PHYSICAL REVIEW B VOLUME 52, NUMBER 9 1 SEPTEMBER 1995-I

Radial distribution function of a new form of amorphous diamond shock induced from C_{60} fullerene

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(Received 29 March 1995)

The radial distribution function of a new form of amorphous diamond, synthesized from C_{60} fullerene by shock compression and rapid quenching, was obtained from an electron diffraction pattern using an imaging plate. The present amorphous diamond was essentially amorphous material based on diffractometry. Analysis of the local structure around an atom revealed that the amorphous material was distinguishable not only from sp^2-based amorphous material but also from some tetrahedrally coordinated amorphous carbon and other amorphous semiconductors previously reported. The carbon atoms in the present material were tetrahedrally coordinated, forming regular tetrahedra that additionally were arranged in the same manner as those of crystalline diamond within a unit-cell size region. The implications of producing the new form of amorphous diamond from C_{60} fullerene also are discussed in the present paper.

INTRODUCTION

Carbon, because of its various bond states, exhibits a wide potential for producing metastable, crystalline, and noncrystalline phases in addition to thermodynamically stable phases. This potential is especially promising under nonequilibrium conditions such as physical and chemical vapor deposition and dynamic shock compression. The noncrystalline forms, which exhibit a diverse range of disordered structures, involve amorphous as well as partially ordered states and possess intermediate characteristics associated with the presence of sp^2 and sp^3 bonds. A peculiar bonding state may, in fact, exist because of the lack of a long-range-ordered structure. These forms are of particular interest in view of understanding the hidden nature of carbon and also for the usefulness of their physical and chemical properties. Intensive studies have focused on the preparation of amorphous carbon materials by various deposition techniques, as well as on characterization of those materials using spectroscopy and diffractometry.[1–10] An amorphous form of diamond has been envisioned as analogous to amorphous silicon (*a*-Si) and amorphous germanium (*a*-Ge), but the existence of such a form was questionable because of bonding constraints and thermodynamic considerations.[2] Actually, the most common amorphous carbon has been represented by some disordered form of graphite, composed mainly of the sp^2 bond.[3,4] Even diamondlike carbon films, in which the fraction of sp^3 bonds certainly has increased, contains a large amount of hydrogen (10–20 %), resulting in decreased hardness.[2] Recently, a higher fraction of sp^3 bonds, e.g., tetrahedrally coordinated, amorphous carbon[1] (ta-C), has been attained by some advanced deposition techniques, pulsed-laser deposition,[5] filtered cathodic-arc deposition,[6] and ion-beam spatter deposition.[7] These amorphous materials have been analyzed by determining their radial distribution function (RDF),[8] conducting electron-energy-loss spectroscopy (EELS),[9] and measuring thermal conductivity,[10] and a compressive-stress-induced mechanism also has been presented.[1] Those characterizations clearly showed a higher fraction of sp^3 bonds (approximately 0.9) and a higher density (approximately 2.9 g/cm^3), but the measures still were insufficient to represent true amorphous diamond, since π electrons were observed in the *k*-absorption edge of the EELS results.[9]

A new form of amorphous diamond was fabricated successfully from C_{60} fullerene[11,12] by a shock-compression and rapid-quenching techniques.[13] This material was characterized by x-ray and electron diffractometry as amorphous in the long-range order and by EELS as diamond in the short-range order.[11,12] The plasmon loss and fine structure of the *k*-absorption edge revealed by EELS were quite similar to those of a typical diamond. It therefore became necessary to confirm the structure in the short-range order by another technique, i.e., by establishing the RDF based on diffractometry, which gives the most probable distances between atoms

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and the number of pairs.

Earlier reports have emphasized that electron diffraction has some advantages over other forms of radiation for the structural investigation of small samples.[8] The present research was aimed toward obtaining the RDF from the electron-diffraction pattern by using an imaging plate (IP), because each specimen chip had to be checked by EELS to determine whether it exhibited the sp^3 bond alone. The conventional film method possesses inherent shortcomings such as lower sensitivity and lower quantitativeness in regard to intensity measurement, whereas, the IP method is advantageous for its sensitivity, dynamic range, and its linearity in the dynamic range.[14] The IP dynamic range can encompass measurements from strong incoherent scattering at a lower angle to abruptly lowered intensity at a higher angle. In the present study, use of the IP made it possible to obtain the RDF of the new form of amorphous diamond from the electron-diffraction pattern and to discuss the nearest-neighbor data in comparison with those for crystalline diamond, as well as for *a*-Si and *a*-Ge. Moreover, the implications of fabricating the amorphous diamond from C_{60} fullerene also were considered.

