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## LETTER TO THE EDITOR

# The electronic structure of diamond-like amorphous carbon

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**Abstract.** The electronic structure of diamond-like amorphous carbon is investigated using a tight-binding molecular dynamics method. The study shows that bonding and antibonding of  $\pi$ -states associated with pairs and quartets of threefold 'defected atoms' embedded in the fourfold matrix yield a band gap of about 2 eV as observed in optical absorption experiments. These states are in general very localized. However, coupling between the threefold 'defects' can produce delocalized states near the band gap, which is essential for electronic conductivity in the material.

Diamond-like amorphous carbon films produced by the mass-selected ion beam deposition technique [1] have recently received considerable attention. The unique properties of the material, such as mechanical hardness, chemical inertness, and optical transparency [2], make it potentially useful for technological applications, and particularly as a protective coating in microelectronics. Very recently, Veerasamy *et al* found that these amorphous films can be doped with phosphorus or nitrogen [3, 4]. They showed that within 1% of doping concentration, the conductivity of the films can be increased by six orders of magnitude, while the tetrahedral bonding nature of the undoped films is retained [3, 4]. This discovery suggests that the material may also be important for electronic device applications.

In the last few years, many efforts have been made to elucidate the microscopic structure and properties of this novel form of carbon [1–14]. Experimental studies using electron energy-loss spectroscopy (EELS) and neutron scattering measurements estimated that about 80% ( $\pm 10\%$ ) of the atoms in these diamond-like amorphous carbon films are fourfold-coordinated atoms [1, 5, 6, 8]. Optical absorption measurements indicate that these films have an optical gap of about 2 eV [2, 5], in contrast to the case of  $sp^2$ -dominated graphite-like amorphous carbon, where the optical gap is less than 0.5 eV [2]. However, this band gap is much smaller than the 5.5 eV gap of crystalline diamond. On the theory side, the electronic structure of this disordered material has been a subject of intense investigation [2, 12, 13, 14]. Nevertheless, the origin of the 2 eV band gap and the nature of the electronic states near the Fermi energy are still not well understood.

In this letter, we report on a detailed analysis of the electronic structures of realistic diamond-like amorphous carbon models generated by tight-binding molecular dynamics (TBMD) simulations. The goal is to understand the relationship between the microscopic atomic structure and the electronic properties in this disordered material. Our study suggests that a purely tetrahedral amorphous carbon network would have a gap as large as 4 to 5 eV, and the observed 2 eV optical gap can be attributed to the bonding and antibonding of  $\pi$ -states of pairs and quartets of threefold 'defect' atoms embedded in the fourfold matrix.

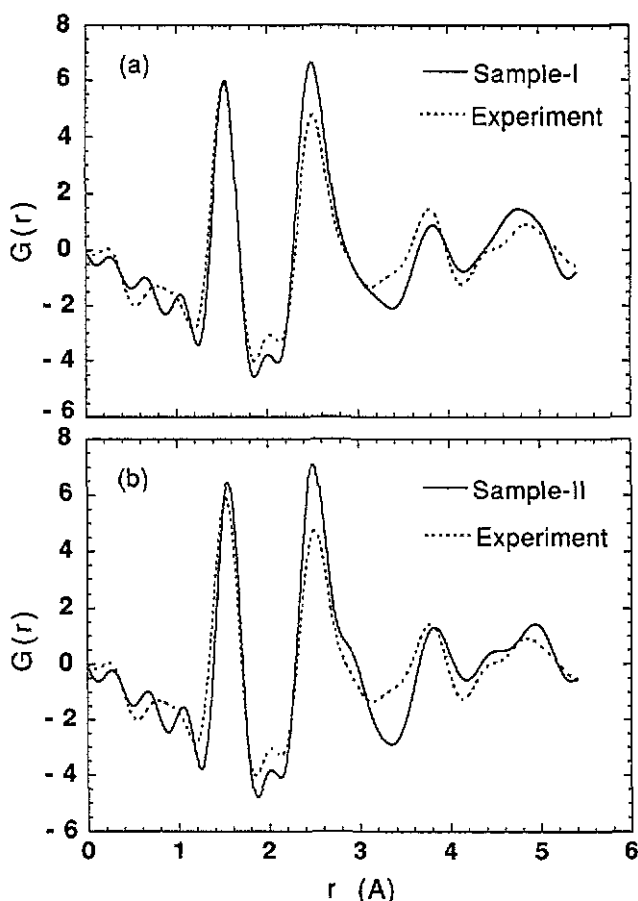


Figure 1. Radial distribution functions  $G(r)$  of the diamond-like amorphous carbon samples generated by TBMD (solid curve) are compared with neutron scattering data from [6] (dotted curve). The theoretical results have been convoluted with the experimental resolution corresponding to the termination of the Fourier transform at  $Q_{\max} = 16 \text{ \AA}^{-1}$ .

