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Characterization of free-standing single-crystal diamond prepared by hot-filament chemical vapor deposition

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ABSTRACT

Hot filament chemical vapor deposition (HFCVD) possesses a large potential to scale-up for the growth of single-crystal diamond (SCD). This study investigates the crystalline qualities of SCD fabricated by HFCVD. A tungsten impurity level of 10^{18} cm^{-3} was detected with secondary ion mass spectroscopy. The full-width at half maximum (FWHM) of the rocking curve (004) was 39.5 arcsec, where that of seed substrates was 42.8 arcsec. A clear free-exciton recombination radiation was observed in cathodoluminescence spectra. The Raman spectra presented a single peak centered at 1333.2 cm^{-1} with a FWHM value of 1.9 cm^{-1}. These results indicate that the HFCVD-grown SCD has good crystalline quality comparable to the seed substrates.

1. Introduction

Diamond semiconducting materials have considerable potential applications in high-power and high-temperature devices because of their superlative physical properties, such as a wide bandgap (5.5 eV), high breakdown electric field (>10 MV/cm) and the highest thermal conductivity (22 W/cm · K) of all materials [1]. Several studies have reported on diamond-based diodes [2,3], and their excellent switching capabilities in high temperature operations [4,5], as well as their low loss of electricity [6], and high blocking voltage [7,8]. The microwave plasma-assisted chemical vapor deposition (MWCVD) method has been extensively utilized for the fabrication of single-crystal diamond (SCD) primarily because of its capacity for high-quality growth, good controllability of the impurity level, and excellent stability of the plasma [9–13]. Recently, a new type of SCD mosaic wafer, named "tiled clones" with an area of a few inches, has been developed by the MWCVD method [14,15]. The commercially available diamond substrates fabricated via the high-pressure high-temperature (HPHT) method are typically limited in size, e.g., around 3 mm^2. The enlarged SCD wafer is thus promising for use in the industrial production of semiconductor devices. However, the MWCVD technique has several disadvantages when growing substrates larger than a few centimeters: (a) restriction of the possible fabrication area by the wavelength of the microwave; for instance, the diameter of the plasma ball is approximately 50 mm when 2.45 GHz microwave frequency is used; (b) concentration of the electrical field to a certain extent at the substrate edges, which may result in crystallographic degradation; [16] and (c) non-uniformity of radicals where growth takes place [17–19], which may result in inhomogeneous growth rate and crystal quality.

The hot filament chemical vapor deposition (HFCVD) method is one way to overcome these disadvantages. This technique is based on the thermal decomposition of growth species by the resistive heating of metal wires, yielding industrially friendly outcomes such as geometric simplification, low cost operation, and a large potential for scaling up to more than 12 in. There have been many attempts to grow polycrystalline diamond films [20–23], as for the homoepitaxial growth of SCD films, few studies have been reported to date, although Chu et al. demonstrated the growth of SCD by HFCVD [24]. SCD films have also been successfully fabricated at various growth conditions of methane concentration [25], α-parameter [26], and different crystal planes [24]. However, the crystalline quality has not been clarified as yet in detail. In this study, freestanding diamond plates were fabricated, and their crystallographic characteristics were investigated.

2. Experimental procedure

Diamond films were homoepitaxially grown by HFCVD (sp^3 Diamond Technology, Inc.). In this study, HPHT-grown type Ib (001) [27] and MPCVD-grown (001) substrates [28] were used. Prior to film

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deposition, the substrates were chemically cleaned by boiling a mixed acid solution of H_2SO_4 and HNO_3 at 250 °C. Tungsten wires of diameter and length of 0.10 and 400 mm, respectively, were employed as the filament materials. The radiative temperature of the heated filaments was checked by an optical pyrometer and found to be 2100 °C. The gas flow was 1000 sccm of H_2 and 30 sccm of CH_4 at total pressure of 30 Torr. The distance between the filaments and substrates was 10–15 mm. To investigate the crystalline quality of the grown films, free-standing diamond plates were fabricated by the lift-off process using C^+ ion implantation. The details of the lift-off method are explained in a previous study [29]. The thickness of the free-standing plates was measured with a micrometer. The surface morphology of the grown films was investigated via differential interference contrast microscopy, laser microscopy, and scanning electron microscopy (SEM). The crystalline quality was examined by secondary ion mass spectrometry (SIMS), X-ray rocking curves, cathodoluminescence (CL), and Raman spectroscopy. SIMS measurements were carried out by O_2^+ ion etching at an applied voltage of 11.0 kV. The etching was started from the grown upper face. Tungsten concentration was quantitatively calibrated by using a standard sample, which was essentially a certain amount of tungsten atom ion implanted into a type Ib (001) substrate. The rocking curve full-width at half maximum (FWHM) omega scans were conducted with a 4-bounce high-resolution X-ray diffraction system (Bede D1) equipped with a Ge (220) channel-cut collimator crystal and a Si (220) dual-channel analyzer crystal (DCA). (004) symmetric reflection of diamond obtained using CuKα1 radiation was used for the measurements. CL measurements were performed at 90 K. The acceleration voltage and electron beam current for excitation were set to 15 kV and 200 nA, respectively. Raman spectra were measured using a HORIBA Jobin Yvon system with a Nd:YAG laser source with a wavelength of 532 nm. The laser intensity, exposure time, and integration time for the Raman spectrum were the same for all the examined films.

