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Modeling the structure of amorphous tetrahedrally coordinated semiconductors. I[*]

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A continuous random network (CRN) consisting of 238 tetrahedrally coordinated atoms has been constructed so as to contain only even-membered rings. The structural properties of the model (density, bond-length distribution, bond-angle distribution, dihedral-angle distribution, radial distribution function) are in satisfactory agreement with experimental results for amorphous Ge, Si, and the III-V compounds. The present model eliminates the conflict between the Polk CRN model, which contains approximately 50% of odd-membered rings, and experimental photoemission, optical, and heat-of-crystallization results for the amorphous III-V's, which indicate the absence of a significant number of such rings. Comparison of the CRN models suggests that a determination of the experimental dihedral-angle distribution of each material is very important for a unique definition of its structure.

The problem of modeling the structure of amorphous Si and Ge has been discussed in several recent papers.[1,2] It was shown that the continuous random network (CRN) built by Polk[3] and adjusted to reduce bond-length variations has a radial distribution function (RDF) that compares satisfactorily with experiments on Si and Ge, thus confirming the earlier but less conclusive work of Polk[3] and Shevchik and Paul.[4] An important and characteristic part of the Polk model is the considerable number of odd-membered rings, which for binary compounds would necessarily lead to the existence of "wrong bonds." Experimentally, Shevchik and Paul showed that the RDF's of all of the III-V compounds that they measured were very similar to those of Si and Ge, reflecting tetrahedral bonding, and that some of them had a wider distribution of nearest-neighbor distances.[5] They therefore suggested that these latter data were generally consistent with wrong bonds in the proportion found in the Polk model. Such numbers of them, however, are expected to produce observable effects in the electronic density of states of both the valence-band and core levels and in the heat of crystallization, but such effects have not been seen.[6-8] Other experimental observations favoring the existence of wrong bonds in the III-V's are the measured energy gaps and the energy-gap pressure and temperature coefficients,[9] which, in contrast to Si and Ge, are very different from those for the crystal; however, only a small fraction of wrong bonds is required to explain these experiments. This article describes a tetrahedrally coordinated CRN that has no odd-membered rings and no wrong bonds when the atoms of a binary compound are assigned to lattice positions so as to avoid such bonds. Its structural parameters provide new insights into the question of the uniqueness of the amorphous structure and suggest what experimental tests could establish the existence of odd-membered rings, or at least their relative frequency of occurrence in different materials.

A roughly spherical model was constructed from 238 plastic tetrahedra interconnected by aluminum rods. Noncrystallinity was achieved through variations in the tetrahedral angle and through the relative rotation of adjoining tetrahedra into configurations other than the staggered or eclipsed. The model had no broken bonds and no odd-membered rings. It appeared that whenever a surface configuration occurred that could lead to a fivefold or sevenfold ring, a reorganization of the adjacent surface atoms would eliminate it. Later, it will be seen that this type of reorganization apparently minimizes the number of eclipsed configurations in the network, an important criterion in the growth of a real system.[10]

The coordinates of each atom were measured and the distances to the coordinating atoms determined. A computer program was then used to reposition the atoms so that the variance of the bond lengths was equal to that due to static distortion measured experimentally in amorphous Ge.[11] The new coordinates, which will be published elsewhere, were then used to determine the structural parameters of the model.

The density was determined as a function of distance from the center of mass, and the RDF of the model, $J_{\mathrm{mod}}(r)$, was calculated. The RDF of an infinite model was then obtained by dividing $J_{\mathrm{mod}}(r)$ by the spherical characteristic function $\gamma_0(r/2a) = 1 - 1.5(r/2a) + 0.5(r/2a)^3$, where $a = 4.47 r_1$ is the effective radius of our approximately spherical model and r_1 is the bond length. $\gamma_0(r/2a)$ is the probability that a point at a distance r in an arbitrary direction from a given point in a sphere of radius a will itself also be in the sphere.[12] The corrected RDF was then broadened, using experimentally determined thermal broadening parameters,[11] to give the final RDF, $J(r)$. Partial RDF's,

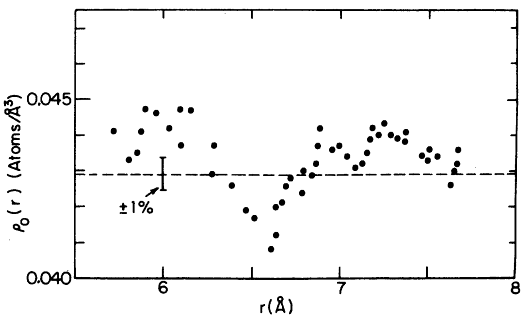

FIG. 1. Density of the present model as a function of radius. The horizontal line is the average density of diamond crystalline Ge scaled to a 2.47-Å bond length.

