Topology of Amorphous Tetrahedral Semiconductors on Intermediate Length Scales

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Using the recently proposed "activation-relaxation technique," we develop a structural model for *a*-GaAs almost free of odd-membered rings, i.e., wrong bonds, having an almost perfect coordination of four. This model is found to be superior to structures from tight-binding or quantum molecular dynamics simulations. Comparing with *a*-Si, as described by a Polk-type continuous random network, we find that the cost of wrong bonds is such that the two materials should have different topologies. Our study provides direct information on the intermediate-range topology of amorphous tetrahedral semiconductors. [S0031-9007(97)02522-2]

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The structure of amorphous materials on short and intermediate length scales remains largely unresolved in spite of decades of work on the problem [1–7]. While diffraction experiments can *in principle* provide the desired information, they still lack the sensitivity necessary to distinguish between various possible conformations of the structure. They must be backed up, therefore, by accurate structural models in order to allow a meaningful interpretation of the data. Models, however, are difficult to construct because they require an accurate description of the interatomic forces, which in turn limits the time scale over which simulations can be carried out. Since glasses relax very slowly, this is an extremely serious problem that can only be addressed through the use of judicious optimization methods.

Amorphous tetrahedral semiconductors, either elemental or compound, are potential candidates for the fabrication of micro- and opto-electronic devices. Advances in this area have, however, been hindered by the limited understanding of their structure, and thus electronic properties, even at the most elementary level. For instance, in the case of amorphous silicon (*a*-Si), the average number of nearest neighbors is still not known precisely, even though evidence (experimental and theoretical) accumulates that it is very close to 4. Thus, it would appear that the fundamental "building block" of these materials is a tetrahedron—a single atom and its four nearest neighbors arranged in a pattern that closely resembles that found in the crystals. It is in the arrangement of those tetrahedra, i.e., on intermediate (and larger) length scales, that differences between amorphous and crystalline materials arise [5,6] and on which, therefore, attention should be focused.

The case of compound III-V materials, such as GaAs and InP, is more problematic because the building blocks are not as clearly defined. Indeed, the chemical identity of the atoms constituting the tetrahedron may vary: While in the zinc-blende crystal each atom of a given species is surrounded by four atoms of the other species, this is not necessarily so in the amorphous material, because of disorder. Thus, there is a possibility that "wrong bonds" are present in the amorphous phase, i.e., bonds between like atoms. This will result in some distortion of the tetrahedra, and therefore on their relative arrangement. However, III-V compounds are partly ionic and the cost in energy of wrong bonds is expected to be significant; the number of them, therefore, will be determined by the competition between elastic deformation and chemical disorder. There is currently no experimental method for measuring this number in *a*-GaAs [8].

In this Letter, we aim at determining the optimal density of wrong bonds in amorphous III-V semiconductors through a comparison with elemental materials, where such defects do not exist. We illustrate our ideas by considering the prototypical materials *a*-Si and *a*-GaAs. We note first that wrong bonds are closely related to the presence of "odd-membered rings" in the structure, i.e., closed paths between an atom and itself containing an odd number of bonds. Evidently, only even-membered rings are present in zinc-blende crystals. Also, it is always possible to "decorate" an amorphous network containing only even rings with two types of atoms such that there are no wrong bonds. Thus, we may formulate the question in the following manner: are odd-membered rings energetically favorable, i.e., necessary to the stability of amorphous tetrahedral semiconductors, be they elemental or compound? And is it possible to construct a tetrahedrally bonded amorphous model *without* odd-membered rings?

Anticipating our results, we find that it is indeed quite possible, albeit difficult, to construct such an all-even-ring network. For elemental materials, however, there is nothing to be gained by such a constraint and the resulting network is therefore *not* appropriate. In contrast, a model that contains odd rings is found to be inappropriate for III-V materials, because of the cost in energy associated with wrong bonds. Thus, *odd-membered rings must be present in a-Si and absent in a-GaAs.* This constitutes, to our knowledge, the first evidence of a *topological difference* (i.e., without regards to chemical identity) between the two materials. We find, also, that the presence (or absence) of odd-membered rings is extremely difficult

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to extract from such quantities as the radial distribution function or distribution of dihedral angles, and therefore realistic structural models are a necessity for proper interpretation of experimental data.

