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Fluctuation microscopy analysis of amorphous silicon models

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ABSTRACT

Using computer-generated models we discuss the use of fluctuation electron microscopy (FEM) to identify the structure of amorphous silicon. We show that a combination of variable resolution FEM to measure the correlation length, with correlograph analysis to obtain the structural motif, can pin down structural correlations. We introduce the method of correlograph variance as a promising means of independently measuring the volume fraction of a paracrystalline composite. From comparisons with published data, we affirm that only a composite material of paracrystalline and continuous random network that is substantially paracrystalline could explain the existing experimental data, and point the way to more precise measurements on amorphous semiconductors. The results are of general interest for other classes of disordered materials.

1. Introduction

While FEM has been repeatedly confirmed as a powerful "fingerprint" for medium-range order in amorphous materials, it remains difficult to simply interpret the results. For example, if we focus on the archetypal amorphous silicon, and the paracrystalline [1] versus continuous random network (CRN) [2] models, several questions have been difficult to separate. The paracrystalline model assumes a conglomerate of small crystallites that are imperfect. In fact in the classic model where the amorphous material is a compact of paracrystallites the degree of order decays as a function of distance from any atom [1]. Real models of nanocrystals have distortions that increase near the grain boundaries and the decay length is approximately the same as the length scale of the grain size. However, it is also possible that the real material is a composite of paracrystals embedded in a random network. In that case key parameters would be the grain-size or correlation length and the volume fraction of paracrystalline material. Using the "ansatz" model proposed by Gibson et al. [3], several authors have had consistent results in measuring the correlation length from the dependence of the normalized intensity variance on the probe size (also known as "variable resolution microscopy") e.g. Bogle et al. [4]. There has been controversy about the volume fraction. Some authors not using FEM have claimed that, while ordered regions may be present, they are only in trace concentrations (e.g. Wang et al. [5]). It has thus become important to develop the FEM technique so that it can separately determine; 1) the structure of ordered regions; 2) the size or correlation length of the order; and 3) the volume fraction of ordered regions. Based on a variety of previous works, and some new ideas discussed here, we feel confident that these should be independently measurable by experiment. We support our claim in this paper through simulations on a variety of models for amorphous silicon. We expand on these three issues next

1) The "crystal structure"[1] of ordered regions.

From the pioneering work of Kam [6] it is known that the correlation function,

$$C = \frac{\langle I(\underline{k}_1)I(\underline{k}_2)\rangle}{\langle I(\underline{k}_1)\rangle\langle I(\underline{k}_2)\rangle},$$

recovers the single-particle correlation function, assuming a distribution of randomly-oriented ordered clusters. The "correlograph", introduced for electron microscopy by Gibson and Treacy [7], based on ideas of Cheng et al. [8], is the azimuthal autocorrelation function of C. We previously noted, in contrast to the related x-ray approach of Wochner et al. [9], that the ensemble-averaged C was essential to reveal single particle correlation functions. Probing individual images before averaging in a correlograph can be interesting, but coincidental and unreal

[1] We use quotes around "crystal structure" because there is no long-range order constraint, and non-periodic packing symmetries, such as dodecahedral, are possible.

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symmetries can be displayed due to particle overlap. These are averaged out in the correlograph [7]. The correlograph is effective for directly revealing the structure of the average unit, such as the structure of paracrystals. We have shown, and elaborate here, that the paracrystalline model, amongst those models currently proposed, is the only model that comes close to fitting the experimental correlograph.

The FEM normalized intensity variance plot can be used to deduce the crystal structure through simulations, but this is indirect and places a premium on the construction of comprehensive families of physically realistic structures. Experimentally-constrained Monte Carlo approaches using FEM variance appear to be effective, requiring very little a priori model building [10–12]. In all cases the paracrystalline structure was found to be a good fit to data and, in at least one case, it was the only acceptable fit [11]. In one study [10], a CRN model that contained voids was found to fit also (vide infra). In another study [12] a complication arose because the procedure for obtaining the normalized variance was inconsistent between experiment and modeling (vide infra). However, we will see that FEM data obtained with only one probe size, without knowledge of scaling, is not sufficiently constraining. The fluctuation map [3] (i.e., the 3-dimensional plot of normalized variance against scattering vector and probe size) is far more constraining, but has not yet been used to our knowledge in experimentally-constrained energy-minimization. Furthermore, the correlograph contains much more information, about symmetry for example, and should also be considered as an experimental constraint for minimization.