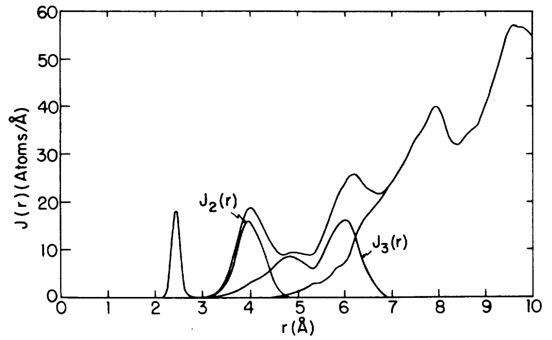

FIG. 3. Radial-distribution function of the present model, $J(r)$, and its n-bond neighbor distributions $J_n(r)$, for $n=2$ and 3. Subtracting $J_3(r)$ from $J(r)$ yields the leading edge of the sum of the $J_n(r)$ distributions for $n \geq 4$.

that is, the first-, second-, and third-bond neighbor distributions, $J_1(r)$, $J_2(r)$, and $J_3(r)$, respectively, were similarly determined. Finally, the bond-angle and dihedral-angle distributions were obtained. In the remainder of this paper, the average nearest-neighbor distance has been scaled to 2.47 Å, the value for amorphous Ge,[11] and the discussion will be focused on this material.

The density $\rho_0(r)$ is shown in Fig. 1 for a range of r in which atoms are fully coordinated. The density of diamond Ge, with a nearest-neighbor distance of 2.47 Å, is also plotted. It is evident that the density of the model is within about 1% of this value, as is the density of the Polk model. It is therefore unlikely that future CRN models with intermediate-ring statistics will have vastly different densities. Conversely, density cannot be used to link a model to experiment in a unique way. Further, it would seem that the gross changes in density, observed experimentally, are a result of defects[11] rather than of different CRN's.

The RDF is shown in Fig. 2. For comparison, the RDF's of amorphous Ge[11] and the Polk model[2] are also shown. The prominent experimental features are present to some degree in both models. Both models reproduce the experimental nearest-neighbor distribution excellently. In the Polk model, the peaks at 4 and 6 Å are narrower than in experiment, and the one near 6 Å is shifted to lower r. On the other hand, the present model describes the 4-Å peak reasonably well, but near 6 Å, the structure is broadened and shifted to higher r. Be-

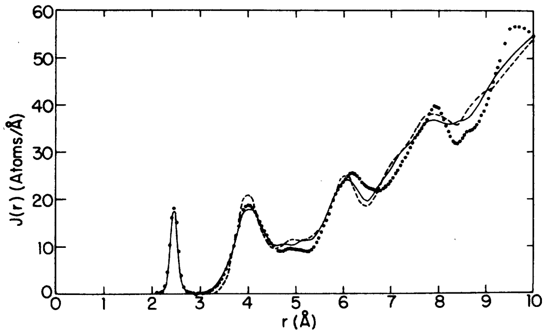

FIG. 2. Radial-distribution functions of the present model (dotted curve) and the Polk model (dashed curve, Ref. 1) compared to experiment (solid curve, Ref. 11).

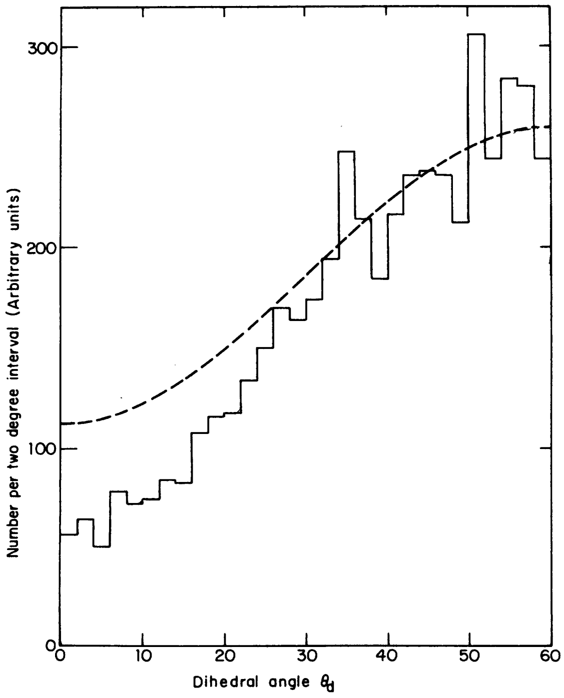

FIG. 4. Dihedral-angle distribution of the present model (histogram, 2° intervals) and of the Polk model (dashed curve). The curves do not have the same normalization.