EXPERIMENTAL

The new form of amorphous diamond examined in the present study was synthesized from C_{60} fullerene by shock compression and rapid quenching. The material was recovered as transparent glassy chips measuring several tens of micrometers (μm) in size and ~ 10 μm thick.[11,12] At first, the glassy chips were confirmed by EELS (*k*-absorption edge) and energy-dispersive x-ray spectroscopy to consist only of carbon. X-ray and electron diffractometry showed the halo and diffuse bands, respectively, typical of amorphous material. No three-dimensional peak was observed in its diffraction pattern; the material was thus defined essentially as amorphous on the basis of diffractometry. Raman spectroscopy revealed the absence of sp^2 bonds, and EELS also revealed no trace of π reelectrons in the fine structure of the *k*-absorption edge. The plasmon-loss spectrum obtained by EELS exhibited σ electron peaks of the sp^3 bond at 27.4 and 34.2 eV, which energy values are totally equivalent to those of typical diamond.[15] The fraction of sp^3 bonds and the bond nature of the present material thus were quite similar to those of diamond, according to the EELS studies of the carbon materials.[1,16] Density, measured by the flotation method, was higher than 3.3 g/cm^3, since the material sank completely into di-iodomethane (CH_2I_2, specific gravity 3.3). Hardness could not be measured quantitatively because of the irregular shape and small size of the sample, but a scratch test showed that the present material was harder than sapphire.

Data were collected by using an IP system combined with transmission electron microscope (TEM) (PIXsys-TEM, JEOL). Figure 1(a) shows a representative electron-diffraction pattern of the present material obtained by the IP method. A distinct variation in intensity with the scattering angle was observed because of the large dynamic range, instead that only diffuse bands were revealed by the conventional film method.[11,12] The radial intensity profile was obtained by averaging over this whole pattern. The camera length was corrected using an electron-diffraction pattern of polycrystalline gold obtained under the same conditions. The scattering intensity, normalized to the units of cross section (nm^2) per atom, was obtained by the Krogh-Moe-Normann method,[17,18] as used in the x-ray study. The normalized intensity is given in Fig. 1(b). The component of coherent scattering I_{coh} was estimated by removing the incoherent intensity from the normalized value, where the incoherent intensity had been calculated from the Compton scattering factor for x rays. The atomic scattering factor and the Compton scattering factor of a carbon atom were derived from the International Tables for Crystallography.[19] The structure function $i(S)$ was deduced based on the following equation for a single-atom system: $i(S)=(I_{\text{coh}}-f_c^2)/f_c^2$. Here f_c is the atomic scattering factor of carbon. The *S*-weighted structure function, $S \cdot i(S)$, thus obtained is plotted against $4\pi\sin\theta/\lambda$ in Fig. 2. The radial distribution function