3. Results and discussion

3.1. Crystalline quality

SCD films were developed at 3% methane concentration on MWCVD-grown mosaic diamond wafers (001), and the free-standing plates after lift-off were used for crystallographic characterization. The thickness of the plates after 38 h growth was 65 μm, which corresponds to the growth rate of 1.7 μm/h. Fig. 1 shows the UV-Vis transmittance spectra of the free-standing plates. Type IIa and Ib (100) substrates were also measured for comparison purposes. The plates exhibited a sharp off-set edge at 225 nm, similar to the situation for IIa substrates. The offset wavelength was in accordance with the bandgap of diamond (5.5 eV). The transmittance in the visible wavelength region was lower than that in type IIa or Ib substrates, principally because of the effect of surface roughness. Surface polishing was not performed for the plates that were lifted off, thus causing unintended reflection.

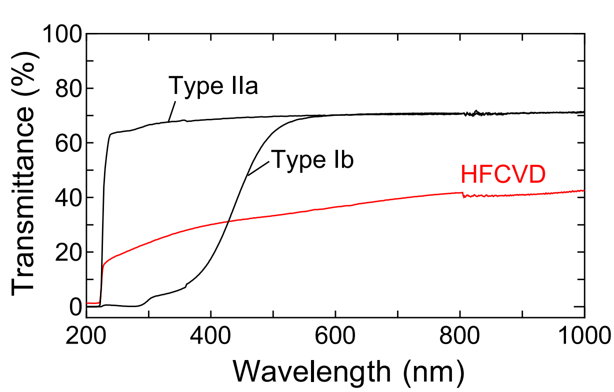

Fig. 1. UV–VIS transmittance spectra of the HFCVD-grown freestanding plates. Type IIa and Ib (100) substrates are shown together for comparison.

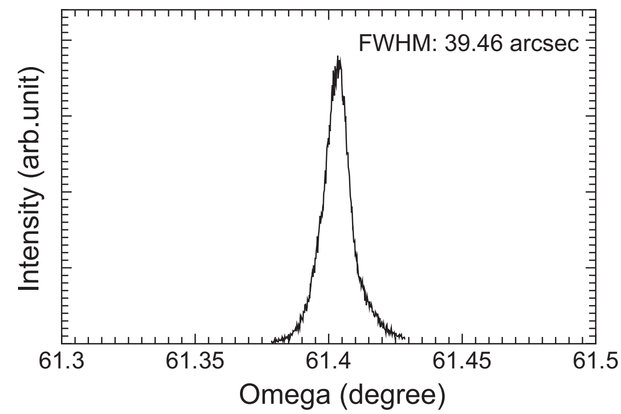

Fig. 2. Typical X-ray rocking curve (004) profile of freestanding SCD plates prepared by HFCVD.

The X-ray rocking curve of the free-standing plate was evaluated using (004) symmetric reflection. Fig. 2 shows the result of the omega scan of the free-standing plates. The seed crystal, which was used as the underlayer substrate for homoepitaxial growth, was also measured for comparison. The FWHM values of the free-standing plate and seed substrate were 39.5 and 42.8 arcsec, respectively. The HFCVD grown films were of good quality comparable to the seed substrate. Better crystalline quality may result from the utilization of higher quality seed substrates. Raman spectra of the plates and seed substrates are shown in Fig. 3(a) and (b), respectively. The plates exhibited a single Raman shift attributable to the presence of diamond. The Raman peak was centered at 1333.2 cm^{-1} with a FWHM of 1.9 cm^{-1}. No broad component peaks arising from the G band or D band, which can be attributed to

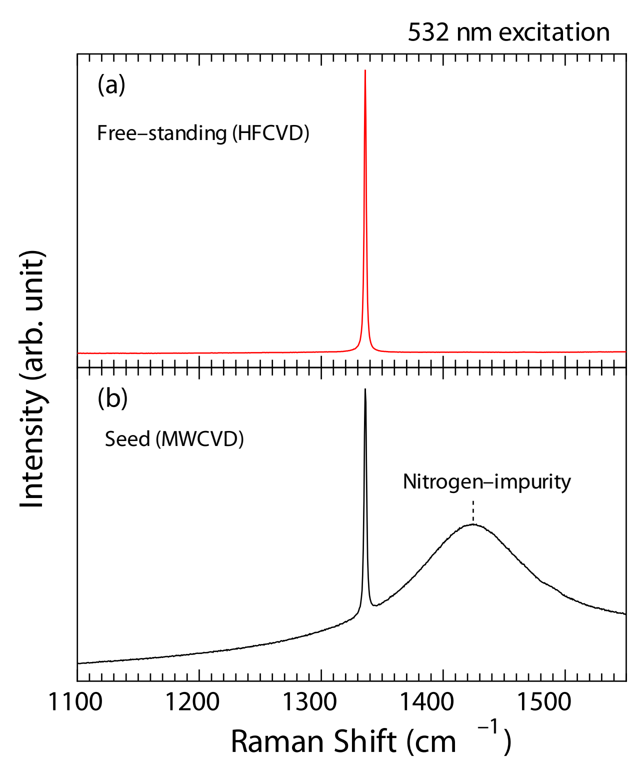

Fig. 3. Raman spectra of (a) SCD plates grown by HFCVD and (b) seed substrates grown by MWCVD.