New Diamond and Frontier Carbon Technology
Vol. 17, No. 1 2007
MYU Tokyo

NDFCT 528

Growth of Heavily Boron-Doped Polycrystalline Superconducting Diamond

Hitoshi Umezawa[1, 3], Tomohiro Takenouchi[1], Kensaku Kobayashi[1],
Yoshihiko Takano[2], Masanori Nagao[2], Minoru Tachiki[2],
Takeshi Hatano[2] and Hiroshi Kawarada[1]

[1]School of Science and Engineering, Waseda University,
3-4-1 Okubo, Shinjyuku-ku, Tokyo 169-8555, Japan
[2]National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[3]National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

(Received 21 January 2007; accepted 24 April 2007)

Key words: diamond, superconductivity, heavily boron-doped, transition temperature

The introduction of a high concentration of boron into polycrystalline diamond films is realized by the chemical vapor deposition of the films. The growth parameter α, which is determined as the growth direction, depends on growth conditions such as the methane concentrations and B/C ratio. With an increase in methane concentration or B/C ratio, <111>-faceted growth is frequently observed. From X-ray diffraction measurement, the <111>-textured growth of the film is confirmed under high-α conditions. The diamond film grown, which has an extremely low resistivity (1.23 mΩ·cm), shows a transition to superconductivity at 5.6 K. For films grown under high-α conditions, for which the surface energy of the {111} face is low, a higher T_c is observed.

1. Introduction

Diamond is the most promising material for future electronic devices because of its superior material properties such as its wide band gap (5.5 eV), high thermal conductivity (22 W/cmK), high breakdown field (10 MV/cm), high mobility (4500 and 3800 cm^2/Vs for electrons and holes, respectively) and chemical/physical stability. Consequently, the expected applications of diamond in various fields are numerous, including application in high-power/high-frequency devices, high-temperature electronics, biomedical sensors and electrochemical electrodes. Consequently, considerable attention has been focused on realizing high-quality diamond growth and controlling impurity doping. In 1955, the

---

[*]Corresponding author: e-mail: hitoshi.umezawa@aist.go.jp

first reproducible synthesis of diamond was realized by Bundy *et al.*(1) The technique they used was the high-pressure and high-temperature (HPHT) method, which imitated the conditions deep underground such as a pressure of 10 GPa and a temperature of 2000 K.(1) However, the HPHT method requires large equipment, the synthesized diamonds are small with a bulk structure, and the level of impurities is not controllable. On the other hand, chemical vapor deposition (CVD) is a technique that is highly suitable for synthesizing diamond for electronic devices and enables large-area thin-film growth and impurity control. The major innovations of the hot-filament method and plasma CVD method were developed by Matsumoto *et al.* and Kamo *et al.* in 1982(2) and 1983,(3) respectively.

High-purity diamond is a band insulator with a wide band gap of 5.5 eV. However, by introducing impurities such as boron into the substitutional sites, semiconducting diamond with 0.37 eV activation can be obtained. An increase in boron concentration decreases the activation energy,(4) as a result a "metallic conduction" is obtained when the doping level is higher than $1–3 \times 10^{20}/\text{cm}^3$ according to the impurity band formation. In 2004, Ekimov et al. discovered that heavily boron-doped (4.9×10^{21} cm^{-3}, 2.8 at.%) metallic-transport diamond synthesized by the HTHP method exhibits type II superconductivity at 2.3 K (zero resistance).(5)

As we mentioned above, the fabrication of heavily boron-doped diamond films by CVD is a more suitable technique for improving the quality of diamond films and controlling the density of boron. Moreover, the low-temperature deposition of CVD diamond makes it possible to fabricate superconducting devices easily. In 2005, we successfully introduced a high boron concentration and a carrier density of 9.4×10^{20} cm^{-3} in polycrystalline diamond films by controlling the growth orientation to (111), and we realized a T_c of 4.2 K.(6) This value is higher than the T_c of 2.1 K for heavily boron-doped (1.9×10^{21} cm^{-3}) diamond deposited on (100) single-crystal diamond.(7)

On the basis of the advantages of the very high Debye temperature (1860 K) of diamond, some theoretical studies on the potential of a higher superconductivity transition temperature (T_c) have been carried out.(8–11) In this paper, the control of the growth parameter of polycrystalline diamond films is discussed to understand the superconducting transition system of heavily boron-doped diamond.

