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High energy-resolution electron energy-loss spectroscopy analysis of dielectric property and electronic structure of hexagonal diamond

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ABSTRACT

Electron energy-loss spectroscopy measurements of a hexagonal diamond (h-DIA) were performed using a transmission electron microscope equipped with a monochromator. From the measurements, the dielectric function of h-DIA was derived using Kramers–Kronig analysis (KKA) for the first time. The results of KKA showed that the band gap energy of h-DIA was 4.2 eV, which is 1.3 eV smaller than that of a cubic diamond (c-DIA). The peak energies that appeared in the imaginary part of the dielectric function were assigned to the interband transition energies predicted by theoretical calculations. The K-shell excitation spectrum of h-DIA, which was apparently different from that of c-DIA, also showed good agreement with the reported theoretical prediction.

1. Introduction

Since the discovery of hexagonal diamond (h-DIA) in 1966 [1], syntheses of h-DIA have been attempted by compressing of graphite along [0001] [1–3] and shock wave method [4,5]. These studies have revealed that h-DIA is a metastable crystal phase, and high pressure and high temperature are indispensable for its formation. Only a few nanometer size h-DIA crystals have been synthesized with impurities of cubic diamond (c-DIA) and graphite. The h-DIA (lonsdaleite) was also discovered in meteorites [6]. This implies that synthesis conditions of h-DIA are indicative of the space environment, that the meteorites experimented [6,7]. From the standpoints of industrial applications, diamond has attracted attention in optoelectronic devices for ultraviolet emission [8,9]. The c-DIA crystal has been successfully used in developing light-emitting diodes [8,9]. Moreover, h-DIA may be used in optoelectronic devices. However, the application of h-DIA in optoelectronic devices has not been achieved because it is difficult to synthesize large h-DIA crystals. In addition, the fundamental physical properties of h-DIA have not been experimentally investigated in detail.

The local structure of h-DIA is characterized by tetrahedrally arranged carbon atoms with sp^3 bonding orbitals same as that of c-DIA. The atomic arrangements farther than the third nearest neighbor atoms in h-DIA are different from those of c-DIA. Consequently, the electronic structure of h-DIA may be different from that of c-DIA. Band calculations for h-DIA using ab initio methods [10,11] and the local density-approximation [12,13] reported that h-DIA has an indirect band gap of 3–4 eV, which is 1–2 eV smaller than that in c-DIA (5.5 eV). The minimum direct transition energy of h-DIA was also reported to be 4–5 eV, which is also smaller than that of c-DIA (7.2 eV) by 2–3 eV [10–13].

Electron energy-loss spectroscopy (EELS) based on transmission electron microscopy (TEM) can investigate the electronic structure of an h-DIA crystal even if its size is smaller than a few micrometers and it coexists with other materials of c-DIA, graphite, and amorphous carbon, However, up until now, the TEM–EELS has not succeeded in the investigation. Schmid [14] reported that a plasmon excitation of whole valence electrons was observed at an energy level 0.6 eV lower than that of c-DIA. This was attributed to the low quality of the h-DIA crystals produced by the shock-wave conversion of graphite. Schmid also reported the K-shell excitation spectrum of h-DIA., in which intensity distribution was slightly different than that of c-DIA. However, the spectral features intrinsic to h-DIA were not clearly observed. On the other hand, the calculation of the K-shell excitation spectrum, including the core-hole effect reported by Gao et al., clearly showed a difference in the intensity distribution between h-DIA and c-DIA [15].

The difficulties in investigating the electronic structures of h-DIA by EELS are due to not only the low quality of specimens but also the insufficient energy resolution (about 2 eV) of the EELS experiments. Recently, a TEM equipped with a monochromator (hereafter called "monochromator TEM") has been developed [16,17]. The monochromator in conventional TEM can achieve a nanometer-sized electron

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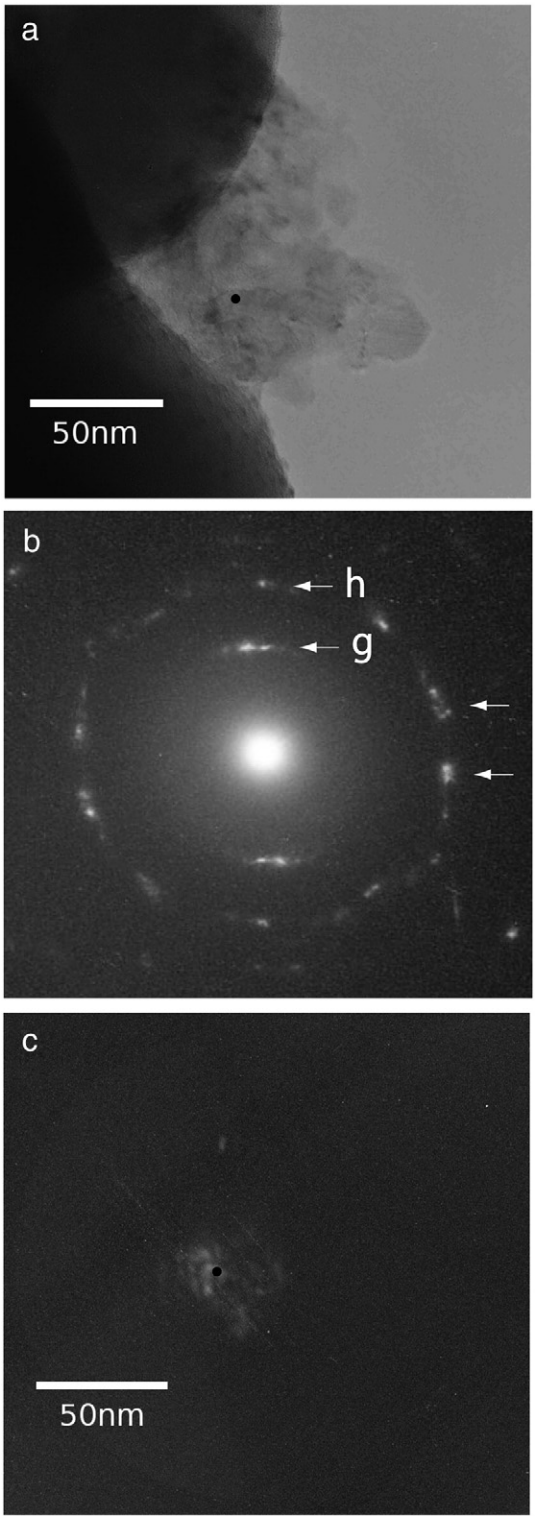