yond about 7.5 Å, the RDF of a 238-atom model is increasingly dominated by partially coordinated atoms, and the relaxation procedure is thus not subject to the same number of constraints at these large r. The sharpness of the structure near 8 Å in the RDF is therefore unreliable and would likely be absent or greatly reduced in a larger model.

Figure 3 shows a breakdown of $J(r)$ into the $J_n(r)$ for $n=1$, 2, and 3. A surprising result is the relatively large height of $J_3(r)$ near $r_2 = 4.0$ Å, the second-neighbor distance, arising from opposite atoms in distorted "boat-like" six-membered rings. In fact, a weak shoulder in $J_3(r)$ is evident in this vicinity. Previous analyses of experimental $J(r)$ curves to determine the experimental bond-angle distortion $\Delta\Theta_b$ have assumed $J_3(r)$ to be zero at 4.0 Å and obtained $\Delta\Theta_b = 10°$.[11] For the $J_3(r)$ of Fig. 3, a $\Delta\Theta_b \approx 12°$ would be a better fit to experiment. Similarly, the height of $J_3(r)$ for $r < 4.0$ Å would explain the experimental result of more than six atoms in the $r < 4.0$-Å half of the second-neighbor peak.[11] In contrast, $J_3(r) \approx 0$ below 4.0 Å in the Polk model as a result of the "shorting out" of boatlike rings by five-membered rings.

The numbers of n-bond neighbors, N_n, determined from $J_n(r)$ for $n=1$, 2, and 3 are $N_1 = 4.03$, $N_2 = 11.36$, and $N_3 = 23.78$ atoms, in good agreement with the diamond and wurtzite structures. The width of $J_2(r)$ corresponds to a $\Delta\Theta_b = 10.7°$. $J_3(r)$ is a two-peaked function, having maxima at 4.85 and 6.05 Å. These maxima correlate with, and could be predicted from, the shape of the dihedral-angle distribution, shown in Fig. 4.[11,13] (The dihedral angle Θ_d is 0° for tetrahedra in the eclipsed configuration and 60° for tetrahedra in the staggered configuration.)

The staggered configuration is approximately four times more probable than the eclipsed configuration. In the Polk model, however, the eclipsed configuration is relatively more probable, as is indicated in Fig. 4, and, as noted by Steinhardt *et al.*,[2] essentially all of this difference is associated with fivefold rings. It would therefore seem that an experimental determination of the dihedral-angle distribution is crucial to establish the proportion of odd-membered rings in a particular material.

Steinhardt *et al.*[2] constructed a 201-atom model in which each adatom was placed in its position of minimum energy under bond-stretching and bond-bending forces alone. The model so constructed had a dihedral-angle distribution and ring statistics that were similar to those of the Polk model. Pauling, however, indicates that an additional term resulting from the overlap of the two sets of bond orbitals that originate on nearest-neighbor atoms and proportional to $\cos 3\Theta_d$ should be included in a calculation of the position of minimum energy.[10] We therefore argue that the effect of its inclusion on the structure would be a reduction in the number of eclipsed configurations and fivefold rings. The possibility then arises that different materials, which have similar RDF's, could have very different dihedral-angle distributions and ring statistics, depending on the relative importance of the dihedral-angle term in the energy minimization. However, if the ring statistics and dihedral-angle distribution are to be obtained from the experimental RDF's, further structural modeling is needed to understand the variation of the RDF with these distributions.

Neither the RDF of the present model nor of the Polk model fits the experimental RDF of amorphous Ge[11] within experimental error. However, it would seem that the structure of amorphous Ge might, in fact, be intermediate between these models, since an average of the two agrees better with experiment than either alone. On the other hand, the experimental RDF's of the amorphous III-V's[5] indicate that they have a somewhat larger bond-angle distortion than amorphous Ge and agree better with the present model than that of Polk. We therefore conclude that it is entirely possible that there is only a small fraction of wrong bonds in these compounds. The present model thus allows a successful reconciliation of the experimental photoemission, optical, and heat-of-crystallization data mentioned earlier, with a CRN structure with no wrong bonds.

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