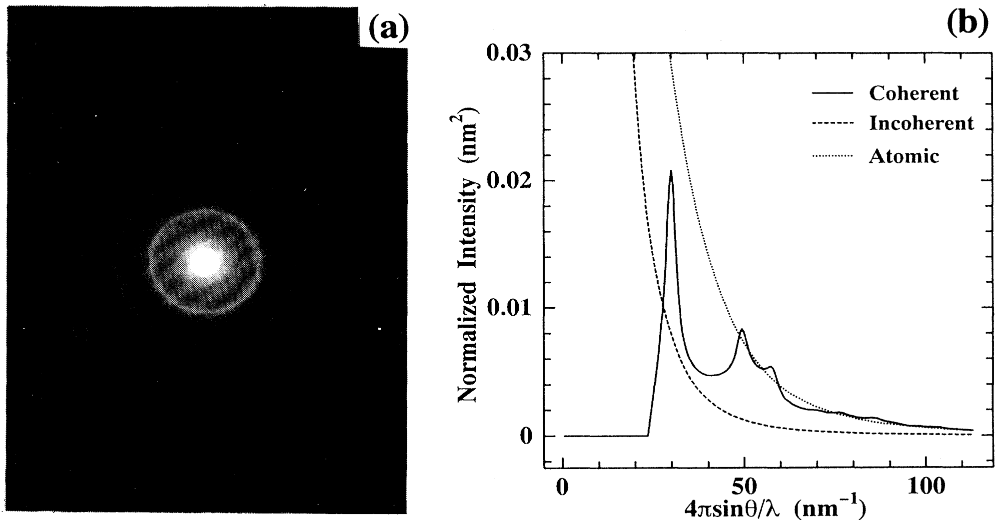

FIG. 1. (a) Intensity distribution collected on an IP. (b) Normalized coherent intensity together with incoherent and independent atomic scattering components.

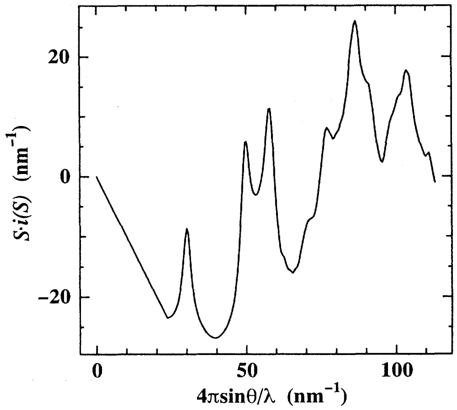

FIG. 2. S-weighted structure function, $S \cdot i(S)$, vs $4\pi \sin\theta/\lambda$.

(RDF), $4\pi r^2 \rho(r)$, around a carbon atom was obtained by the Fourier transformation of $S \cdot i(S)$:

$$4\pi r^2 \{\rho(r) - \rho_0\} = (2r/\pi) \int S \cdot i(S) \sin sr \, ds \ .$$

The correlation function, $G(r) = 4\pi r^2 [\rho(r)/\rho_0]$, is shown in Fig. 3(a). A region of r less than 0.12 nm was cut off by a frequency filter. Distances determined by the peak positions and the number of atomic pairs estimated from the peak area are listed in Table I, together with those of crystalline diamond and graphite. Now it becomes possible to discuss the local structure around a carbon atom based on the $G(r)$ obtained.

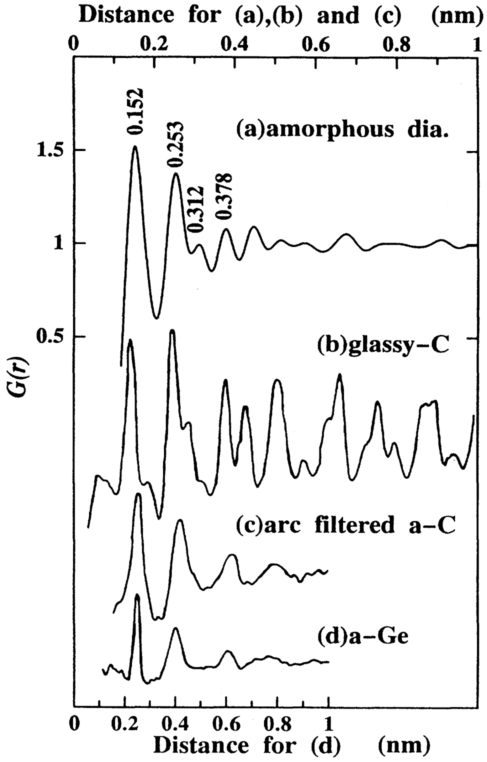

FIG. 3. (a) Correlation function $G(r)$ vs r of the amorphous diamond. For comparison, (b), (c), and (d) are reduced RDF's for a glassy carbon (Ref. 8), for an arc filtered a-C (tetrahedrally coordinated amorphous carbon) (Refs. 1 and 8) and for an a-Ge (Ref. 8), respectively. For a-Ge (d), the scale is changed so as to align the first nearest-neighbor peak to that of (a).