2. Experimental Procedure

The growth of heavily boron-doped diamond films was carried out utilizing a microwave-assisted CVD system with a quartz-tube chamber. Polycrystalline diamond film growth was performed on a high-resistivity Si (001) substrate. Methane gas was utilized as the carbon source and trimethylboron (TMB) as the boron source in dilute hydrogen. The methane concentration (CC) was 0.5–3% in hydrogen, with the concentration ratio of the boron source comparable to that of the carbon source in the gas phase (B/C) of 2000–24000 ppm. The chamber pressure was controlled at 50 Torr. The substrate temperature was increased by the exposure of plasma (600 W) to 800–900°C. The growth time was fixed to 8 h. Films of 0.7–6 μm thickness, depending on growth conditions, were obtained.

To characterize the heavily boron-doped diamond films, we employed Raman spectroscopy, Hall effect measurement, X-ray diffraction (XRD: θ - 2θ) analysis and transport measurement. The measurement of magnetization properties was carried out using a superconducting quantum interference device (SQUID) magnetometer.

Raman measurements were carried out under backscattering configurations using the 632.8 nm line of a He-Ne laser (Renishaw in-Via Reflex system). The cutoff frequency of the notch filter, the number of gratings and the wave number resolution were 50, 1800 and 1.05 cm^{-1}, respectively. Raman spectra were calibrated using a standard Si substrate. Three areas (1 center, 2 edges) for each substrate were used for measurement to confirm the peak positions.

To confirm the quality of the films and the growth orientation, rocking-curve and high-resolution θ - 2θ measurements were carried out. The surface morphology of the films was observed by field-emission secondary-electron microscopy (FE-SEM).

The ohmic electrodes used for all transport measurements were obtained using silver glue contacts. Resistivity-temperature measurement was carried out using commonly used four-point contacts with the I- V- V+ I+ structure. The Van der Pauw method was utilized for Hall effect measurement with four ohmic contacts on every edge of the diamond substrate.

3. Results and Discussion

The growth of heavily boron-doped diamond films was realized under all the growth conditions mentioned above; however, the growth parameter that determines the growth orientation largely depends on CC and B/C. Figure 1 shows the surface morphology of the films for various CC and B/C values. The deposited film surface consists of (111) and (100) facets. A lot of twins are also observed, and icosahedral or decahedral multiply twinned particles (MTPs) are found to be embedded in the layers. The difference in the major facets is explained by the growth parameter α, which is obtained from the growth velocity ratio of the <100> and <111> directions ($\alpha = \sqrt{3}\nu_{100}/\nu_{111}$).(12) In general, an increase in CC and a decrease in temperature reduce the surface energy of the (111) face. Accordingly, the growth velocity in the <111> direction decreases. Our results show the different values of α obtained for changing growth conditions. For a low CC and a low B/C, such as CC = 1% and B/C = 2000 ppm or CC = 0.5% and B/C = 2000 ppm, the majority surface is (100). However, under conditions such as CC > 1% and B/C > 2000 ppm, the majority surface becomes (111). The estimated α obtained from the MTP structure(13) decreased from 2.5–3 to 1.5–2 by decreasing CC and B/C. For fixed CC = 1%, an increase in B/C increases α.

The grain size highly depends on the growth conditions. Figure 2 shows the mean grain size of the film as functions of CC and B/C. An increase in CC increases the grain size; however, an increase in B/C reduces the size. The thickness of the film also decreased with decreasing grain size. The reduction of the growth rate with an increase in the boron source has been reported in previous studies.(14,15) Boron is considered to act as a terminator of growth sites on the surface when B/C is increased. In particular, when boron exists at the center of the tetrahedral sp3 structure, growth species such as C_2 or free radicals cannot connect to the boron because the three bonds of boron are already

