

# Control of electrical conductivity in diamond by boron-implantation using an ECR ion source

H. Yamazaki,<sup>\*1</sup> T. Minamidate,<sup>\*2</sup> M. Kidera,<sup>\*1</sup> A. Yamamoto,<sup>\*3</sup> R. Kato,<sup>\*4</sup> and H. Ueno<sup>\*1</sup>

Diamond is an excellent electrical insulator with a large band gap of 5.5 eV. It becomes a semiconductor when doped with a small amount of boron (for *p*-type) or phosphorus (for *n*-type). When doped beyond the metal-to-insulator transition at a boron density of  $n_B \sim 3 \times 10^{20}$  B/cm<sup>3</sup>, boron-doped diamond exhibits superconductivity in the samples grown by the high-pressure and high-temperature synthesis.<sup>1)</sup> Theoretically, the superconducting critical temperature  $T_c$  can be significantly increased by reducing the effects of disorder in boron-doping processes.<sup>2)</sup> For a higher  $T_c$ , more subtle control of doping using CVD and/or MBE methods is highly required. However, a different method based on ion implantation is also worth investigating as it enables selective ion doping in a controlled manner. This has great potential for future device applications. Successful inclusion of boron ions by the implantation technique has been confirmed using SEM/EDS measurements. The surface image of our sample and its EDS spectrum are shown in Fig. 1. At 0.19 keV, we can see an energy peak from the boron ions embedded in the diamond.

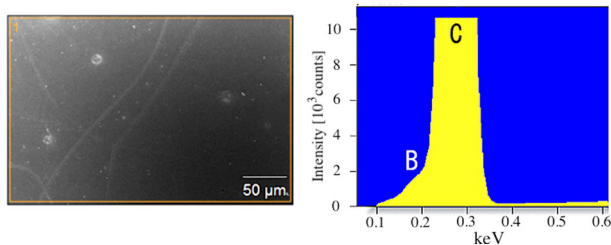


Fig. 1. Left: SEM image of our sample with a boron concentration of  $n_B \sim 6.8 \times 10^{22}$  B/cm<sup>3</sup>; right: EDS spectrum obtained with an acceleration voltage of 7.0 kV. The strongest peak comes from the carbon atoms in the diamond.

For the past few years, we have been trying to control the electrical conductivity in Ib-type diamonds using boron-ion implantation. To reduce the lattice damage produced during the implantation, we performed annealing treatments after implantation. As the phase diagram of carbon shows, the diamond is not stable at low pressures; therefore, we annealed the samples at 800°C and 4 GPa for 1 hour. Contrary to our expectations, the annealed samples exhibited no sign of superconductivity. The laser Raman spectra (632.8 nm

excitation) indicated that the annealing promoted the formation of NV<sup>-</sup> centers, which behave as carrier traps in the diamond.

In this fiscal year, to decrease the NV<sup>-</sup> defect density, we used single-crystals of IIa-type diamond with a nitrogen concentration of less than 8 ppm (Fig. 2, right). We also investigated the dependence of boron-implantation yield on the crystallographic orientation of diamond surface: (100) and (111). Using an ECR ion source,<sup>3)</sup> boron ions were implanted into the diamond crystals at 5 keV corresponding to an implantation depth of  $\sim 10$  nm. Five samples of different concentrations from  $n_B \sim 5 \times 10^{20}$  to  $2 \times 10^{22}$  B/cm<sup>3</sup> were prepared. These samples were annealed under the same conditions as noted above.



Fig. 2. Pristine single-crystals of IIa-type diamond (right) and Ib-type diamond (left, for comparison). The size of each crystal is approximately  $1 \times 1 \times 0.3$  mm<sup>3</sup>.

Figure 3 shows a sample and some parts of high-pressure media after removing the sample. For comparison, the implanted samples without annealing were also prepared. We are now ready to measure the samples with different combinations of the conditions: (a) five different  $n_B$ 's, (b) two types of surface orientations: (100) and (111), and (c) with/without annealing treatment after implantation.



Fig. 3. The boron-implanted diamond (arrowhead) after the process of high-temperature and high-pressure annealing. Parts of high-pressure media are also shown.

<sup>\*1</sup> RIKEN Nishina Center

<sup>\*2</sup> Faculty of Science, Tokyo University of Science

<sup>\*3</sup> Graduate School of Engineering and Science, Shibaura Institute of Technology

<sup>\*4</sup> Condensed Molecular Materials Laboratory, RIKEN

## References

- 1) E. A. Ekimov *et al.*, *Nature* **428**, 542 (2004).
- 2) T. Shirakawa *et al.*, *J. Phys. Soc. Jpn.* **76**, 014711 (2007).
- 3) M. Kidera *et al.*, *Eur. J. Mass Spectrom.* **13**, 239 (2007).