Computer model of tetrahedral amorphous diamond

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We computer generate a model of amorphous diamond using the Wooten-Weaire method, with fourfold coordination everywhere. We investigate two models: one where four-membered rings are allowed and the other where the four-membered rings are forbidden; each model consisting of 4096 atoms. Starting from the perfect diamond crystalline structure, we first randomize the structure by introducing disorder through random bond switches at a sufficiently high temperature. Subsequently, the temperature is reduced in stages, and the topological and geometrical relaxation of the structure takes place using the Keating potential. After a long annealing process, a random network of comparatively low energy is obtained. We calculate the pair distribution function, mean bond angle, rms angular deviation, rms bond length, rms bond-length deviation, and ring statistics for the final relaxed structures. We minimize the total strain energy by adjusting the density of the sample. We compare our results with similar computer-generated models for amorphous silicon, and with experimental measurement of the structure factor for (predominantly tetrahedral) amorphous carbon.

I. INTRODUCTION

A great deal of work has been done on modeling amorphous silicon and germanium. The structure is well understood and widely accepted as being a continuous random tetrahedral network.[1,2] Recently, there has been growing interest in tetrahedral amorphous diamond,[3] largely because McKenzie et al.,[4] and others[5,6] have successfully grown an *amorphous* form of carbon, which is predominantly (85%–90%) fourfold coordinated.

In this paper we describe a computer-generated continuous network model of tetrahedrally bonded amorphous diamond, constructed by a method introduced by Wooten, Winer, and Weaire,[7] and Wooten and Weaire.[8] We hope this large model will serve as a useful reference point for discussions of the observed structures of various forms of amorphous carbon, which in reality (to date) always contain varying amounts of graphitic bonding. Our periodic supercell cell consists of $4096 = 8 \times 8^3$ atoms. For the sake of comparison, we have constructed similar models for amorphous silicon. Furthermore, we make two different structures for both cases; one where four-membered rings are allowed, and the other where four-membered rings are forbidden.

The layout of this paper is as follows. First, we shall briefly describe the Wooten-Weaire method, and give a short overview of relevant properties of amorphous diamond. We then present and compare results for all four models, with the experimental measurements. The discussion and conclusions follow.

II. WOOTEN-WEAIRE METHOD

The method is described in detail elsewhere[8,9] and we give just a brief review here. The starting structure is a perfect diamond crystal. Periodic boundary conditions are imposed so that the structure is fully tetrahedrally coordinated, i.e., there are no dangling bonds anywhere. The bond-bending and bond-stretching forces are described by a Keating potential:[10,11]

$$V = \frac{3}{16}\frac{\alpha}{r_0^2}\sum_{l,i}\left(\mathbf{r}_{li}\cdot\mathbf{r}_{li}-r_0^2\right) + \frac{3}{8}\frac{\beta}{r_0^2}\sum_{l\{i,i'\}}\left(\mathbf{r}_{li}\cdot\mathbf{r}_{li'}+\tfrac{1}{3}r_0^2\right)^2,$$

(1)

where α and β are the bond-stretching and bond-bending force constants, respectively, and r_0 is the *strain-free* equilibrium bond length in the diamond structure. There are 4096 atoms placed in a box of size L. The numerical values of all the parameters used in our work are given in Table I.[10]

The first step after generating the initial crystal structure is to randomize the network sufficiently, so that subsequent annealing will *not* lead the system back to the crystalline state. The randomization process is realized by the introduction of many bond rearrangements (*bond switches*)[8] at a temperature just above the melting point for the model. The *melted* structure had $\Delta\theta \approx 22°$ for the rms bond-angle deviation. A useful criterion as to whether the system is melted or not, is the structure

TABLE I. The values of the parameters used in the models of C and Si. These were obtained from measurements of phonon dispersion relations and elastic constants in crystalline materials (Ref. 10). The most dramatic effect of the higher β/α ratio in diamond is evident in the much stiffer transverse acoustic phonon branch (Ref. 11).

	Silicon	Carbon
α (dyn/cm)	0.485×10^3	1.293×10^3
β/α	0.278	0.655
r_0 (Å)	2.35	1.544
L (Å)	43.42	28.53

factor $I(\mathbf{k})$ associated with the (111) direction for the diamond cubic structure. If this quantity is of roughly comparable intensity for all k values, then the structure is well randomized,[8] and all memory of the original crystalline structure is gone. The bond rearrangements maintain fourfold coordination at each atom, thus introducing large strains in the structure.