In order to establish these results, we proceed as follows. Using the "activation-relaxation" technique [9] (see below), we construct two "generic" continuous-random networks (CRN) [1] with periodic boundary conditions: The first, CRN-A, possesses the same attributes as an infinite Polk model [2] as constructed by Wooten, Winer, and Weaire (WWW) [4], and thus contains odd-membered rings. (In fact, the WWW algorithm consists in amorphizing a crystalline lattice through, precisely, the introduction of odd rings.) Our second model, CRN-B, was constructed with the constraint that odd rings be absent, and thus corresponds to an infinite Connell-Temkin [3] computer model. (The Connell-Temkin model is a hand-built, 238-atom, mechanical model with free surfaces.) Both CRN-A and CRN-B were then "decorated" with either Si or Ga and As—so that we have, altogether, four different structural models—and relaxed to their equilibrium state using conjugate gradients with forces derived from tight-binding (TB) potentials.

It is important to note that there have been numerous attempts at simulating the structure of *a*-Si using molecular dynamics (MD) and a variety of interatomic potentials — from empirical to fully *ab initio.* All lead to a sizable proportion of odd-membered rings. For GaAs, for which there exists no satisfactory empirical potential, calculations have been carried out using either TB [10,11] or Car-Parrinello (CP) [12] MD. Again, here, odd-membered rings—and therefore wrong bonds—are present, in an amount which appears to be quite large (10–12%). Since the period of time that can be simulated using such approaches is inevitably short (of the order of 10–100 ps), there remains a possibility that the large density of defects is the result of incomplete relaxation. In order to resolve this point, a different, much more efficient, optimization method must therefore be used to prepare the structural models.

The activation-relaxation Monte Carlo technique (ART), recently proposed by Barkema and Mousseau [9], provides a powerful and efficient way of searching configuration space for a global minimum. Full details of the method can be found in Ref. [9]; it can be summarized as follows: Starting with a random distribution of atoms, the system is first relaxed to the nearest local minimum on the potential energy surface using standard minimization techniques. It is then "activated" by pushing it to a neighboring saddle point along a valley, i.e., a path of minimal energy. The system is then relaxed, again, to the nearest local minimum, and the process iterated until a global minimum is found.

The potential energy for the ART preparation of CRN-A was taken to be of the Stillinger-Weber form [13], appropriate to Si, except that the strength of the bond-bending term was increased by 50% so as to provide a better description of the structure of the amorphous phase [9]. For CRN-B, the same potential was used—the lattice parameters of *c*-Si and *c*-GaAs are nearly the same—but an *ad hoc* repulsive term between like atoms was added in order to describe the chemical order

$$E_{\mathrm{rep}} = \sum_{\langle ij \rangle} A_{ij} \epsilon \left[1 + \cos\left(\pi \frac{r_{ij}}{s_{ij}} \right) \right], \tag{1}$$

where the sum is over all pairs of atoms, ϵ is the Stillinger-Weber energy parameter, $A_{ij} = 1.2$ for like particles and zero otherwise, and $s_{ij} = 3.6$ Å. Both CRN-A and CRN-B models contain 216 atoms in a cubic cell with periodic boundary conditions. The ART relaxation took about three days on a R8000 workstation for CRN-A and about a week for CRN-B. This should be contrasted with several weeks for a TB simulation of a 64-atom system on a workstation or a CP simulation on a state-of-the-art parallel supercomputer.

After reaching a stable configuration in the ART simulations, the two models were made material specific by further relaxing under TB potentials. *Both* CRN-A and CRN-B models were thus relaxed with *both* the Goodwin-Skinner-Pettifor TB potential for Si [14] and the Molteni-Colombo-Miglio TB model for GaAs [10]. In the case of model CRN-A-GaAs, it is necessary to "label" the atoms. This was done by assigning identities at random, then iteratively minimizing the number of wrong bonds by a "label-switching" process. This led to a proportion of wrong bonds of approximately 14%, corresponding to the theoretical value for optimal ordering on a Polk-type network [15].

It is important to note that the exact form of the empirical potentials used in the ART simulations is, to some extent, unimportant, as long as they lead to physically reasonable structures, e.g., with a coordination of about four, appropriate to tetravalent semiconductors. (Hence the modification to the Stillinger-Weber potential—Ref. [9].) This is true because the "generic" ART models were, in a second and final stage, submitted to further relaxation using realistic TB potentials. The suitability of the approach, and, in particular, the value of the potentials used to prepare the generic models, is thus justified *a posteriori* in terms of stability and configurational energies of the final TB-relaxed structures, as we demonstrate below.

