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Changes in structure and electronic state from C_{60} fullerene to amorphous diamond

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Changes in electronic state and structure from C_{60} fullerene to amorphous diamond under shock compression were examined by electron energy-loss spectroscopy and electron diffractometry for the recovered samples from the 50 to 55 GPa compressions. Three transient states were distinguished. In the first transient state, the fcc structure was almost unchanged, and the π plasmon was prohibited owing to decreasing intercluster distance. In the second state, the basic stacking structure of clusters was barely retained, and intercluster bondings were generated. In the third state, the fullerene structure collapsed to be amorphous, while sp^3 bonding was partly produced. Finally, complete sp^3 bonds were entirely reproduced, whereas the diamond structure in the long-range order was not reconstructed.

I. INTRODUCTION

Amorphization under pressure has been a hot issue in high-pressure science and material science. Also, for C_{60} fullerene, some amorphous phases have been produced by static and shock compressions. Among them, a new transparent material which can be called "amorphous diamond" has been successfully fabricated from C_{60} fullerene by the shock compression and rapid quenching (SCARQ) technique.[1] This material is amorphous in long-range order, according to x-ray and electron diffractometry, while it is diamond in short-range order, consisting only of sp^3 bonds totally equivalent to those of a typical diamond, according to electron energy-losss spectroscopy (EELS) and Raman spectroscopy. Another SCARQ experiment was conducted by the present authors with a lower-grade initial C_{60} fullerene containing impurities and defects.[2] This experiment exhibited the entire transition to the diamond crystallite, probably because of easier nucleation and crystal growth due to the impurities and defects. It also demonstrated that the transition was achieved through an amorphous phase. Several amorphous phases previously reported[3,4] were similar to the above amorphous diamond and different from disordered graphite consisting of sp^2 bonds.[5,6] A transparent amorphous phase was formed by nonhydrostatic compression using a canted diamond anvil cell.[3] Another transparent phase produced by shock compression was so unstable that it turned back to an opaque graphitic amorphous phase in a few days.[4] However, their structures and the electronic states were insufficiently characterized. Besides these products obtained by the recovery experiments, electrical and optical properties were measured under high pressure, and the following various phenomena were reported, which suggest formation of amorphous phases consisting of sp^3 bonds.[7,8] The optical absorption edge showed an irreversible transition to a transparent amorphous phase[7] and the optical reflectively spectrum showed a transition to amorphous carbon.[8] The electrical resistivity decreased as pressure increased, and a subsequent sudden transition to a more insulating phase occurred.[9] On the basis of these experimental results, it can be concluded that an intrinsic behavior of C_{60} fullerene under high pressure is to collapse to an amorphous phase consisting only of sp^3 bonds. Several changes in the electrical and optical properties probably indicate several transient states in a series of changes from sp^2 to sp^3 hybridization states. Therefore to clarify the formation process of sp^3 bonds from C_{60} fullerene is of great interest and urgency.

The amorphous diamond was synthesized with good reproducibility, being quite stable under ambient conditions such as air and light. The amorphous diamond was obtained as transparent glassy chips measuring a few tens of μm to 100 μm in size. The amorphous diamond in the recovered sample was usually more than 90%, coexisting with a small amount of altered C_{60} fullerene. Some larger chips recovered included a black core which consisted of variously altered C_{60} fullerenes caused by the temperature distribution during the shock compression. The variously altered fullerenes quenched together with the amorphous diamond in these chips were the most suitable sample for examining the changes from C_{60} fullerene to amorphous diamond. As a characterizing technique, the electron diffraction pattern (EDP) provides information on the structure in the long-range order, while plasmon-loss spectra of electron energy-loss spectroscopy provide information on the electronic state and/or bonding states in the short-range order. By combining these analyses, we can explore the changes in the structure and the electronic state of the variously altered C_{60} fullerenes and the coexisting amorphous diamond. The present work is intended to clarify the formation process of the amorphous diamond from C_{60} fullerene by using the EDP and EELS, and to discuss the observed transient states concerning the behaviors reported under high pressure and the electronic state.[10]

II. EXPERIMENTS

The SCARQ technique is advantageous for fabricating transient phases such as amorphous diamond. This is because this technique generates adequately high pressure and temperature for an extremely short duration within a