In the second stage of the procedure, the temperature is reduced in small steps, and at each new temperature thermal equilibrium is established. The system is relaxed *geometrically* (the release of the strain energy allowing the stretching and bending of bonds, according to the Keating potential[11]), and *topologically* (creating more bond switches in the system). As a consequence, the total strain energy, rms bond-angle deviation, and rms bond-length deviation are decreased until an optimized amorphous structure is created as the temperature approaches zero. A piece of the structure obtained is shown in Fig. 1.
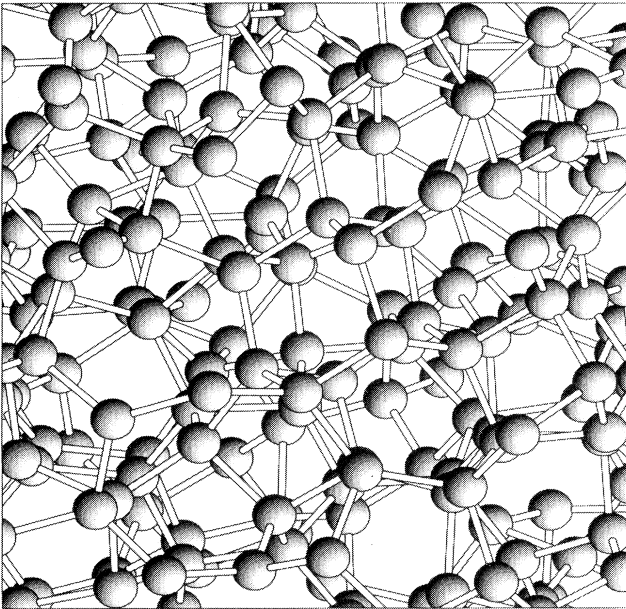

FIG. 1. A piece of computer-generated tetrahedral amorphous diamond structure.

The presence of four-membered rings in the structure makes a successful annealing process easier, while the absence of four-membered rings increases the probability that the system will be trapped in an unsatisfactory metastable state. When four-membered rings are allowed, the final structure contains only a tiny fraction of four-membered rings, even though there was a large number of such rings at the beginning of the process (in the melted structure after the first randomization).

III. DISCUSSION OF AMORPHOUS CARBON

Since McKenzie et al.[12,4] have obtained 85%–90% fourfold coordinated amorphous carbon by plasma-arc deposition, there has been an increasing interest in amorphous diamondlike carbon. These diamondlike carbon films are found to be hard, optically transparent, and chemically inert, which makes them potentially important for applications in coating technology and also for use as wide band gap semiconductors. It is known that amorphous silicon and amorphous germanium exhibit a striking similarity in the shape of their radial distribution functions (see Refs. 13 and 7). In both of these materials the bond-stretching forces are dominant compared to the weaker bond-bending forces. Amorphous carbon is different with respect to both a-Si and a-Ge because of very strong chemical bonding, and because the bond-bending forces are much larger relative to the bond-streching forces. The ratio of bond-bending to bond-stretching forces β/α is 2.4 times larger for carbon than for silicon (see Table I). One might have expected a different amorphous structure of carbon (i.e., different ring statistics, etc.) compared with silicon and germanium, because of the greater bond stiffness of carbon. This was the initial motivation for this work, but our results show that the pair distribution function (PDF) of tetrahedral amorphous diamond is remarkably similar to the PDF's of amorphous silicon and amorphous germanium.

IV. RESULTS AND COMPARISONS

We constructed four different models: two for amorphous carbon, and two for amorphous silicon. We were interested in the ring statistics, and whether the presence of the four-membered rings makes any significant difference in the final structure. So, one amorphous carbon (silicon) model was constructed *with* four-membered rings present and the other *without* four-membered rings. We calculated the total strain energy, rms bond length, rms bond-length deviation, rms bond-angle deviation, and the mean angle between the bonds. Also, we calculated the number of four-, five-, six-, seven-, and eight-membered irreducible rings present. An irreducible ring is one that has no shortcuts across it. That is, given any two atoms (vertices) on the ring, there is no shorter path between the two atoms (as measured by the number of bonds along the path) than a path on the ring itself. One advantage of such rings for topological purposes is that the number of n-membered rings goes to zero for large n, but no topologically important rings are omitted, and the complete table of ring statistics remains finite.[9] All

TABLE II.   The structural parameters for the models discussed in this paper at two densities—the crystalline density $(\rho/\rho_0 = 1.000)$ and the optimal density.   The number of elemental rings per site n_r is independent of the density as the topology is not changed when the density is varied.

