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High energy-resolution electron energy-loss spectroscopy and soft-x-ray emission spectroscopy studies of amorphous diamond transformed from neutron-irradiated graphite

Y Sato¹, M Terauchi¹, K Niwase², K G Nakamura³, T Atou³ and T Iwata⁴

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
²Hyogo University of Teacher Education, Kato-shi, Hyogo 673-1494, Japan
³Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama, 226-8503, Japan
⁴Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan

E-mail: y-sato@tagen.tohoku.ac.jp

Abstract. High energy-resolution electron energy-loss spectroscopy measurements were performed for amorphous diamond (am-DIA), which was synthesized from neutron-irradiated graphite by shock compression, by using a monochromator transmission electron microscope (TEM). Soft-X-ray emission spectroscopy (SXES) measurements were performed by a wavelength-dispersive type spectrometer attached to the monochromator TEM. A volume plasmon peak of am-DIA is observed at 32.5 eV, which is a little smaller than that of crystalline diamond (c-DIA). The smaller plasmon energy of am-DIA indicates a smaller valence electron density of am-DIA than that of c-DIA. From the onset energies of the K-shell excitation and the SXES spectra, the band gap energy of am-DIA is estimated to be 4 eV, which is similar to the value, 3.9 eV, from the valence electron excitation spectrum and reported values, 3.5-4.5 eV, for the am-DIA synthesized from C₆₀ fullerene by shock compression.

1. Introduction
Transformation from carbon materials to diamond is a long time issue and various crystalline sizes of diamond have been synthesized by the techniques of static pressure and shock compression. By the conversion of graphite under a static high pressure and a high temperature, hexagonal diamond (h-DIA) has been synthesized and the electronic structure has been investigated by using a high energy-resolution electron energy-loss spectroscopy (EELS) transmission electron microscope recently [1]. Also, polycrystalline diamond has been synthesized and shown to have extremely high hardness [2]. The ultimate smallest crystalline size of diamond has been synthesized from C₆₀ fullerene by shock compression and rapid quenching (SCARQ) technique [3,4]. The obtained material was transparent, suggesting diamond structure, but the diamond crystalline size is within the range of unit cell. Then, it was labelled “amorphous diamond (am-DIA)” as it is amorphous in the long-range order and diamond in the short-range order [5]. Graphite, on the other hand, has not been found to transform to am-DIA by shock compression but to crystalline diamond by the martensitic mechanism, if shock pressure is
applied parallel to the c axis [6]. Recently, a novel pathway for the transformation from highly oriented pyrolytic graphite (HOPG) into am-DIA has been discovered [7]. The pathway consists of neutron irradiation, shock compression, and rapid quenching. Defects produced by irradiation (Wigner defects) are considered to work as the nucleation sites for diamond.

Here, we aimed to investigate the electronic structure of the am-DIA synthesized from neutron-irradiated graphite by using a high energy-resolution EELS transmission electron microscope (TEM) and a soft-X-ray emission spectroscopy (SXES) instrument attached to the monochromator TEM.

2. Experimental procedure
Am-DIA was synthesized by SCARQ from HOPG, which was irradiated with fast neutrons at about 333 K to a dose of 2.6x10\(^{24}\) n m\(^{-2}\) [7]. The shock pressure was estimated to be 51 GPa. Specimens for transmission electron microscopy were prepared by pasting a piece of am-DIA on a microgrid for TEM and the pasted piece of am-DIA was thinned by using a focused ion-beam (FIB) instrument. High energy-resolution EELS measurements were performed by using a monochromator TEM [8]. The energy resolutions were 80 - 150 meV at an accelerating voltage of 100 kV. SXES measurements were performed by using a wavelength-dispersive type spectrometer [9] attached to the monochromator TEM. The energy dispersion on a CCD detector was 0.34 eV/channel at carbon K-emission energy of 280 eV.