For details of the TBMD method and the tight-binding model used in this study, we refer the reader to our previous publications [14–19]. We note that our tight-binding model describes accurately the energies and properties of the diamond (fourfold), graphite (threefold), and linear-chain (twofold) structures in comparison with self-consistent first-principles density functional calculations [16]. The model has also been successfully applied to the studies of carbon fullerenes [17], liquid carbon [19], and amorphous carbon [14, 18]. In the TBMD simulation, the electronic structure is calculated at every MD step through an empirical tight-binding Hamiltonian; thus, the electronic information of the amorphous network can be obtained simultaneously along with the structural properties.

The diamond-like amorphous carbon samples were prepared by quenching carbon liquid from high temperature under high pressure. The as-quenched samples were then relaxed to a local energy minimum and zero pressure by a steepest-descent procedure. Two samples obtained by different quenching conditions were used for analysis. Sample I consisted of 74% of fourfold and 26% of threefold sites, with a microscopic density of  $3.35 \text{ g cm}^{-3}$ . Sample II, which was obtained by quenching from a higher-density liquid, had 89% of

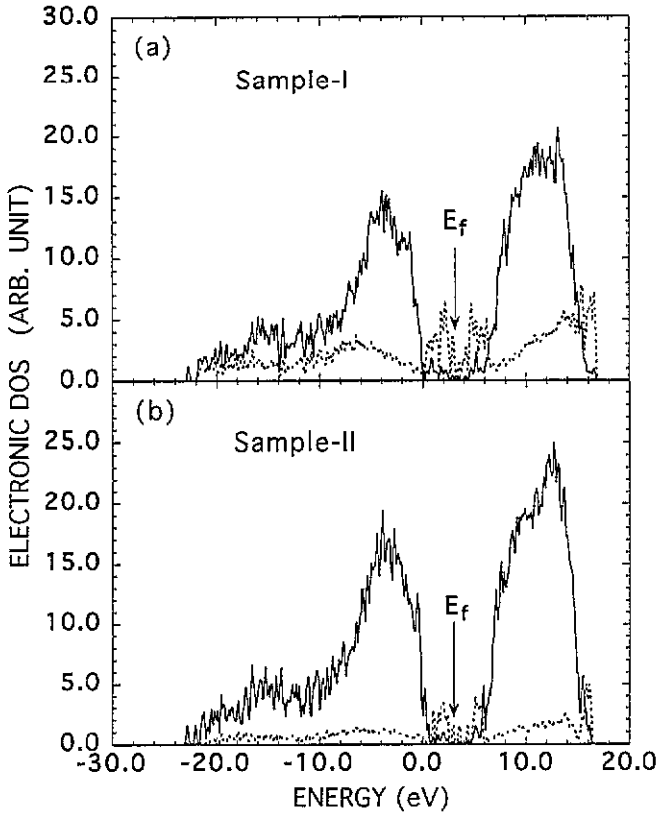
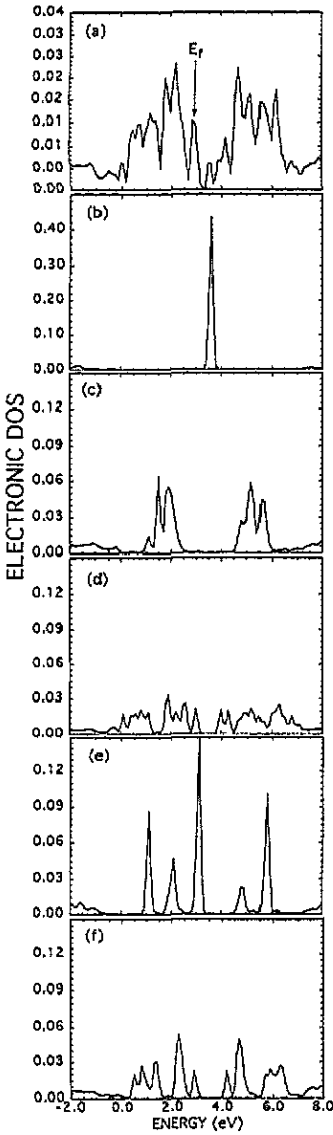