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fraction of a microsecond, and also quenches transformed phases with cooling rates of 10^6 to 10^{10} K/s.[11] The detailed experimental procedure and the initial C_{60} fullerene were described in previous papers.[1] In order to quench a transformed phase, single crystals of the initial C_{60} fullerene were sandwiched by gold or silver heat-sink disks. The sandwich was supported by a protection system and was subjected to shock loading of 50, 54, and 55 GPa. Shock temperature was estimated to be 2000 K for bulk C_{60} fullerene, but some temperature distribution might exist around the initial C_{60} crystals. Shock duration at peak pressure was ~ 0.3 μs. More than 90% of the initial material was transformed to transparent glassy chips. First, it was confirmed that the material was composed only of carbon by EELS (k absorption edge) and energy-dispersive x-ray spectroscopy. It was then characterized by x-ray diffractometry, electron diffractometry, Raman spectroscopy, and EELS. The present study examined by transmission electron microscopy (TEM) and EELS some larger chips including an opaque core, where C_{60} fullerene remained variously altered.

III. RESULTS AND DISCUSSION

The initial C_{60} fullerene [Fig. 1(a)] exhibited a sharp and latticed EDP showing a fcc structure [Fig. 1(b)]. Two bulk plasmon peaks at approximately 6.4 and 26.7 eV were observed in the EELS spectrum [Fig. 1(c)]. The first peak was attributed to the collective excitation due to π electrons (π plasmon), and the second peak to that due to $\pi+\sigma$ electrons ($\pi+\sigma$ plasmon).[12,13] In the slightly altered fullerene [Fig. 1(d)] showing an almost unchanged EDP or a slightly broader one [Fig. 1(e)], the π plasmon peak was extremely weakened or absent, and the $\pi+\sigma$ plasmon peak was shifted to lower energy (24.5 eV) [Fig. 1(f)]. According to Duclos *et al.*'s compression study,[14] C_{60} fullerene is compressed without deformation of the cluster until the intercluster distance nears the intracluster atomic distance. The electron band structure and valence-electron density of fcc C_{60} fullerene have been calculated using the natural lattice constant by Saito and Oshiyama.[10] The π bonding spreads outside the cluster more than the σ bond, and shows intercluster overlap. Therefore the first transient state can be regarded as a compressed C_{60} fullerene in which the basic fcc structure is retained, and only the collective excitation of π electrons is prohibited owing to the decrease of the intercluster distance. The early and sensitive response of the π bonding state compared with the σ bonding is reasonably supported by the band structure and electron density.[10] The shift in the second peak to lower energy indicates a lower density of the initial $\pi+\sigma$ electrons, since the magnitude of the shift of the plasmon peaks to lower energy for carbon materials depends on the density of complete sp^2 or sp^3 bonds.[15]

In the more altered portions [Fig. 2(a)], the π plasmon peak completely disappeared, and new shoulders appeared instead at approximately 12 and 17 eV [Fig. 2(c)]. In spite of this change in the electronic state, these portions still showed a broader but latticed EDP [Fig. 2(b)], which could be indexed as the fcc structure. A lower-symmetry structure[14] and a rhombohedral structure[16] were formed by the static compression. The latter structure was explained by the occurrence of linkage of the clusters. In the EDP presently observed, reduction of d spacing and/or lowered symmetry, if any, were not evaluated because of low resolution of the EDP. In any case, the basic structure composed of stacked C_{60} clusters was retained, although individual clusters might be somewhat deformed. The new shoulders in the EELS are attributed to single-electron excitations of $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, and $\sigma \rightarrow \sigma^*$ transitions by Kuzuo *et al.*[12,13] using their specialized apparatus with high resolution of 0.16 eV and analyzing by the Kramers-Kronig method. Usually the interband excitations of electrons cannot be detected by the conventional EELS apparatus used in the present

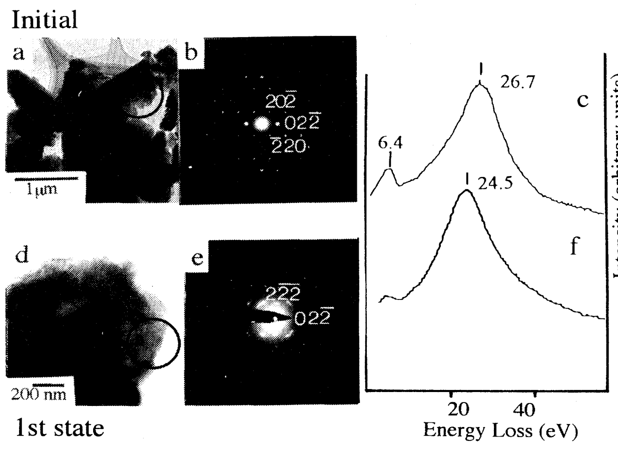

FIG. 1. Representative TEM micrographs, EDP's and EELS spectra. (a), (b), and (c): the initial C_{60} fullerene. (d), (e), and (f): the first transient state.