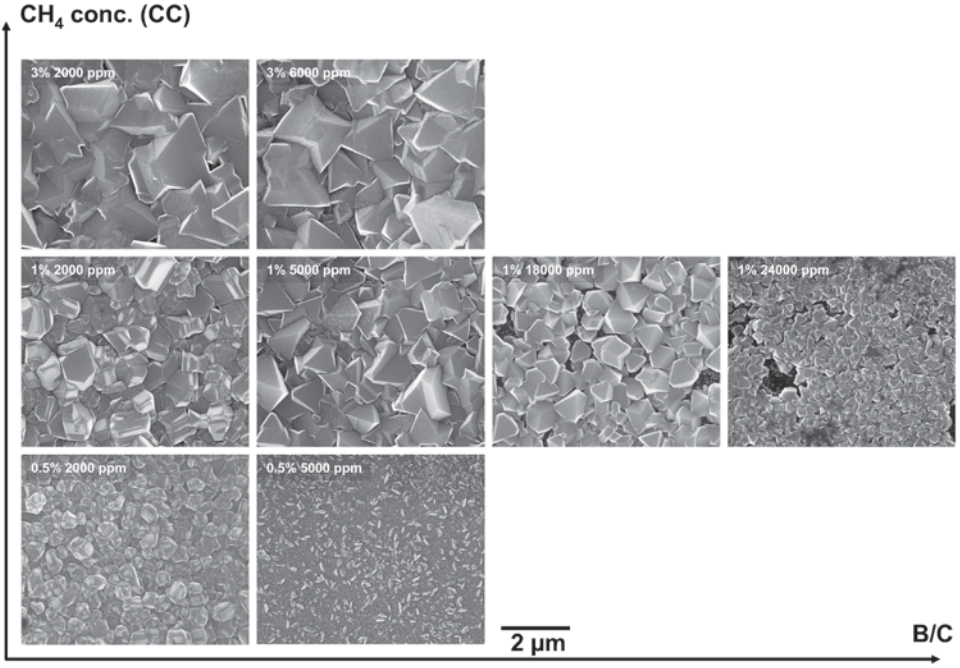

Fig. 1. SEM images of heavily boron-doped polycrystalline diamond films. An increase in α is obtained with an increase in CC or B/C.

connected to the carbons of diamond. Accordingly, the surface energy of the (111) face is decreased when B/C is increased. Results for homoepitaxial growth support this model; the growth rate of heavily boron-doped diamond on (111) is 20% lower than that on (100).

Figure 3 shows typical XRD (powder diffraction) patterns on polycrystalline diamond films deposited under the conditions of (a) CC = 3 % and B/C = 2000 ppm and (b) CC = 0.5% and B/C = 2000 ppm. Diffraction peaks corresponding to (111), (220), (311) and (400) diamond were detected. The XRD pattern obtained from the high-CC film indicates that the growth is (111)-textured, in contrast with the predominant (110)-growth of the low-CC films. For the heavily boron-doped film, (001)-textured growth was not obtained.

Figure 4 shows the Raman shifts of heavily boron-doped polycrystalline diamond film in comparison with those of typical semiconducting and impurity-band-conducting single-crystal diamond. Semiconducting single-crystal diamond, which has a boron concentration of $10^{18}/\mathrm{cm}^3$, shows a narrow peak at 1332/cm due to zone-center optical phonons. No other Raman shift peak is detected. However, when the doping level is increased to $3.0 \times 10^{20}/\mathrm{cm}^3$, which is a sufficient value to form an impurity band, two additional large wide bands at approximately 1200–1280 cm^{-1} (1200/cm band) and 470 –570 cm^{-1} (500/cm band) are detected, as shown in Fig 4(b). These two wide bands are typically observed in heavily boron-doped ($[B] > 3 \times 10^{20}\ \mathrm{cm}^{-3}$) diamonds.(16–18) The

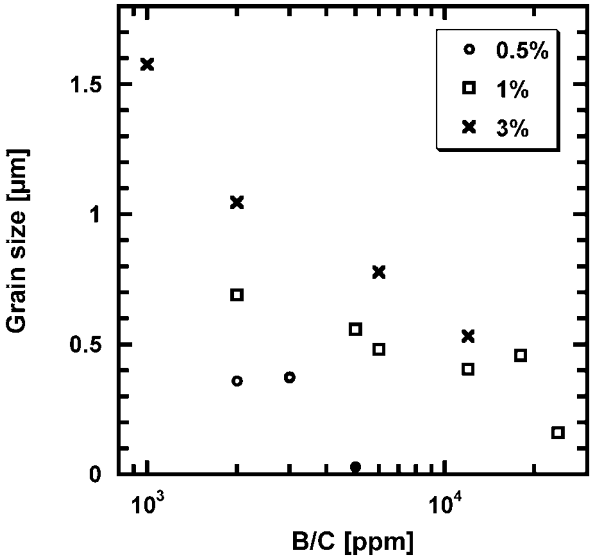

Fig. 2. Grain size of heavily boron-doped polycrystalline diamond films. The grain size of the film is increased with an increase in methane concentration; however, it decreases with an increase in B/C ratio.