	Si(4)		Si		C(4)		C	
ρ/ρ_0	1.000	1.025	1.000	1.033	1.000	1.050	1.000	1.054
$\langle r \rangle / r_0$	0.996	0.988	0.997	0.987	0.996	0.980	0.997	0.980
$\langle \theta \rangle^\circ$	109.24	109.23	109.25	109.23	109.31	109.30	109.31	109.30
$\Delta r / r_0 (\%)$	2.52	2.46	2.65	2.57	4.39	4.31	4.40	4.31
$\Delta \theta^\circ$	10.51	10.54	11.02	11.06	9.29	9.31	9.06	9.08
E (eV)/atom	0.336	0.334	0.367	0.362	0.757	0.741	0.731	0.715
n_4	0.015		0		0.009		0	
n_5	0.491		0.523		0.472		0.457	
n_6	0.698		0.676		0.760		0.800	
n_7	0.484		0.462		0.472		0.498	
n_8	0.156		0.164		0.156		0.143	

results are presented in Table II.

We tested the influence of the sample density on the strain energy, and found that the crystalline density is *not* the optimal one for the amorphous structure. In all cases, a slightly larger density gave a smaller strain energy when using the Keating potential. The Stillinger-Weber potential[14] goes in the opposite direction for silicon: slightly smaller density gave the smallest strain energy.[8] The small density differences should therefore not be taken seriously, although it is proper to optimize the density to give the smallest strain energy within a given model. The optimal density was determined by fitting a parabola to a plot of strain energy as a function of density, and finding the minimum, given in Table II.

From the coordinates of the final amorphous structure obtained for the optimal density, we calculated the PDF, which is given as

$$P(r) = \frac{G(r)}{4\pi r^2 \rho_0}, \qquad (2)$$

where $G(r)$ is the radial distribution function

$$G(r) = \frac{1}{N} \sum_{ij} \delta \left(r - |\mathbf{R_i} - \mathbf{R_j}| \right) \qquad (3)$$

and ρ_0 is the number density of the system

$$\rho_0 = \frac{N}{L^3}, \qquad (4)$$

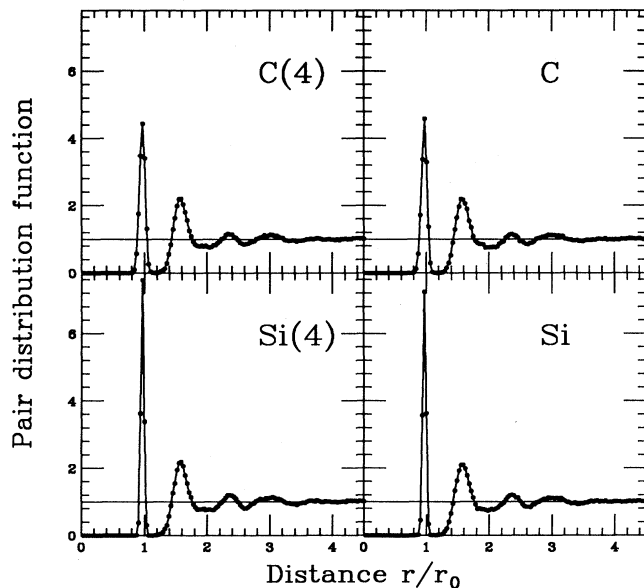where $N = 4096$, and L is the *actual* size of the supercell