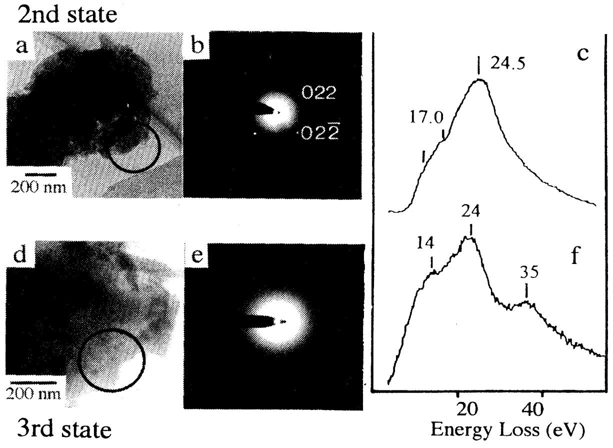

FIG. 2. TEM micrographs, EDP's, and EELS spectra. (a), (b), and (c): the second state. (d), (e), and (f): the third state.

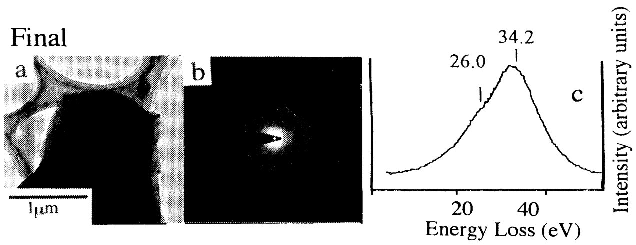

FIG. 3. TEM micrograph, EDP, and EELS spectrum for the final state of amorphous diamond.

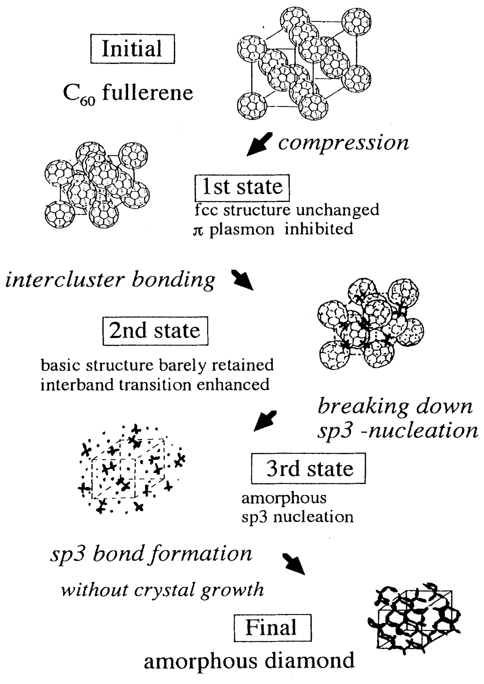

FIG. 4. Schematic illustration of the formation process of amorphous diamond from C_{60} fullerene.

study, because they have much lower intensities than those of the plasmon. The excitations of electrons, however, were distinctly distinguished in the second state. This means that the interband transitions were enhanced, while the initial collective excitation of π electrons ceased. Both the electronic state and the structure maintaining the basic stacking sequence suggest that a certain intercluster bond was produced by a further decrease of the intercluster distance. The transition to an insulating phase detected by the change of electronic resistivity was explained also by the intercluster bonding of neighboring clusters.[9] The production of intercluster bonding is reasonable, considering the compression behavior[14] and the electron states.[10]

The highly altered portion [Fig. 2(d)] represented the EDP of a halo [Fig. 2(e)], indicating breakdown of the structure. An additional peak rose at approximately 35 eV beside the 14, ~20, and 24 eV peaks in the EELS spectrum [Fig. 2(f)]. For a typical diamond, a peak at 34.5 eV and a shoulder at ~25.5 eV appear; the former is assigned to the bulk plasmon peak of σ electrons, and the latter is differently explained as a surface plasmon,[17] interband transition,[18] or sp^2 contamination.[19] The appearance of the former peak at ~35 eV implies directly that the sp^3 bond was produced in the portion where the long-range order structure was already broken.