TABLE I. Distances and the numbers of atomic pairs of amorphous diamond, crystalline diamond, and graphite.

	Amorphous dia.		Crystalline dia.		Graphite
Peak	Distance (nm)	Number of pairs	Distance (nm)	Number of pairs	Distance (nm)
1	0.152	4.5	0.154	4	0.142
2	0.253	13	0.252	12	0.246
3	0.312	10	0.296	12	0.284
			0.356	6	0.336
4	0.378	(17)			0.365
			0.388	12	0.376
	0.68				

RESULTS AND DISCUSSION

The first (0.152 nm), second (0.253 nm), and third (0.312 nm) nearest-neighbor distances obtained for the present material are essentially near those of crystalline diamond. No evidence of a characteristic peak at ~0.14 nm, associated with a graphitelike structure [e.g., glassy-C in Fig. 1(b)] and the C_{60} fullerenelike structure, was observed in the correlation function. Although the distance of the third peak, 0.312 nm, also could be attributed to the diameters of the six-member rings of the graphite structure (0.284 nm) or to a C_{60} cluster, it is more reasonable to attribute it to the third-nearest-neighbor distance of crystalline diamond (0.296 nm), since the most typical distance of ~0.14 nm for graphite and the C_{60} cluster was not observed. This conclusion also is understandable in view of all the spectroscopic-analysis results, the density, and the transparency, which demonstrate that the present amorphous material was not an sp^2-based material.

The first-neighbor distance (0.152 nm), the number of atomic pairs (4.5), and the second-neighbor distance (0.253 nm) indicate that a carbon atom in the material was accompanied by four carbon atoms as nearest neighbors. In addition, these four carbon atoms formed a nearly regular tetrahedron, because the ratio of the two distances was near that of a regular tetrahedron. The numbers of pairs of second and third peaks (13 and 10), despite being slightly larger or smaller than those of crystalline diamond, showed that each apex atom of the tetrahedron was further surrounded by another tetrahedron. The configuration of these tetrahedra was almost the same as that of crystalline diamond, although the third distance (0.312 nm) between adjacent tetrahedra was slightly larger than that of crystalline diamond (0.296 nm). The distance of the fourth peak (0.378 nm) represents an intermediate value between the fourth distance (0.356 nm, i.e., the unit-cell size) and the fifth (0.388 nm) of crystalline diamond, and its number of pairs (17) is roughly comparable to the sum of the two peaks (6+12=18) of crystalline diamond. These facts suggest that a certain disordering in the atom configuration became appreciable around the region. These topological analyses showed, in summary, that the carbon atoms in the present material were tetrahedrally coordinated, and that the tetrahedra were arranged in the same manner as those of crystalline diamond within a region corresponding to a unit-cell size of crystalline diamond, even though the distances among the tetrahedra were slightly larger (in other words, the packing of the tetrahedra was slightly looser). The present material is in itself amorphous but its degree of order is so high as to evaluate the third peak, indicating highly ordered amorphous. Therefore, this material can be called *amorphous diamond.* A peak distinguished at ~0.68 nm in the correlation function suggests the plausibility of a certain cluster less than ~0.7 nm in size.

Comparing the correlation function of the present amorphous diamond with those of other tetrahedrally coordinated amorphous materials [Fig. 3(c) and 3(d)],[1,8] shows that the present amorphous diamond is characterized by the third peak, clearly distinguished, at 0.312 nm. In the other amorphous materials, this peak commonly is absent. The third distance (0.312 nm) corresponds to the diameter of a zigzag six-member ring of crystalline diamond, i.e., the distance from the center atom of a tetrahedron to the apexes of the neighboring tetrahedra. The existence or absence of the 0.312 nm peak thus indicates whether or not the configuration among the tetrahedra is similar to that of crystalline diamond. The present amorphous diamond therefore displays a closer similarity to the crystalline form than do the *a*-Ge and ta-C. The exact definition of *amorphous* has been argued and remains unclear, especially in the medium-range order. The present material is perfectly amorphous, according to conventional diffractometry, in which structural periodicity in the long-range order is not evaluated. This material, however, can be distinguished clearly from an amorphous form with randomly distributed tetrahedral clusters. The configuration of the tetrahedra is the same as that in crystalline diamond within the unit-cell size cluster. The nearest-neighbor data obtained in the present work infer an amorphous nature in which highly ordered amorphous clusters, measuring less than 1 nm, are randomly packed.