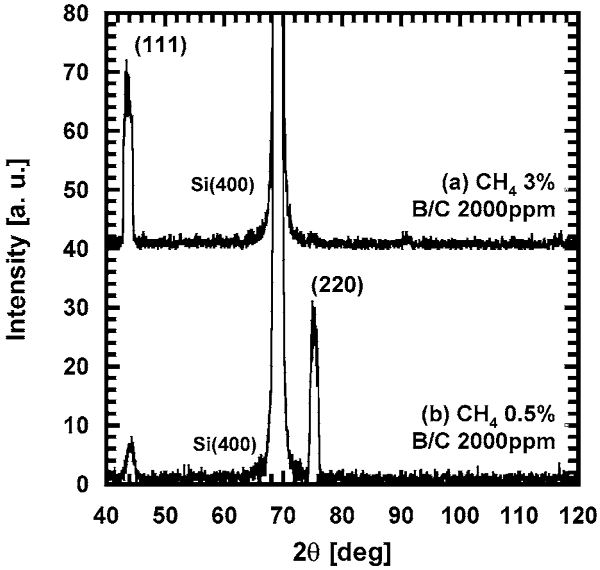

Fig. 3. X-ray diffraction peaks of (a) high-α and (b) low-α diamond films. The high-α condition is obtained under CC = 3% and B/C = 2000 ppm. The low-α condition is obtained under CC = 0.5% and B/C = 2000 ppm.

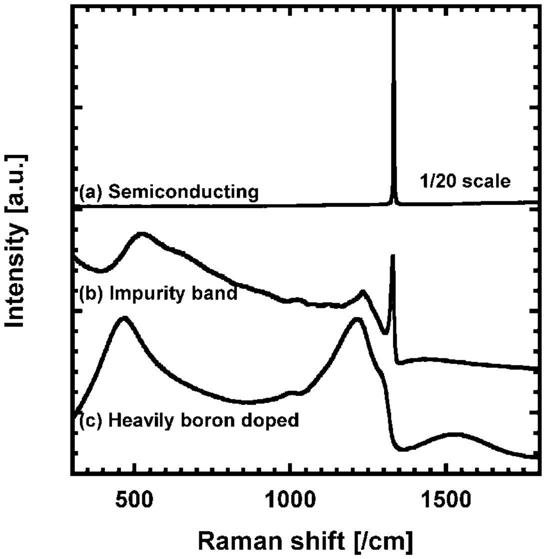

Fig. 4. Raman shifts of (a) semiconducting single crystal, (b) impurity-band conducting single-crystal and (c) heavily boron-doped polycrystalline diamond films. An increase in boron concentration shifts the 1200 and 500/cm bands to lower wave numbers.

intensity of the zone-center optical phonon line is decreased and shifted to a lower wave number of 1330/cm. The Raman shift of (c), a heavily boron-doped diamond film, ($p\sim$ 1.59 × 10^{21}/cm^3), which was grown under a high-α condition and has an extremely low resistivity (ρ = 1.23 mΩ·cm), is similar to that of (b), an impurity-band conducting diamond film ([B] = 3.0 × 10^{20}/cm^3); however, both wide bands of 1200 and 500/cm shift to the lower wave numbers of 1150–1250 and 400–500/cm, respectively, and the zone-center optical phonon line is observed as a shoulder of the 1200/cm band. The origins of the 1200 and 500/cm bands have been discussed in previous studies.(17,18) Gonon et al. attributed the 1200/cm band to the maxima in the one-phonon density of states of diamond, and suggested that this band is a result of regions that are disordered by heavy boron doping.(17) The 500/cm band is explained by Bernard et al. as being a result of the local vibration modes (LVMs) of boron pairs.(18) They also point out that this band shifts to lower wave numbers depending on the density of the boron pairs in the diamond. In our case, the peak position of the 500/cm band is located at 440–470/cm in most of the heavily boron-doped polycrystalline diamond films. The formation of many B-B pair defects is expected to have occurred in our diamond films. The broad band at 1500/cm corresponds to high-resistivity surface amorphous carbon. No graphitic layer was observed on any of the diamond films. The surface amorphous carbon layer can be removed by oxygen plasma treatment after the deposition of diamond films and does not contribute to conductivity. Not only boron pair defects, but also other defects are expected to form in heavily boron-doped diamond films.