3. Results and discussion
Figure 1 shows a valence electron excitation spectrum of am-DIA. A spectrum of cubic diamond (c-DIA) is also shown for comparison. A volume plasmon peak of am-DIA is observed at 32.5 eV, which is a little smaller than that of c-DIA. Since the volume plasmon energy is proportional to square root of valence electron density, the lower plasmon energy of am-DIA indicates that the valence electron density of am-DIA is smaller than that of c-DIA (0.71 x 10\(^{24}\) electrons/cm\(^3\)). The spectral structure of am-DIA around 22 eV indicated by a vertical lime is attributed to σ-σ* transitions, which is broader than that of c-DIA. This suggests that oscillation strength of the σ-σ* transition is broader in energy than that of c-DIA. The onset of the spectrum intensity of am-DIA is assigned at 3.9 eV, which correspond to the band gap energy of am-DIA. This energy of am-DIA is apparently smaller than that of c-DIA (5.5 eV).
Figure 2 shows K-shell excitation spectra of am-DIA and c-DIA, which correspond to the partial density of states (DOSs) with p-symmetry of conduction bands (C.B.). Weak intensity around 280 – 286 eV might come from sp² components of amorphous carbon layer overlaying am-DIA specimen, which is produced by ion-beam irradiation of FIB process. Onset energy of am-DIA is assigned to be at 287 eV as indicated by an arrow. A sharp peak at 289 eV of c-DIA corresponds to an exciton peak. Exact energy position of conduction band bottom of c-DIA without the exciton peak intensity was evaluated to be at 289.2 eV, where the exciton peak was fitted by Gaussian (dashed line) and density of states of conduction bands were by parabolic band model (solid line) [12]. Therefore, energy position of C.B. bottom of am-DIA is approximately 2 eV lower than that of c-DIA.

Figure 3 shows SXES, carbon K-emission, spectra of am-DIA and c-DIA, which correspond to the partial DOSs with p-symmetry of valence bands (V.B.). The widths of those spectra are attributed to energy distribution of individual sp² bonding levels. One peak is observed at 278 eV in the spectrum of am-DIA and any other structures are not observed. Top of valence band of am-DIA is at 282 eV, which is 2 eV lower than that of c-DIA at 284 eV.

Figure 3 shows SXES, carbon K-emission, spectra of am-DIA and c-DIA, which correspond to the partial DOSs with p-symmetry of valence bands (V.B.). The widths of those spectra are attributed to energy distribution of individual sp² bonding levels. One peak is observed at 278 eV in the spectrum of am-DIA and any other structures are not observed. Top of valence band of am-DIA is at 282 eV, which is 2 eV lower than that of c-DIA at 284 eV.
(indicated by an arrow), which is 2 eV lower than that of c-DIA at 284 eV. Width of V.B. of am-DIA is 9.4 eV, which is narrower than that of c-DIA (10.8 eV).

Figure 4 shows the carbon K-emission and the carbon K-shell excitation spectra of am-DIA and c-DIA, which experimentally show a distribution of partial DOSs of V.B. and C.B. The energy positions of the SXES spectra were calibrated in order that the top of valence band of c-DIA was located at 5.5 eV (band gap of c-DIA) lower than the bottom of C.B. It is revealed that the band gap energy of am-DIA is 4.0 eV, which shows good agreement with the estimation of 3.9 eV from the onset energy of valence-electron excitation spectrum shown in Fig.1.

Am-DIA synthesized from the neutron irradiated graphite have been shown to be optically transparent and exhibited no diamond Raman peak at 1332 cm\(^{-1}\) [7,10]. These features are similar to the one synthesized from C\(_{60}\) fullerene [3,4]. Also, the band gap of am-DIA investigated in the present study is similar to the one synthesized from C\(_{60}\) fullerene, as the value for the latter has been estimated to be 3.5-4.5 eV [11]. Both the values of am-DIAs are smaller than that of c-DIA (5.5 eV). By utilizing the combined method of neutron irradiation and shock compression, we may fabricate a series of materials for which the band gap is controlled arbitrarily. Moreover, the present technique will be useful in future to estimate electronic properties, especially for small-sized materials or ones which can be obtained only in small amounts.

4. Conclusions
A novel pathway for the transformation from highly orientated pyrolytic graphite foils irradiated with neutrons into am-DIA platelets has been discovered previously. The pathway consists of neutron irradiation, shock compression, and rapid quenching. We performed high energy-resolution EELS and SXES measurements for the am-DIA. We revealed the band gap energy of am-DIA is about 4 eV, a value which is similar to the one reported for the am-DIA synthesized from C\(_{60}\) fullerene by shock compression. By changing the neutron dose and the shock condition in the present method, it may produce various states of am-DIA with various electronic structures, and further investigations are awaited.

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