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MODELS OF PARACRYSTALLINE SILICON WITH A DEFECT-FREE BANDGAP

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Recently there have been attempts to create physically realistic models for para/polycrystalline silicon (containing randomly oriented c-Si grains embedded in a disordered matrix) by means of empirical molecular dynamics. These models demonstrate acceptable geometrical and vibrational properties but fail to reproduce the correct electronic bandgap due to the presence of numerous "frozen-in" coordination defects. We propose a new procedure for the preparation of more realistic models of paracrystalline silicon based on a modification of the bond-switching method of Wooten, Winer and Weaire. Our new method allows us to create interfaces between the crystalline and disordered phases of Si with no coordination defects. Models with 400, 1000, and 4000 atoms were constructed. All the models have ~10 atomic % of the crystalline phase. The two smaller models contain a single crystalline grain and the largest model contains 4 randomly oriented grains. Our models show good geometrical and vibrational properties compared to good continuous random networks models of a-Si and also display excellent optical properties, correctly reproducing the electronic bandgap of amorphous silicon.

Recent fluctuation electron microscopy experiments have shown signatures of ordered structure at length scales on the order of 10 Å in as-deposited amorphous semiconductor thin films.[1,2] Structure at this length scale in Si is called medium-range order (MRO). Computer modeling provides a powerful tool for investigating the structural properties of semiconducting materials and understanding the degree

of geometrical structural order in them. Previously we have conducted numerical simulations of the MRO for two families of models:[3] continuous random network (CRN) models, constructed by Barkema and Mousseau,[4] and paracrystalline models developed by Keblinski *et al.*[2,3] The paracrystalline models contain randomly oriented topologically crystalline silicon grains[5] embedded in a more disordered silicon matrix. These grains are strongly strained so few of the atoms sit precisely on their crystalline lattice positions, making the model as a whole exhibit a pair correlation function that is a good match to experimental results for a-Si. The CRN models displayed little or no MRO, while the results obtained for paracrystalline models were in reasonable agreement with the fluctuation microscopy experiments.[2]

However, only a model that agrees with a whole set of experiments (structural, optical, and vibrational) can reliably describe a semiconducting material.[6] While complying with structural and vibrational experimental data, the earlier Keblinski-method paracrystalline models do not have acceptable electronic properties.[3] The empirical MD "quench from the melt" procedure used with the Stillinger-Weber potential for the preparation of these models[7] creates an *unphysically* large density of coordination defects in the network. This creates localized electronic states which fill the bandgap, making these models look more like bad metals than semiconductors.

The aim of the computational project presented here is to create models of paracrystalline silicon that not only agree with fluctuation microscopy experiments but also correctly reproduce the semiconductor bandgap. In order to do that we employed the bond-switching algorithm of Wooten, Winer and Weaire,[8] modified by Barkema and Mousseau,[4] which produces the best CRN models in the field. In the method of Barkema and Mousseau, atoms are randomly placed into a cubic box with periodic boundary conditions at crystalline density and subject to the condition that no two are too close together. The atoms are then connected by "artificial" bonds[a] in such a way that a perfectly tetravalent network is created. This network is then subjected to a large number of bond-switching transpositions followed by local structural rearrangements which result in a highly relaxed, low strain configuration.

In our approach we generally follow this procedure, but before randomly putting atoms into the box we position a crystalline grain (or a set of grains, randomly oriented with respect to each other) inside it. The grains are created by starting with a spherical section of crystalline Si and keeping only those atoms that have two and more nearest neighbors which *also belong* to the grain. For reasons described below we also require the grain to contain an even number of atoms that have exactly three nearest neighbors.

When the grain is positioned inside the box, a nearest neighbor list is created for it and 2- and 3-fold coordinated atoms are identified. After the grains are set in place the remaining volume is randomly seeded with "matrix" atoms, which are

[a]These bonds exist only in a form of a neighbor list constructed for each atom. They can be unphysically long.

then connected into a perfectly 4-fold network. The grains, which contain some atoms that need to form additional bonds, are at this point disconnected from the disordered matrix and need to be incorporated into it, but in such a way that all the atoms have exactly four nearest neighbors. This is done in two steps. First, for any 2-fold grain atom the closest bonded pair of matrix atoms is found, the bond between the matrix atoms is broken and two new bonds between each of the matrix atoms and the grain atom are formed. Second, for each 3-fold grain atom the closest additional 3-fold grain atom is found, then the bonded pair of amorphous atoms closest to both 3-fold grain atoms is found, and the bond between these atoms is broken and two new 3-fold grain atom/matrix atom bonds are formed. This requires an even number of 3-fold grain atoms. The algorithm creates a number of unphysically long bonds, but these high energy bonds are sure to be broken during the bond-switching transpositions.

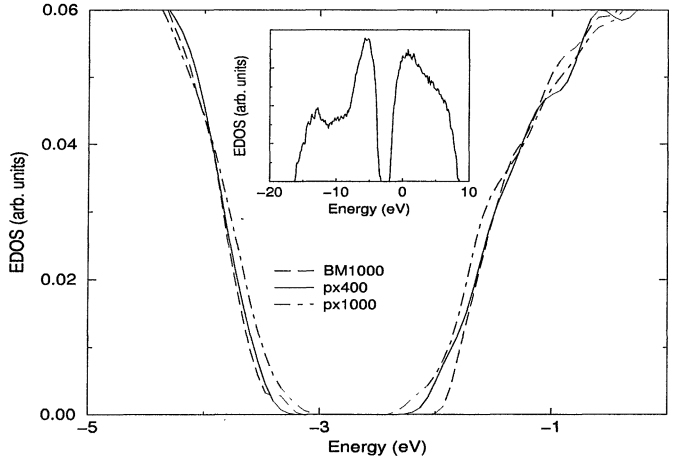

Figure 1: The bandgap region of the electron density of states (EDOS) for px400, px1000 and BM1000 models. The total EDOS is shown on the insert.