The superconducting transition is confirmed on extremely low resistivity heavily boron-doped diamond films. The superconductivity characteristics are shown in Fig. 5. The diamond film is grown under the high-α condition of CC = 3% and B/C = 2000 ppm. The thickness and resistivity of the film are 6.0 μm and 1.23 mΩ·cm, respectively. The carrier concentration of the film is estimated to be $1.59 \times 10^{21}/\text{cm}^3$ from the Hall effect measurement. The superconductivity transition temperature is determined from the temperature dependence of the resistance. $T_{c(\text{onset})}$ and $T_{c(\text{offset})}$, which are determined as the temperature at which resistance starts to deviate from normal-state resistance and that of zero resistance, respectively, are estimated to be 6.9 and 5.6 K, respectively. The inset of Fig. 5 shows the temperature dependence of the magnetic susceptibility under zero-field cooling (ZFC) and field cooling (FC) using the SQUID magnetometer. The transition to superconductivity is also confirmed at 5.4 K, from the onset of the diamagnetic transition under the ZFC measurement.

Figure 6 shows the temperature dependence of magnetic susceptibility under ZFC for polycrystalline diamond films grown under different CC conditions of 1, 2 and 3% with B/C = 2000 ppm. No decrease in the resistivity of the films is obtained with an increase in CC; however, an increase in T_c with an increase in CC is clearly observed. The T_c values of the films are 2.4, 3.2 and 5.4 K for CC = 1, 2 and 3%, respectively. This phenomenon indicates that an increase in the growth parameter α is not effective to decrease the electric conduction at room temperature but is effective for improving the superconductivity characteristics.

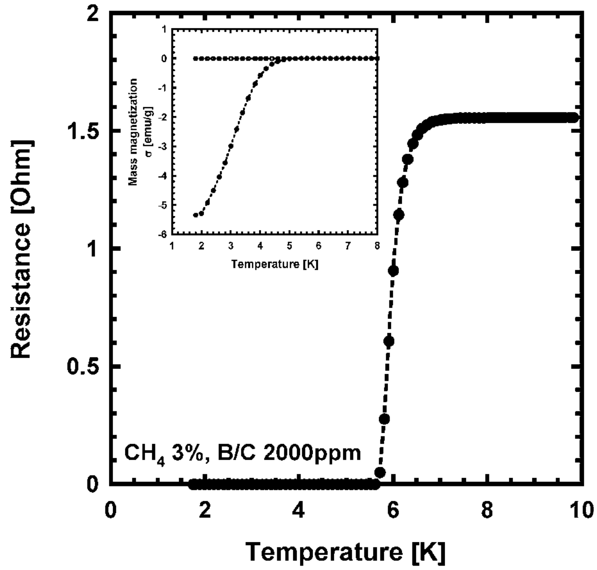

Fig. 5. Electrical resistance curve of heavily boron-doped diamond grown under high α conditions and zero magnetic field. The $T_{c(\text{onset})}$ and $T_{c(\text{offset})}$ are 6.9 and 5.6 K, respectively. The inset shows the mass magnetization of the film measured under zero-field cooling (ZFC) and field cooling (FC) at 10 Oe.