Fig. 1. (a) TEM bright field image, (b) electron diffraction pattern, and (c) dark field image. The diffracted spot h corresponds to the $10\bar{1}0$ of h-DIA and spot g corresponds to the 0002 of graphite. The black dots in (a) and (c) indicate the area of the EELS measurements.

probe with an energy resolution better than 0.1 eV for EELS analysis. Then, it is interesting to apply such a monochromator TEM to study the electronic structure of small crystalline h-DIA.

This study investigates the electronic structure of h-DIA obtained by using a monochromator TEM in detail. The dielectric function of h-DIA was experimentally derived for the first time by Kramers–Kronig analysis (KKA) from the valence electron excitation spectrum. The K-shell excitation spectrum was also obtained, which provides information on the partial density of states (DOS) of the conduction bands. These results were compared with those of c-DIA and the theoretical calculations. The characteristic electronic structures of h-DIA were also assigned.

2. Experiment

An h-DIA was synthesized using a Kawai-type high-pressure apparatus [26]. An anvil assembly of tungsten carbide cubes with a truncated edge length of 5 mm was used. A 10 mm regular octahedron of sintered MgO containing 5% Cr_2O_3 was used as the pressure medium. A graphite sample was compressed at 20 GP and 1400 °C for 20 min [3]. According to the X-ray powder diffraction profile, the specimen was a mixture of h-DIA, c-DIA, and graphite [3]. The mass fractions of h-DIA, c-DIA, and graphite were in the ratio 37:38:25. The average crystallite size of the h-DIA particles was evaluated to be a few nanometers on the basis of Rietveld refinement of the diffraction profile.

The specimen for the TEM observation was prepared by crushing the synthesized materials and dispersing the fragments on a microgrid. TEM images and electron diffraction patterns were obtained by using a JEM-2010 transmission electron microscope at 100 kV. To reduce damage due to irradiation damage and contamination, the specimen was maintained at approximately 100 K using a liquid-N_2 cooling holder. The monochromator, which is equipped with TEM, is located between the extraction anode of the ZrO/W emitter and the accelerating tube. The monochromator consists of two dodecapole-type Wien filters and an energy selection slit, which is inserted between the two Wien filters. The column part of a JEM-2010FEF transmission electron microscope is utilized as the illumination lens system, specimen goniometer, and imaging lens system, in which an omega-filter is used as an analyzer. The imaging plates, which are large to enable the one-step capture of a wide energy range and a large dynamic range ($1.0\times10^{-14}-1.0\times10^{-10}$ C/cm^2), were used to record the intensity of the spectrum. The EELS measurements were performed at an accelerating voltage of 100 kV, at which the electron probe size and energy resolutions were approximately 1 nm in diameter and 0.08–0.12 eV, respectively.

3. Results and discussion

Fig. 1 shows (a) a bright field image, (b) an electron diffraction pattern, and (c) a dark-field image. The black dot in (a) and (c)

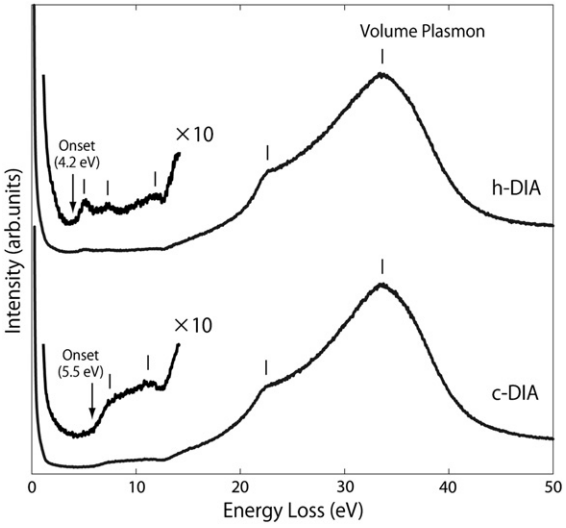

Fig. 2. Low-loss spectra of h-DIA and c-DIA. The energy resolution was 80 meV.