After the perfectly 4-fold network, containing both the crystalline grains and the matrix is constructed, it is subjected to the bond-switching moves in order to minimize system's energy. Unlike the method of Wooten, Winer and Weaire, we impose a number of "bond breaking" constraints on our system, aimed at preserving the crystalline topology of the grains during energy minimization. In particular, bonds between grain atoms are not allowed to break; only bonds between a grain atom and a matrix atom or between two matrix atoms can be broken. An additional constraint is imposed on the positions of the grain atoms: during the initial phase of the relaxation while strain in the system is relatively high, the grain atom coordinates are fixed. The grains to this point are truly crystalline. When the energy of

the system with fixed grain atoms reaches its minimum, the grain atoms are allowed to move and the energy is minimized again.

Using this procedure we have constructed three models of paracrystalline silicon. The first 400 atom model, called px400, has one grain consisting of 44 atoms, positioned in the center of a 20 Å cubic box. This model was created mostly for testing purposes. The second model, px1000, has 1000 atoms, out of which 86 belong to a single grain placed in the center of a cubic box with a side of approximately 28 Å. The third 4000 atom model, px4000_4, has 4 crystalline grains of roughly the same size (100 atoms), randomly oriented with respect to each other and positioned at the vertexes of a tetrahedron the center of which lies at the center of the cubic supercell, which has a side of approximately 43 Å. All the models are 100% 4-fold coordinated.

In Fig. 1 we present the bandgap region for the electron density of states (EDOS) of px400, px1000 and a 1000 atom CRN model of Barkema and Mousseau called BM1000 here. The total EDOS is shown on the insert; at this scale it is indistinguishable for all three models. The EDOS for all the models has been calculated with FIREBALL local-basis *ab initio* tight binding code.[9] Our calculations show that our paracrystalline models have a clean bandgap comparable in width with the gap for the best CRN models for a-Si.

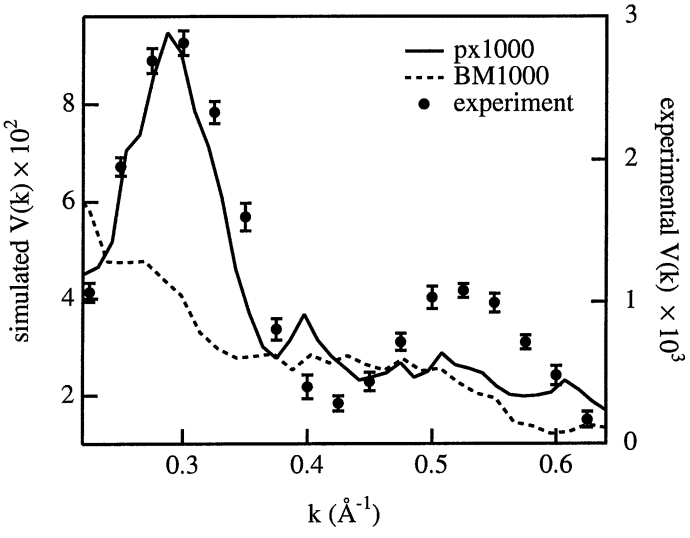

Figure 2: Fluctuation electron microscopy simulations for px1000 and BM1000 models.

In Fig. 2 we shows the fluctuation electron microscopy signal[1,3] $V(k)$ calculated for the models and measured for a sputtered a-Si thin film[10]. $V(k)$ is the variance of dark-field electron micrographs acquired with mesoscopic (~15 Å) resolution and provides a measure of MRO. k sets the diffracting condition probed in the images.

A large $V(k)$ with significant structure in k indicates a physical structure with significant MRO, while a small $V(k)$ with little structure in k is indicates a structure with little or no MRO.[11] BM1000 shows the mostly featureless $V(k)$ typical of CRN models. px1000 shows the prominent peak at $k = 0.3$ Å^{-1} that is observed in the data and is a measurable signature of paracrystallinity. It does not reproduce the second peak at $k = 0.55$ Å^{-1} seen in the data, indicating that it has somewhat less MRO than this sample. The degree of MRO in paracrystalline models can be varied by changing the volume fraction and density of the topologically crystalline grains, which will be the subject of future simulations. Both models show a much higher variance than experiment due to their small size compared to the 200 Å thickness of the sample. We have also calculated the vibrational density of states, the pair correlation function $g(r)$, and the bond-angle distribution for our models which are all in good agreement with experimental results for a-Si.

Our results presented in Figs. 1 and 2 show that we have succeeded in creating a family of models for paracrystalline Si which not only have structural MRO in qualitative agreement with experiment, but also have good electronic and geometrical properties. We believe that the evidence presented here proves that our models can serve as a reasonable description for tetravalent semiconducting material, containing topologically crystalline grains embedded in a more disordered medium.

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