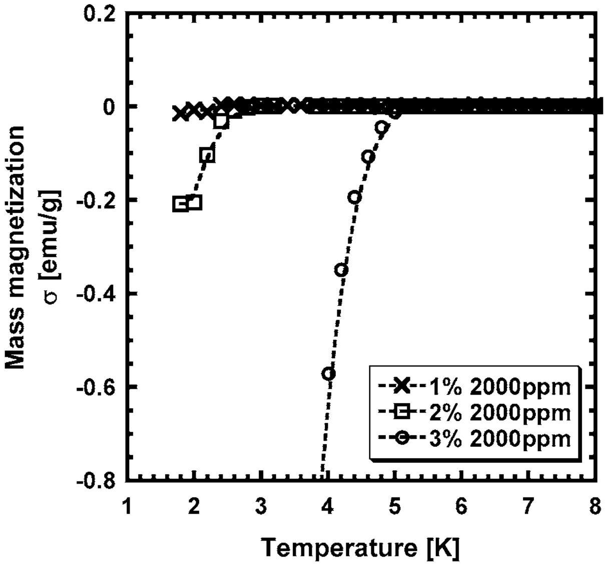

Fig. 6. Mass magnetization of heavily boron-doped polycrystalline diamond films grown under 1, 2 and 3% methane concentrations. Measurements were carried out under ZFC. An increase in T_c with methane concentration is obtained.

4. Conclusions

The growth of heavily boron-doped polycrystalline diamond films has been realized by CVD. Grown polycrystalline diamond films show fine grains with (111) and (100) faces. By controlling methane concentration and B/C ratio, the surface energy of (111) and (100) faces can be controlled. Increases in methane concentration and B/C ratio decrease the surface energy of the (111) face and increase the growth parameter α. The <111>-textured growth of the film under a high-α condition was confirmed by XRD measurement. An extremely low resistivity of less than 5 mΩ·cm is obtained when the doping level is higher than 2000 ppm. A superconducting transition at 5.6 K is obtained from the film grown under a high-α condition. This value is higher than that of the films grown under lower-α conditions.

Acknowledgements

This work is partially supported by a grant from the Japan Society for the Promotion of Science (JSPS). This work is also supported in part by the Advanced Research Institute for Science and Engineering, Waseda University and a Grant-in-Aid for Center of Excellence (COE) Research from the Ministry of Education, Culture, Sports, Science and Technology.

References

1) F. P. Bundy, H. T. Hall, H. M. Strong and R. H. Wentorf: Nature **176** (1955) 51.
2) S. Matsumoto, Y. Sato, M. Kamo and N. Setaka: Jpn. J. Appl. Phys. **21** (1982) L183.
3) M. Kamo, Y. Sato, S. Matsumoto and N. Setaka: J. Cryst. Growth **62** (1983) 642.
4) T. H. Borst and O. Weis: Phys. Status Solidi A **154** (1996) 423.
5) E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Melnik, N. J. Curro, J. D. Thompson and S. M. Stishov: Nature **428** (2004) 542.
6) Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H. Umezawa and H. Kawarada: Appl. Phys. Lett. **85** (2004) 2851.
7) E. Bustarret, J. Kacmarcik, C. Marcenat, E. Gheeraert, C. Cytermann, J. Marcus and T. Klein: Phys. Rev. Lett. **93** (2004) 237005.
8) L. Boeri, J. Kortus and O. K. Andersen: Phys. Rev. Lett. **93** (2004) 237002.
9) K. W. Lee and W. E. Picket: Phys. Rev. Lett. **93** (2004) 237003.
10) H. J. Xiang, Z. Li, J. Yang, J. G. Hou and Q. Zhu: Phys. Rev. B **21** (2004) 212504.
11) G. Baskaran: cond-mat 0404286 (2004).
12) C. Wild, R. Kohl, N. Herres, W. Mueller-Subert and P. Koidl: Diamond Relat. Mater. **3** (1994) 373.
13) J. Buhler and Y. Prior: J. Cryst. Growth **209** (2000) 779.
14) P. Gonon, A. Deneuville, F. Fontaine, E. Gheeraert, A. Campargue, M. Chenevier and S. Rodophe: J. Appl. Phys. **78** (1995) 7404.
15) N. Tokuda, T. Saito, H. Umezawa, H. Okushi and S. Yamasaki: Diamond Relat. Mater. doi :10.1016/j.diamond (accessed Aug 13, 2006).
16) K. Ushizawa, K. Watanabe, T. Ando, I. Sakaguchi, M. Nishitani-Gamo, Y. Sato and H. Kanda: Diamond Relat. Mater. **7** (1998) 1719.
17) P. Gonon, E. Gheeraert, A. Deneuville, F. Fontaine, L. Abello and G. Lucazeau: J. Appl. Phys. **78** (1995) 7059.
18) M. Bernard, C. Baron and A. Deneuville: Diamond Relat. Mater. **13** (2004) 896.