G(r)$ for model MC X TDV [calculated directly from the atomic coordinates provided in the supporting online material for (*1*)],

smoothed so as to show comparable widths of the first coordination peak. Clearly, the model deviates significantly from pure a-Si; arrows indicate positions of sharp peaks in the model that do not correspond to sharp features in the measured $G(r)$. Only the peak at 4.45 \AA corresponds to a feature visible in high-resolution RDFs (*9*), but it appears upon annealing, whereas the FEM intensity is known to reduce upon annealing (*4–6*). The first shell coordination number of the paracrystallite models (~ 3.6) is significantly less than the measured value (3.88 ± 0.01 in annealed a-Si), and the width of the distribution of tetrahedral angles of the models (16°) (*3*) is nearly twice the measured value ($9.63^\circ \pm 0.08^\circ$). These deviations are so significant as to invalidate the claim that the models provide a correct fit to the a-Si RDF. In contrast, the blue curve, corresponding to a 1000-atom CRN model (*10*), fits the experimental $G(r)$ much better. Similar conclusions are drawn when comparing the data and models in reciprocal space, as depicted in the inset, which shows the corresponding interference functions. The MC-X-TDV model agrees with the data up to $Q = 15 \text{ \AA}^{-1}$, but for larger values it does not exhibit the strong damping shown by both the experimental data and the CRN model. Such a strong disagreement was not found for CRN models containing voids, which also succeeded in explaining the FEM data (*7*).

Other evidence should be taken into account. The absence of a large small-angle x-ray scattering signal (*11*) argues against a mixed phase (PC-disordered) structure, and so do the observations from impurity segregation (*12*) and crystallization through nucleation and growth (*13*), demonstrating that a first-order phase transition separates a-Si from c-Si. A mixed-phase model for a-Si, such as PC, is fundamentally incompatible with these observations.

Thermal annealing of a-Si induces structural relaxation, and many of its aspects (tetrahedral and dihedral bond ordering, defect removal, and changes in the vibrational spectrum) can and have been understood in terms of the relaxation of defected

Fig. 1. Black curve: RDF from pure a-Si [after (*8*)]. Red curve: RDF for model MC X TDV, according to atomic coordinates provided with (*1*) and smoothed to the same first-peak width. Blue curve: RDF for a 1000-atom CRN model (*10*). Arrows indicate peaks in the model RDF that do not correspond to features in the experimental data or the CRN. The inset shows the corresponding interference functions; the vertical line near $Q = 15 \text{ \AA}^{-1}$ is the upper limit of the diffraction data considered in the reverse Monte Carlo modeling.



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CRN models. If the FEM from as-prepared a-Si were due to small crystallites embedded in a CRN (because of incomplete transformation to the amorphous phase), and if one views these crystallites as prenucleation subcritical (and therefore unstable) embryos (14), then one would expect the FEM amplitude to decrease upon annealing because most of those nuclei would dissolve. This is exactly what is observed (4–6), and it indicates that in well-annealed a-Si the volume fraction of paracrystalline matter is insignificant.

It is entirely true that the ideal, fully connected, four-fold coordinated CRN is never realized. It is equally true that the perfect crystal

does not exist, except in our imagination. Real crystals are best viewed as ideal crystals with defects and imperfections. Likewise, a-Si is best viewed as a CRN with imperfections—for example, vacancies or voids. High-resolution x-ray measurements support this view fully.

References

1. M. M. J. Treacy, K. B. Borisenko, *Science* **335**, 950 (2012).
2. M. M. J. Treacy, J. M. Gibson, L. Fan, D. J. Paterson, I. McNulty, *Rep. Prog. Phys.* **68**, 2899 (2005).
3. K. B. Borisenko *et al.*, *Acta Mater.* **60**, 359 (2012).
4. B. Haberl, thesis, Australian National University, Canberra (2010).
5. B. Haberl *et al.*, *J. Appl. Phys.* **110**, 096104 (2011).
6. J.-Y. Cheng, J. M. Gibson, D. C. Jacobson, *J. Mater. Res.* **16**, 3030 (2001).
7. P. Biswas, R. Atta-Fynn, S. Chakraborty, D. A. Drabold, *J. Phys. Condens. Matter* **19**, 455202 (2007).
8. K. Laaziri *et al.*, *Phys. Rev. B* **60**, 13520 (1999).
9. S. Roorda *et al.*, *Phys. Rev. Lett.* **108**, 255501 (2012).
10. G. T. Barkema, N. Mousseau, *Phys. Rev. B* **62**, 4985 (2000).
11. D. L. Williamson *et al.*, *Appl. Phys. Lett.* **67**, 226 (1995).
12. D. C. Jacobson, J. M. Poate, G. L. Olson, *Appl. Phys. Lett.* **48**, 118 (1986).
13. U. Köster, *Phys. Status Solidi* **48**, 313 (1978).
14. K. F. Kelton, A. L. Greer, C. V. Thompson, *J. Chem. Phys.* **79**, 6261 (1983).

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