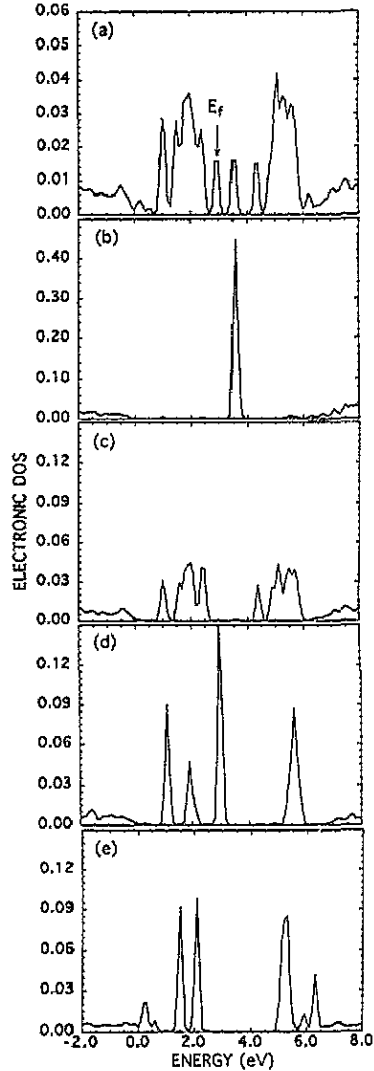
Figure 2. The EDOS of the TBMD-generated diamond-like amorphous carbon samples. Solid and dotted curves show the EDOS from the fourfold and threefold atoms respectively.

fourfold and 11% of threefold sites, with a microscopic density of  $3.4 \text{ g cm}^{-3}$ . Both samples contained 216 atoms in a cubic supercell with cubic periodic boundary conditions. Structural analysis shows that these two samples have overall structural properties that resemble those of diamond-like amorphous carbon films observed in experiments. In figure 1, the radial distribution functions  $G(r)$  ( $= 4\pi r\rho[g(r) - 1]$ ) of the two theoretical samples are plotted in comparison with neutron scattering data of Gaskell *et al* [6]. The agreement between the theoretical results and the experimental data is fairly good.

The electronic densities of states (EDOS) of the above two samples obtained by our TBMD calculations are plotted in figure 2. As one sees from the plot, the EDOS of the fourfold-coordinated atoms has a large pseudogap of about 5 eV for both samples I and II (solid curves). This result suggests that pure tetrahedrally bonded amorphous carbon structures would have a band gap almost as large as that of diamond. It is apparent that the smaller band gap (about 2 eV) of the diamond-like amorphous carbon films observed in experiments is attributable to the presence of threefold 'defects' in the diamond-like amorphous network. Our calculations show that the threefold 'defects' in the diamond-like amorphous carbon network do indeed tend to open up a gap of about 2 eV, although the gaps obtained from our samples are not 'clean', i.e. there are some states in the gap region (see the dotted curves in figure 2). We note that sample II has far fewer residual states in the gap than does sample I, indicating that the residual gap states are sensitive to the concentration of



**Figure 3.** The local electronic density of states (LEDOS) of sample I in the vicinity of the Fermi energy. The LEDOS of (a) all threefold atoms; (b) isolated threefold atoms (dangling bonds); (c) pairs of threefold atoms; (d) the large cluster of 22 threefold atoms; (e)  $C_3$  chains; (f)  $C_4$  chains. The spectra have been smoothed using a Gaussian function with a standard deviation of 0.075 eV. The intensities of the spectra have been renormalized to that of one atom.



**Figure 4.** The LEDOS of sample II in the vicinity of the Fermi energy. The LEDOS of (a) all threefold atoms; (b) isolated threefold atoms (dangling bonds); (c) pairs of threefold atoms; (d)  $C_3$  chains; (e)  $C_4$  chains. The spectra have been smoothed using a Gaussian function with a standard deviation of 0.075 eV. The intensities of the spectra have been renormalized to that of one atom.

the threefold 'defects'.

In order to understand the nature of the electronic structure of the threefold 'defects'

in the diamond-like amorphous carbon samples, we have performed detailed analysis of the local EDOS for the threefold atoms in samples I and II. Sample I contains 58 threefold atoms which consist of one isolated threefold atom (dangling bond), six pairs of atoms, one C<sub>3</sub> chain, five C<sub>4</sub> chains, and a large cluster of 22 atoms. Sample II has only 24 threefold atoms, 16 of which form pairs and the rest of which are divided into one C<sub>3</sub> chain, one C<sub>4</sub> chain, and one isolated threefold atom (dangling bond). We have calculated the local density of states for the different types of threefold atoms as classified above.