The RDF analysis revealed that the present amorphous diamond is wholly different from sp^2-based structures and also can be distinguished from the ta-C and other tetrahedrally coordinated amorphous semiconductors previously reported. This characteristic structure probably originates from the initial bond nature C_{60} fullerene. C_{60} fullerene is composed of fcc-stacked C_{60} balls that possess highly modified hybridization, nearer to sp^3 than to sp^2, because the bond angle 108°, in the five-member rings is comparable to the bond angle of 109° 28′ in an ideal sp^3 bond.[20] According to compression studies of C_{60} fullerene, compression brings the C_{60} balls closer together without causing deformation,[21] and a certain interball bonding then is produced by further compression.[22] This interball bonding involves the formation of an embryo of the sp^3 bond. Finally, the C_{60} fullerene structure collapses to become amorphous, forming a vast number of sp^3 bonds or diamond embryos simultaneously and homogeneously throughout the collapsed C_{60} fullerene. The C_{60} fullerene therefore seems to produce an sp^3 band more easily than do other graphite-based materials. This result is supported by previous compression studies on many graphite-based materials; those graphite-based materials did not exhibit sp^3 bond formation or diamond transition under the same conditions used for fabricating the amorphous diamond.[23] The ~0.7 nm peak in the amorphous diamond was not observed for other amorphous materials reported. That size of 0.7 nm or less was comparable to the size of a C_{60} cluster or of the body diagonal of a unit cell in crystalline diamond. If the peak represents intrinsic information about the present material, it can be speculated that this cluster size probably derives from the C_{60} balls.

The present work on RDF analysis by use of the IP method resulted in a comprehensive understanding of the structural nature of the amorphous diamond synthesized from C_{60} fullerene by shock compression and rapid quenching. The present results emphasize that the local structure of the present material closely resembles crystalline diamond within a unit-cell size region, despite the fact that the essence of the material is amorphous. A high-resolution TEM observation in a future work can truly confirm its amorphous nature.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture, and by the Asahi Glass Foundation.

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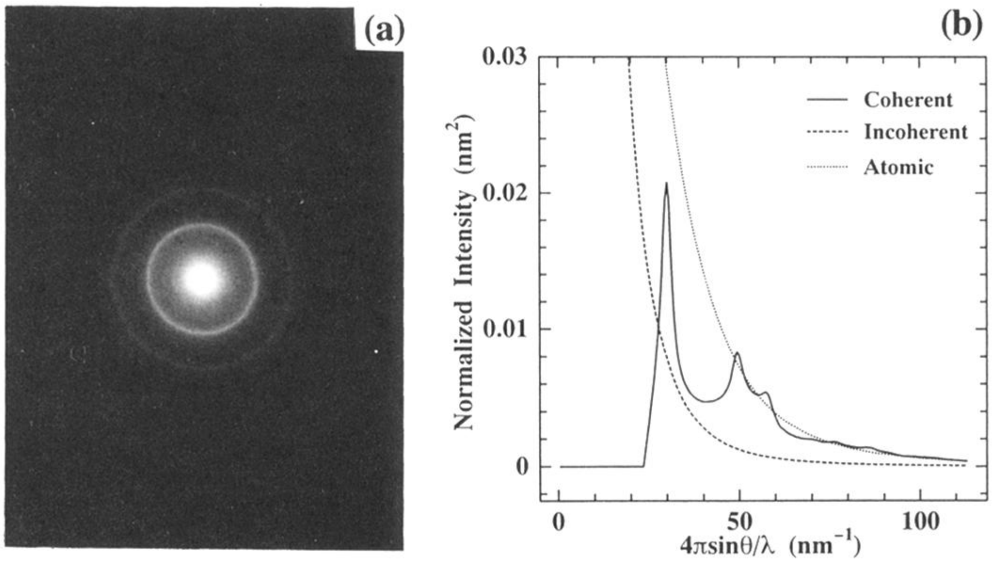

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