Figure 3(a) shows a representative amorphous diamond with a homogeneous and dense mass. The EDP showed two quite diffuse bands with maxima at approximately 0.22 and 0.12 nm [Fig. 3(b)]. The EELS spectrum exhibited a shoulder (26.0 eV) and a peak (34.2 eV), which were totally equivalent to σ electrons in a typical diamond. Although the long-range order structure is not built up, the bonding state of sp^3 was completely reproduced. The transparent phases found by the measurements of the optical absorption edge[7] are probably the same material as the amorphous diamond, because they exhibited the same Raman spectra.

Figure 4 represents an elemental and tentative scheme of the progression from C_{60} fullerene to amorphous diamond. The first transient state can be recognized as a compressed fullerene. The fcc structure is unchanged, and only the π plasmon is prohibited owing to a decrease of the intercluster distance. The most striking feature of the second state is the production of the intercluster bonding, and the basis stacking sequence of the structure is barely retained. The second state calls to mind a polymerization of C_{60} clusters[16,20] and a hypothetical structure envisioned as "C_{60} zeolite," which is built up by C_{60} clusters joined by intercluster bonding.[21] A drastic change in the structure and the bonding state occurs in the third state. The C_{60} fullerene structure collapses to be amorphous, and complete sp^3 bonds are partly produced. Subsequently, a vast number of sp^3 bonds forms homogeneously throughout the material, and this state is quenched without crystal growth. In this way, the transition was accomplished. If further thermal energy is supplied or some other factors facilitate diamond nucleation (namely, sp^3 bond formation), diamond crystals might grow. In any case, an interesting feature in this phase transition is that the electronic and bonding states change prior to a structural transition in which rearrangement of atoms is necessary over a longer distance. The present work, a combination of EELS with EDP analyses, has developed a comprehensive understanding of the transition behavior of C_{60} fullerene. As future work, a theoretical calculation and an *in situ* measurement will be required in order to confirm the postulated electronic states and cluster motions.

ACKNOWLEDGMENTS

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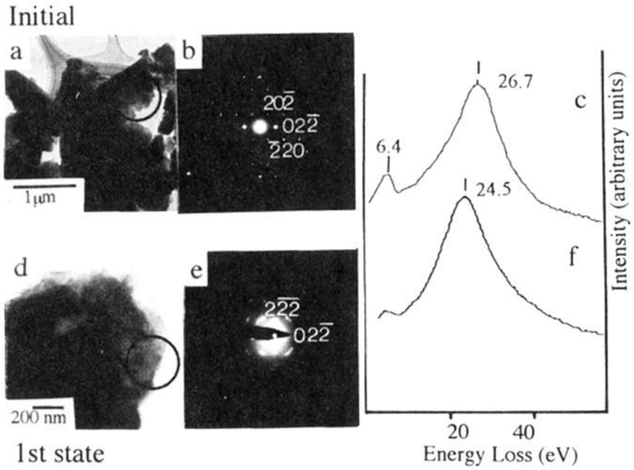

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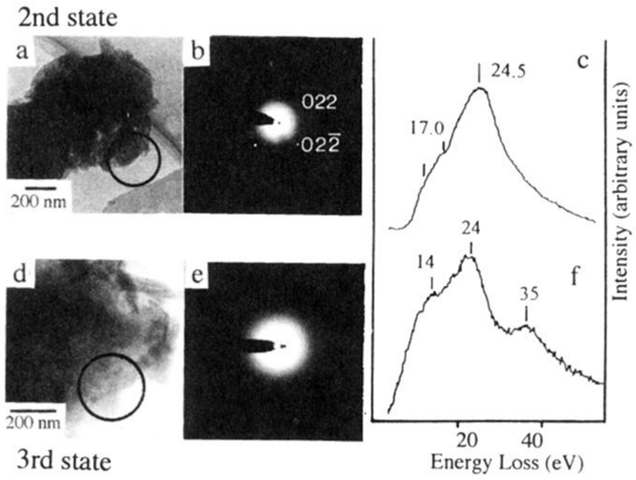

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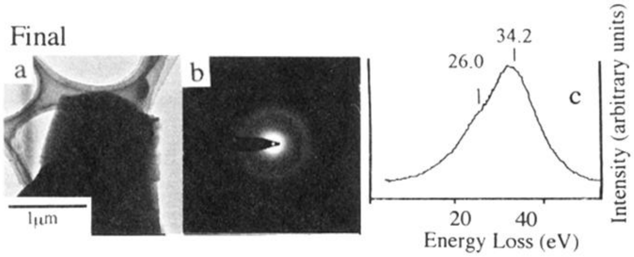

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