FIG. 2.   Pair distribution functions $P(r)$ for amorphous carbon and amorphous silicon models, with, and without four-fold rings. All models are at the optimized density.
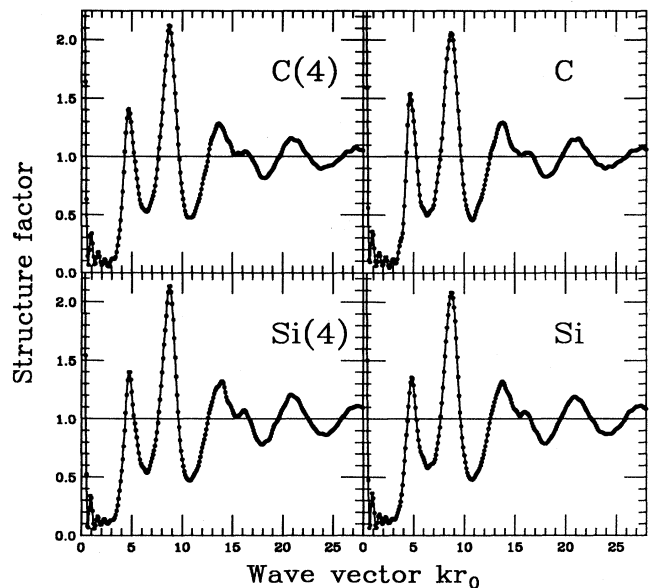

FIG. 3.   Structure factors $I(k)$ calculated from the corresponding pair distribution functions shown in Fig. 2.

(either the original supercell size as given in Table I, or the optimized one). For comparison, we rescale the PDF of silicon to that of carbon, with the distance scaled by r_0, the nearest neighbor distance in the crystalline form. The four PDF's are shown in Fig. 2.

Using a Fourier transformation, the structure factor can be written

$$I(k) = 1 + \frac{4\pi\rho_0}{k} \int_0^\infty r[P(r) - 1]\sin(kr)dr, \qquad (5)$$

where r_0 is the strain-free nearest neighbor distance for the crystalline structure as given in Table I. We calculate the structure factor for the four models, which are shown in Fig. 3. Because there is no contribution to the integral (5) when $P(r)$ approaches unity, it can be seen from Fig. 2 that this integral should (and does) converge well, with only a few *termination* ripples at small k.

V. DISCUSSION

The most striking feature of the results in Table II is that there are *no major differences* between amorphous carbon and amorphous silicon. We considered two densities; the crystalline density and the density that minimizes the total strain energy. The rms bond lengths, $\langle r \rangle / r_0$, of carbon and silicon are about the same, and slightly *smaller* than in the crystalline diamond structure. The rms bond-length deviation, $\Delta r / r_0$, is *larger* for carbon by 44%. This is one of the most significant differences between carbon and silicon. The rms bond-angle deviation, $\Delta\theta°$, is *smaller* for carbon by 18%, as would be expected because of the larger angular force reflected through the larger value of β/α. Ring statistics are also very similar, except that there are more six-membered irreducible rings[8] in carbon, and fewer five-membered rings than in silicon.

The optimal density results given in the second subcolumns in Table II, show the following features. The energy is minimized, in all cases, at a slightly *higher* density than the crystalline one. The rms bond length, the mean bond angle, and the rms bond length, are slightly *decreased*, while the rms bond-angle deviation is slightly *increased*.

Looking at Fig. 2, one can see a surprisingly good matching between the PDF's of carbon and silicon. The general shape is the same. The first peak is shifted towards to a value slightly smaller than unity; the crystalline value. This is true even at the crystalline density, and corresponds to the rms relative bond length, which is smaller than one in the crystalline state, i.e., the mean bond length in the amorphous structure is slightly smaller than in the crystal (1.544 Å). The carbon first peak is broader than the silicon first peak, which is correlated with the larger rms bond-length deviation in carbon. This represents a different apportioning of the strain energy between bond-length strain and bond-angle strain in carbon and silicon. The ratio of the strain energy associated with the bond angle (second term in the Keating potential) and the bond length (first term in the Keating potential) for carbon is found to be 1.57, while for silicon it is 2.73. This means that relatively *more*
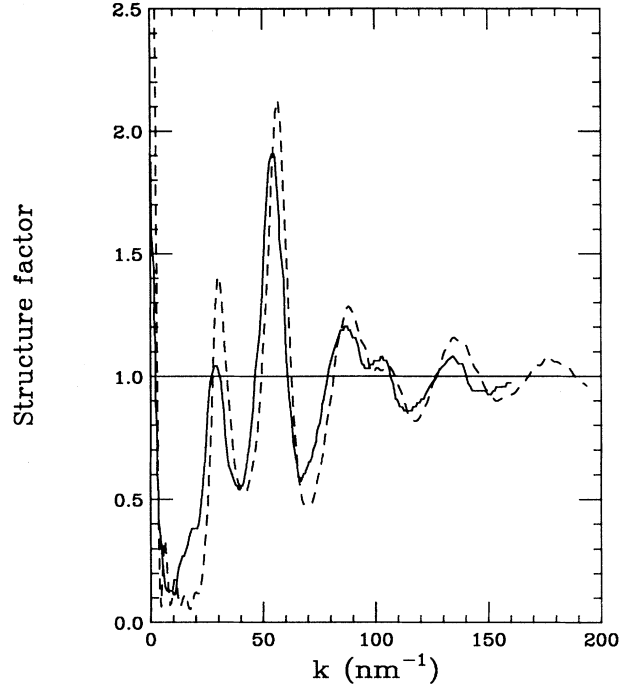