The energies of our four different TB-relaxed models are listed in Table I. It was observed that the topology of the models is little affected by the final TB relaxation, indicating that the ART simulations effectively took the systems very close to the global minimum.

Considering Si first, it is clear that the two types of networks are essentially equivalent in energy. However, because of the additional constraint preventing the existence of odd rings in CRN-B-type models, there exists considerably fewer ways for an ensemble of Si atoms to arrange in a CRN-B pattern than in a CRN-A pattern. Thus, on the basis of entropy, CRN-A models are favored in the case elemental semiconductors.

TABLE I. Energy (eV/atom) of the two networks relaxed with TB. For GaAs, we also give the results from the TB-MD simulations of Seong and Lewis (SL), Ref. [11].

	TB parameters		
Network	Si	GaAs	GaAs (SL)
CRN-A	−13.172	−13.450	
CRN-B	−13.163	−13.561	−13.450
Crystal	−13.389	−13.802	−13.802

For GaAs, now, we find the opposite result: As indicated in Table I, it is much more interesting for this material to adopt the CRN-B structure, free of odd-membered rings and therefore wrong bonds, than the CRN-A structure. Thus, the energy gained by the elimination of wrong bonds—0.11 eV/atom, corresponding to an activation temperature in excess of 1300 K, i.e., close to melting—should *largely compensate* the entropic cost of eliminating odd-membered rings.

The structural properties of the two optimal models—CRN-A for Si and CRN-B for GaAs—are summarized in Table II. Evidently, for Si, we achieve an excellent-quality model, with an *almost perfect coordination* of 4, sharply peaked at this value, i.e., a structure which, while amorphous (see below), is *almost free of topological defects.*

Likewise, our CRN-B-GaAs model, with less than 4% of wrong bonds and an almost perfect coordination of 4, is by far the closest realization of a perfect, infinite, Connell-Temkin-like CRN ever achieved. The present model compares very favorably with experimental static-structure-factor data [8], as demonstrated in Fig. 1 as well as with the results from TB-MD or CP-MD simulations, as can be seen in Tables I and II. Using MD and exactly the *same* TB model, Seong and Lewis (SL) [11] obtained an amorphous model whose energy lies significantly *above* that of the present model. (It is not possible to compare energies from the CP [12] and TB models.) The density of wrong bonds in the present model is also much lower than that obtained in the TB-MD and CP-MD simulations. In addition, the distribution of coordination numbers here is sharply peaked at about 4, while it is much broader in the other models. These results suggest that the usual melt-and-quench MD approach may not yield a fully relaxed configuration, while ART simulation approaches this point much more effectively. ART relaxation under TB or first-principles forces is, however, presently not available.

TABLE II. Distribution of coordination numbers Z and average value, nearest-neighbor distance r_{NN}, and density of wrong bonds (WB) in our two optimized models, compared with other models—SL: TB-MD of Ref. [11]; CP: CP-MD of Ref. [12]. For CRN-A, the density of wrong bonds is that of the GaAs-decorated lattice as discussed in the text.

	CRN-A-Si	CRN-B-GaAs	GaAs (SL)	GaAs (CP)
$Z = 3$	0.032	0.051	0.242	0.219
$Z = 4$	0.954	0.944	0.598	0.781
$Z = 5$	0.014	0.005	0.129	0
$Z = 6$	0	0	0.024	0
$Z = 7$	0	0	0.007	0
$\langle Z \rangle$	3.981	3.954	3.94	3.83
r_{NN} (Å)	3.0	3.0	3.0	2.8
WB (%)	14.2	3.9	12.2	10.0

It is of interest to examine our models in terms of a possible structural signature of the presence of odd-membered rings (or wrong bonds), not based on knowledge of the system at the atomic level, that would provide (e.g., from experiment) information on intermediate-range correlations. One possibility is the radial distribution function, $G(r)$, which we show in Fig. 2 for our two best models, CRN-A-Si and CRN-B-GaAs. In spite of the fact that these models differ markedly in their medium-range topology, as we have seen, *the differences between the two curves are clearly very small.* This is a bit of a surprise in that it contradicts the current view that differences between the two structures should be clearly visible beyond the second peak [16]. In fact, it was argued by Connell and Temkin [3] that the signature of a CRN-B-type network would be, in comparison to CRN-A, (i) a broader second peak, (ii) a deeper minimum between the 2nd and 3rd peak, as well as (iii) a shifted and (iv) broader 3rd peak. This is not what we find here, as can be seen in Fig. 2: although there are some differences—not necessarily in agreement with the above criteria—they remain small and could easily be within the accuracy of the models. Thus, $G(r)$ exhibits no clear signature of the presence of odd-membered rings (even though the differences we observe between the two structures are within experimental resolution).

