Low resistivity p$^+$ diamond (100) films fabricated by hot-filament chemical vapor deposition

S. Ohmagari [a],[*], K. Srimongkon [a],[b], H. Yamada [a], H. Umezawa [a], N. Tsubouchi [a], A. Chayahara [a], S. Shikata [a],[1], Y. Mokuno [a]

[a] National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
[b] Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

ARTICLE INFO

ABSTRACT

By hot-filament (HF) chemical vapor deposition (CVD), heavily boron (B)-doped single-crystal diamond (100) films were fabricated and their structural and electrical properties were studied. We did not observe the soot formation, which is frequently observed and limits the performances in the case of microwave plasma (MWP) CVD. The B concentration was successfully controlled over the range from 10^{19} to 10^{21} cm^{-3}. Hillock-free films were obtained, whose mean surface roughness measured by atomic force microscopy (AFM) was less than 0.1 nm. From the reciprocal space mapping (RSM) around 113 diamond reflection, it was revealed that the films possess the smaller lattice expansion than that expected from the Vegard's law. The room-temperature resistivity was decreased lower than 1 m$\Omega \cdot$cm for B concentration $\sim 10^{21}$ cm^{-3}. These results indicate that the HFCVD possesses large potential for fabricating the device-grade p$^+$ diamond.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Diamond is attractive for high-power, low-loss, and high-temperature power devices operable under harsh environments. So far, several trials with diamond-based devices have demonstrated high blocking voltage (>10 kV) [1], high-temperature durability (973 K) [2], and fast-switching (15 ns) [3] characteristics. The diodes have been also reported showing high current density of more than 1 kA/cm^2 [4–6]. However, the actual operation current is less than 5 A [7,8], which limits the usage of diamond in industrial applications.

B-doping is a well adapted technique to produce p-type conduction in diamond, and heavily B-doped (p$^+$) substrates have been fabricated via both high-pressure high-temperature (HPHT) gradient method [9, 10] and MWP CVD [11,12]. In most of these attempts, the B concentration and the resistivity of the p$^+$ layers are limited to be less than $\sim 10^{20}$ cm^{-3} and larger than 10 m$\Omega \cdot$cm, respectively. The highest B concentration and the lowest resistivity, which have ever been reported for thin films, are $\sim 10^{22}$ cm^{-3} and ~ 0.6 m$\Omega \cdot$cm, to the best of the author's knowledge [13–16].

The preparation of p$^+$ substrates via MWPCVD suffers from several technical shortcomings such as the soot formation [12,17] and limited growth area [18–20]. These problems are still open issues. The HPHT is also considered to be an impractical method to grow large size crystals. On the other hand, HF CVD is now widely adapted to grow poly-crystalline diamond coatings even with a low resistivity [21–24]. However, this method is considered to be unsuitable for the homoepitaxial growth owing to a possibility of the impurity-induced non-epitaxial growth. Recently, we demonstrated the fabrication of single-crystal freestanding diamond plates by HF CVD [25]. It was revealed that hillock-free and high-quality undoped films could be homoepitaxially grown, if one optimizes growth parameters appropriately, such as the substrate temperature, the methane concentration, and the substrate off-axis angle. This result indicated the advantages of HFCVD, i.e., simplicity of the system and extremely large growth area, e.g., 12 inch square, could be utilized for practical homoepitaxial growth. In this study, aiming at the fabrication of high-quality p$^+$ substrates over large areas, heavily B-doped single-crystal diamond (100) films were prepared. Electrical and structural properties were comprehensively investigated. The result indicates that the film resistivity was successfully decreased to 1 m$\Omega \cdot$cm. From the structural analysis based on the X-ray diffraction (XRD), transmission electron microscopy (TEM) and AFM, key factors for fabricating the p$^+$ diamond by HFCVD are discussed.

---

2. Experimental

Heavily B-doped p$^+$ diamond films were fabricated by HFCVD (sp3 Diamond Technology, Inc.). Approximately 1-μm thick p$^+$ films were grown on (100) insulating single-crystal substrates, whose misorientation angles are around 3°. Two kinds of substrates, i.e., HPHT-grown substrate and CVD-grown one, were used. The substrate surface was treated in an appropriate manner by scaife polishing or lift-off technique using C$^+$ ion plantation. The surface roughness was less than 0.1 nm of Ra. Before film growth, the substrates were chemically cleaned using a mixed acid solution of H$_2$SO$_4$ and HNO$_3$ at 250 °C. Tungsten wires with a diameter and length of 0.12 and 400 mm, respectively, were employed as filament materials. The filament temperature was maintained around 2100 °C during the growth. The CH$_4$ and H$_2$ gases were regulated by mass flow controllers at 30 and 995 sccm, respectively. The total pressure was 30 Torr. The distance between the filaments and substrates was fixed to be 15 mm. The growth time was 5 h for each experimental condition. For the B source, 2% trimethylborate (TMB) gas diluted with hydrogen was used. The B concentration in the gas phase [(B/C)$_{gas}$] was controlled by changing the TMB flow amount. The B concentration in the films was measured by secondary ion mass spectroscopy (SIMS) using Cs$^+$ ion at an acceleration voltage of 15.0 kV. The film morphology was investigated by AFM. The lattice structure was investigated by RSM around 113 diamond reflection with scattering planes along both [001] and [110] direction using CuKα1 radiation. 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) was used for the measurement. The TEM observation was performed by a Hitachi H-800 at an operating voltage of 200 kV. Focused ion beam (FIB) sample preparation was performed using a XVision200DB, SII Nanotechnology, which carried out Ga ion milling at 1–30 kV. As for the electrical properties, the uncompensated acceptor concentration was evaluated by transmission-type Fourier transform infrared spectroscopy (FTIR) using JASCO IRT-5000 equipped with the FT/IR 6100 system. The B-related peak appearing at 1250–1300 cm^{-1} was used for the evaluation [26]. The film resistivity was evaluated using a Hall-effect system with van der Pauw geometry. The Ti/Au electrodes were formed at the four sample corners using an electron-beam (EB) evaporator with a mechanical mask.
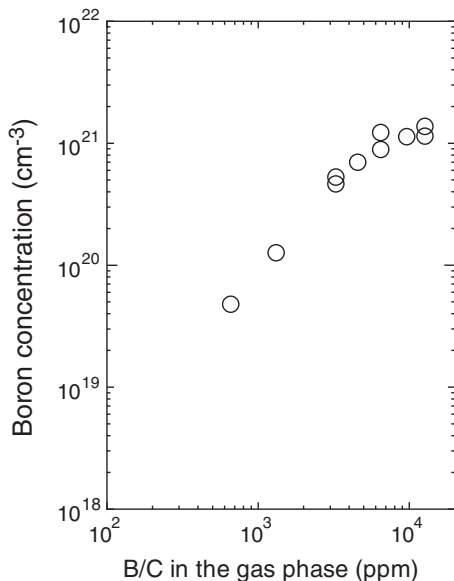