FIG. 4. A comparison of the structure factor from our computer-generated model of amorphous tetrahedral diamond *with* fourfold rings (dashed line), and the structure factor measured by Gaskell *et al.* (solid line) (Ref. 6), on samples containing 10%–15% graphitic regions.

energy is stored as bond-bending strain in carbon, when compared with silicon. Nevertheless the overall features of PDF's are essentially unchanged between carbon and silicon.

Figure 3 shows again great similarity in the structure factor for carbon and silicon. Furthermore, it fits relatively well the measured structure factor for amorphous, diamondlike carbon, as shown in Fig. 4 (see Ref. 6, p. 159). It should be remembered that these experiments are on samples containing 10–15 % graphitic bonding so that a detailed comparison between our model and experiment is not appropriate at this time. Graphitic regions can be incorporated into computer-generated models using molecular dynamics and other techniques.[15] However, these models are much smaller than ours (the model in Ref. 15 contains 216 atoms) so that a detailed comparison of these models with experimental structure factors is also premature. It must also be realized that carbon films[6] contain some hydrogen, which will have some effect on the PDF and structure factor.

VI. CONCLUSION

Although carbon has much stiffer bond-bending forces than silicon (i.e., a much larger value of β/α, the ratio of bond-bending to bond-stretching force constants in the Keating model), this does not influence the pair distribution function significantly. The bond-angle deviations are slightly smaller in amorphous tetrahedral dia-

mond compared with amorphous silicon and amorphous germanium, but they cannot be *too* small, as the atoms are constrained to be in a fully tetrahedrally coordinated random network. Indeed our experience in constructing random networks leads us to believe that a rms bond-angle deviation of at least 7° is required if the network is not to contain crystalline regions and so be a two-phase mixture.

The coordinates and neighbor table of the four models discussed in this paper can be obtained from the authors by sending a request to *thorpe@pa.msu.edu* on the Internet.

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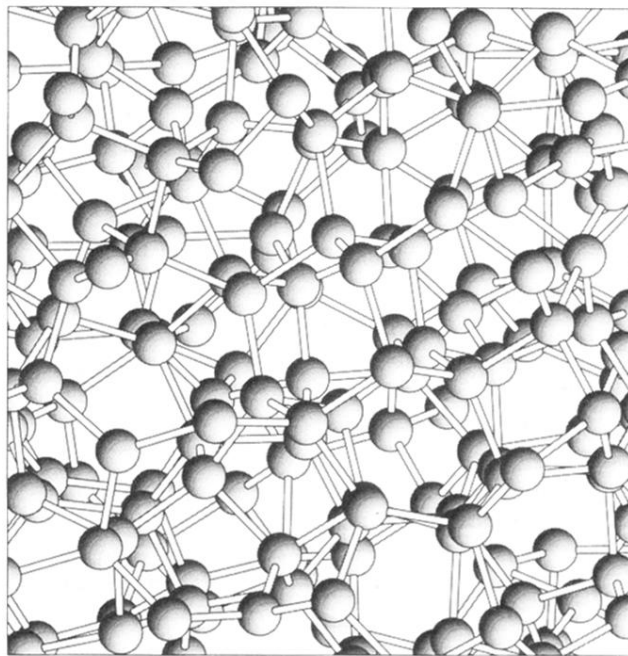[15] C. Z. Wang and K. M. Ho, Phys. Rev. Lett. **71**, 1184 (1993).

FIG. 1. A piece of computer-generated tetrahedral amorphous diamond structure.