We show, in the inset to Fig. 2, the distribution of dihedral angles (i.e., between second nearest-neighbor bonds) in our two models. In the Connell-Temkin model [3] (corresponding to our CRN-B), staggered configurations

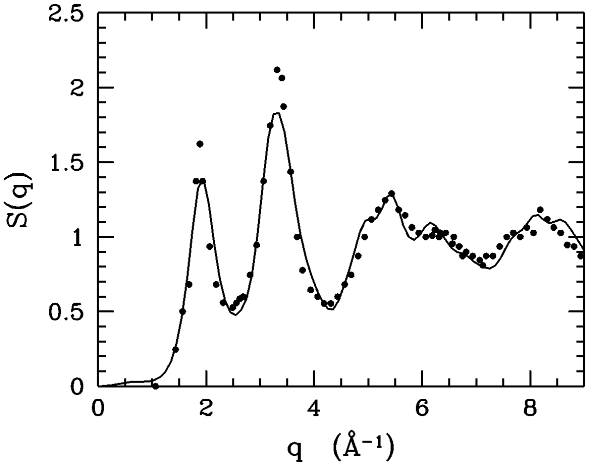

FIG. 1. Total static structure factors for the CRN-B-GaAs model (full line) and from experiment (dots, Ref. [8]).

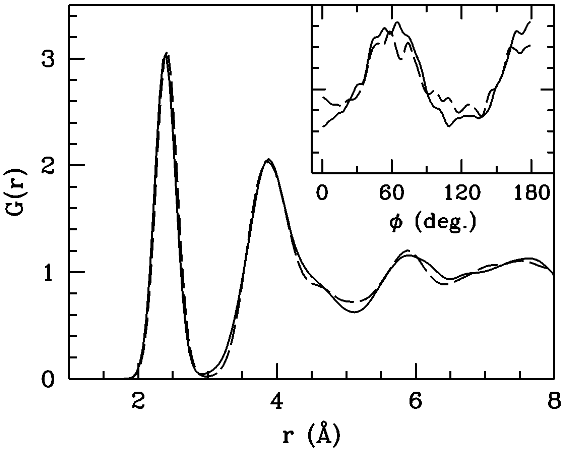

FIG. 2. Radial distribution functions for the CRN-A-Si (dashed line) and the CRN-B-GaAs (full line) models. The GaAs curve has been rescaled along r so as to match the first-neighbor peak of Si. The inset shows the distribution of dihedral angles for the same two models.

($\phi = 60°$) are found to be much more probable than in the usual Polk CRN [2], which contains odd-membered rings. Our models demonstrate that the differences are, in fact, very small and again not significant. In particular, both models seem to like staggered configurations with comparable probability. Thus, the distribution of dihedral angles is *not* a good measure of intermediate-range correlations.

It follows from the above discussion that the nature of intermediate-range correlations cannot easily be determined with current experimental techniques, so that *atomic-level* models, which have the power to resolve different possible structures yielding the same structure factor on the basis of total-energy calculations, remain the only resort for proper interpretation of experimental data. Thus, while such a method as "reverse Monte Carlo" (Ref. [17]) can provide almost perfect agreement with diffraction data, it clearly cannot resolve two structures that yield comparable structure factors because it does not include a total-energy component.

In conclusion, using the newly proposed activation-relaxation technique, we have been able to construct a structural model appropriate to a-GaAs that contains almost *no wrong bonds* (i.e., is free of odd-membered rings) with an almost *perfect coordination* of four. This Connell-Temkin-like model is found to be superior, from both structural and energetic viewpoints, to structures obtained from TB and quantum MD simulations, at a fraction of the computational cost. In contrast, in the elemental system a-Si, where wrong bonds do not exist, the traditional Polk-like CRN is found to be appropriate. Our study thus provides, for the first time, direct and solid information on the nature of intermediate-range correlations in amorphous tetrahedral semiconductors, and, in particular, establishes clearly that these materials cannot be described by a single topological model. It underlines, moreover, the fact that state-of-the-art total-energy computer models are essential for reliable interpretation of experimental diffraction (and other) data. Finally, our study gives unambiguous evidence for the ability of ART to yield the optimal structure of strongly disordered systems, thus opening a new way into "complexity."

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