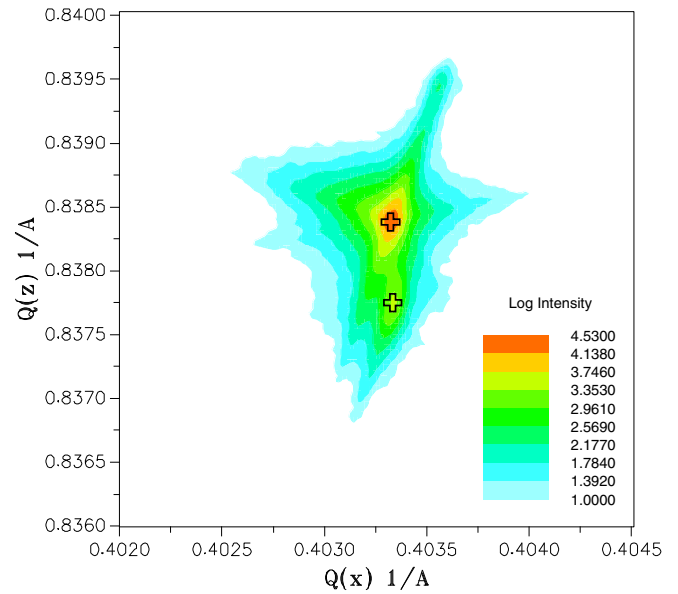**Fig. 1.** Dependence of B concentration in the films on B/C molar ratio in the gas phase.

Fig. 2. RSM image around 113 asymmetric reflection of p$^+$ film prepared at (B/C)$_{gas}$ of 6535 ppm.

3. Results and discussion

3.1. Structural property

3.1.1. Boron incorporation efficiency

The heavily B-doped diamond films were prepared at wide (B/C)$_{gas}$ ranges between 200 and 12,820 ppm. Non-epitaxial crystallites and pyramidal hillocks were not generated. Note that soot formation was not confirmed in our system, which enables long-time operation, e.g., >100 h. The B concentration in the films was evaluated by SIMS. Fig. 1 shows the dependence of the B concentration against (B/C)$_{gas}$. The B concentration in the films was increased monotonously with increased (B/C)$_{gas}$. The amount of doped B was successfully controlled over a wide range from 4.7×10^{19} to 1.2×10^{21} cm^{-3}. The incorporation efficiency of B from gas phase to solid is found to highly maintain even when the heavily-doping was undertaken.

3.1.2. Lattice structures evaluated by RSM and TEM

The lattice structure of the p$^+$ film/substrate interface was investigated by RSM. Fig. 2 shows the 113 asymmetric RSM image of the p$^+$ epitaxial layer grown at 6535 ppm possessing the B concentration of 1.2×10^{21} cm^{-3}. The RSM spots coming from substrate and p$^+$ film could be distinguished. This indicates that the occurrence of lattice strain between the substrate and the p$^+$ film due to heavily B-doping. The spot was separated toward normal-direction, which indicates the pseudomorphic growth. The lattice expansion (Δa/a) of p$^+$ films was estimated to be +0.08%. According to the Vegard's law [27], which describes lattice expansion based on the difference of covalent bonding radii between the host element and the impurity atom, the Δa/a can be calculated to be +0.10% for the B concentration of 1.2×10^{21} cm^{-3}. This indicates that our films possess slightly smaller lattice expansion than that expected from Vegard's law. As for the possible explanation for the smaller lattice expansion, it has been proposed the contribution of free holes and the negative deformation potentials at the valence band maximum (VBM) [28]. The effect of B clusters or interstitial B incorporation, which do not contribute to generate free holes, is unlikely since the electrical measurements (see Section 3.2.) have confirmed that all incorporated B atoms are electrically active. As for the heavily B-doped diamond (~10^{21} cm^{-3}), a high density of free