2) The "crystal" size, or correlation, length

Given the existence of ordered regions, measurement of their size or correlation length Λ is among the most reliable and widely used experimental methods. Gibson et al. [3] proposed an "ansatz" model for the measurement of the correlation length, the validity of which has repeatedly been demonstrated experimentally and by simulation e.g. [4,13]. The ansatz model approximates the simulation of variance by assuming that the contributions arising from probe size (beam convergence) and scattering vector are decoupled – literally, a separation of variables where we declare that $V(r_p, k) \equiv R(r_p)K(k)$. This has been shown to be an excellent approximation when the probe size is larger than the correlation length, i.e. $r_p \gg \Lambda$. In this paper we also demonstrate that an even more direct measurement of the correlation length can be obtained by identifying the probe size that yields the maximum overall variance. This occurs at $r_p \approx \Lambda$. For the case of static amorphous silicon models, we find that experimentally observed fluctuation maps are consistent only with a paracrystalline structure – neither the CRN nor the CRN with voids show the characteristics of medium-range order. Nor do they show a peak and decay in the variance versus probe size. Of course this does not rule out the possibility of a composite paracrystalline and CRN-type model, and that question is addressed next.

3) Volume fraction of ordered regions

This has proven to be the most difficult to measure reliably. While theoretically there is a strong correlation between the fraction of order and the magnitude of the variance peaks, there are suspicions that "decoherence" effects strongly reduce these experimental variance amplitudes in an as-yet unpredictable way [14,15]. The structure details would also affect the variance peak heights so that questions 1 and 3 are difficult to decouple. Several approaches have been suggested. Bogle et al. [4] observed a correlation between the relative heights of the first and second variance peak, at least for Si, but this depends also on the probe size. Yi et al. [16] proposed detailed fitting of peak heights and probe size, based on a reasonably sophisticated dispersed crystal model of a composite, but this appears vulnerable to details of the structure (e.g. faulting and intergrowths).

An intriguing, and highly informative, metric to examine is the correlograph. Gibson et al. [7] showed that the characteristics of correlographs were affected significantly by volume fraction, and used that sensitivity to estimate a paracrystalline volume fraction of greater than 50% in a typical sputtered amorphous Si sample. On the other hand, Raman data has been used to suggest a much smaller volume fraction [5]. Cheng et al. [8] proposed diffraction intensity cross-correlations (covariance) as a more informative measure than the simple variance, which measures the intensity autocorrelation. Li et al. [17] went further and proposed cross-correlations as an approach to study volume fraction. Below we suggest that the variance of the correlograph looks like a powerful and independent method to determine volume fraction on the assumption (which can be verified by conventional diffraction) that there is a random orientation distribution of paracrystals.

From our modeling of amorphous silicon it seems clear that the paracrystalline structure (possibly diluted with CRN) is the only model that can explain FEM data, including correlographs, experimentally observed in amorphous silicon. This assertion is also consistent with experimentally-constrained energy minimization [11]. The 2-body function is not discriminating enough to distinguish these models, as has already been clearly demonstrated [11,12]. However, detailed comparison with fresh experiments, including measurements of the correlograph variance, is desired to make more precise conclusions.

2. Theoretical and simulation background

Simulations were carried out including the curvature of the Ewald sphere under the kinematical approximation. To deal with small model sizes simulations were carried out at 20 kV accelerating voltage, which replicates the conditions of multiple scattering at 100–200 kV in a typical thickness of 10–20 nm. For comparison, full multi-slice calculations and weak-phase object calculations were also made using the same Mathematica-based software package written by the first author, JMG. In general we saw reduced peak heights, but no major changes in thin samples arising from multiple scattering, and little accelerating voltage dependence apart from Friedel's-law issues arising from the curvature of the Ewald sphere. Models up to 20 nm in size were simulated. In order to expand the size of smaller models, these were rotated through 90° , shifted and assembled into a larger cube, from which cubes of size $\sqrt{3}$ times the original model size could be carved after random re-orientation. About 1000 image/diffraction calculations were carried out for each model and for each probe size.

Variance is calculated by the technique listed as number 4 ("Annular mean of variance image") by Daulton et al. [18],

$$V = \frac{\left\langle \left\langle I^2(\underline{k}) \right\rangle_r \right\rangle_\phi}{\left\langle \langle I(\underline{k}) \rangle_r^2 \right\rangle_\phi},$$

where $< >_\phi$ is the average over the azimuthal angle, ϕ, and the average, $< >_r$, is over the ensemble (that is, over different probe locations, $\mathbf{r}$).

This method produces much higher variance overall than the first method enumerated by Daulton ("Normalized variance of the annular mean"), which evaluates the angular average of $I(\underline{k})^2$ before averaging over the ensemble, and so method 4 is much preferable to method 1. We should note here that method 1 was initially used in hollow-cone dark-field in the earliest FEM work because the angular averaging automatically occurred. The angular averaging was originally seen as an advantage as it provided a way to adjust the illumination spatial coherence, and the method was