The results of the local density-of-states analysis are shown in figure 3 and figure 4 for sample I and sample II respectively. We found that in both samples the sharp state in the middle of the band gap comes from the dangling bond, and the state at the Fermi energy is a state of the C<sub>3</sub> chain. The larger cluster of threefold atoms in sample I yields very broad  $\pi$ - and  $\pi^*$ -bands and gives only a very small gap. In contrast to the above 'defects', pairs of threefold atoms embedded in the fourfold-coordinated network can form fairly sharp bonding and antibonding  $\pi$ -states with gaps ranging from 2 to 4 eV, depending on the details of the local geometries. Pairs of threefold atoms with longer bond lengths and larger  $\pi$ -bond angles (defined as the angle between the two planes formed by each threefold atom and its fourfold neighbours) tend to have smaller gaps because the overlap between the  $\pi$ -states is reduced. Among the 14 pairs of threefold atoms in the two samples, we found that only one pair of atoms in sample II produces a gap smaller than 2 eV (about 1.9 eV). Structural analysis shows that the configuration of this pair of atoms is quite different from that of the others. The bond length between the two atoms is 1.3810 Å, which is longer than the average bond length of 1.3701 Å for all pair threefold atoms in this sample. The  $\pi$ -bond between the two atoms is also severely twisted, with a  $\pi$ -bond angle of 70.2°, while the average  $\pi$ -bond angle of the eight pairs of threefold atoms in this sample is only 28.7°. The magnitude of the band gap and the width of the  $\pi$ - and  $\pi^*$ -bands produced by the pair of threefold atoms are also dependent on the environment of the pair. If there are other threefold 'defects' nearby, interactions between the threefold 'defects' will broaden the  $\pi$ - and  $\pi^*$ -peaks, leading to a smaller gap. In our present study, the overall contributions of pairs of threefold atoms in the above two samples can lead to a clean band gap of about 1.9 eV and have a  $\pi$ -to- $\pi^*$  (peak-to-peak) transition of about 3.5 eV.

Besides the pairs of threefold atoms, we found that the C<sub>4</sub> chains can also open up a clean band gap of about 2 eV, although the  $\pi$ - and  $\pi^*$ -bands of the C<sub>4</sub> chains are much broader than those of pair threefold atoms. We noticed that the EDOS of the C<sub>4</sub> chains in sample I exhibits two sharp states inside the 2 eV gap near the band edges. Using Mulliken population analysis, we found that about 68% of the amplitude of these two states is localized on a C<sub>4</sub> chain while another 12% is on a nearby C<sub>4</sub> chain, indicating that the two C<sub>4</sub> chains are interacting with each other. The interaction makes the cluster effectively bigger and the  $\pi$ -band splitting smaller.

By analysing the inverse participation ratio and Mulliken population of the eigenstates in the two samples, we found that the  $\pi$ -states arising from the relatively isolated small clusters of threefold atoms (e.g. C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>) are very localized, with more than half of the amplitude on a few atoms. Therefore, these states should contribute very little to electronic conductivity when the sample is doped. The dramatic increase of electronic conductivity when phosphorus or nitrogen is lightly doped (less than one per cent of concentration), as observed in experiments [3, 4], seems to suggest that there are larger threefold clusters in the diamond-like amorphous carbon samples. The presence of larger threefold clusters can produce delocalized  $\pi$ -states, but cannot open a clean gap of 2 eV. Another possibility is that the introduction of phosphorus or nitrogen increases the coupling among the small clusters of threefold atoms in the original diamond-like amorphous carbon films and induces

delocalized  $\pi$ -states which are essential for increasing electronic conductivity in the material. Further experimental and theoretical studies seem to be necessary to clarify this issue.

In conclusion, our calculation results suggest that the gap-opening mechanism in the diamond-like amorphous carbon is the formation of bonding and antibonding  $\pi$ -states of the threefold atoms in the network. Pairing distribution of the threefold 'defects' in the diamond-like amorphous sample is crucial for a clean gap of about 2 eV. The states in the gap region are primarily from small odd-numbered ( $C_1$  and  $C_3$ ) and larger threefold clusters. The presence of larger threefold clusters or coupling between small threefold clusters can produce delocalized  $\pi$ -states and can enhance the electronic conductivity of the material. Since the details of the electronic states in the vicinity of the Fermi energy are very sensitive to the concentration and the distribution of threefold-coordinated sites in the amorphous network, the details of electronic structure of diamond-like amorphous carbon should be very strongly dependent on the sample preparation conditions.

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