Control of electrical conductivity in diamond by boron-implantation using an ECR ion source —Crystallographic orientation and crystal quality dependence II—

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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). Further, when doped beyond the metal-to-insulator transition at a boron density of $n_{\rm B} 3 \times 10^{20} \text{ B/cm}^3$, boron-doped diamond exhibits superconductivity in the samples grown by the high-pressure and high-temperature synthesis.¹⁾ For a higher $T_{\rm c}$, more subtle control of doping using CVD and/or MBE methods is highly required. However, a different method based on ion-beam implantation, such as that used in doping of Si, is also worth investigating. This is because it enables selective ion-doping in a controlled manner, thereby providing a great potential for future device applications. Since the 1970s, trials of the ion-doping of diamond by ion-beam implantation under all types of possible conditions have not made good progress. In most cases, trials resulted in the graphitization of diamond. Therefore, in our study, we focuced on an application of hightemperature and high-pressure (HTHP) annealing in the diamond-stable region (Fig. 1) following ion-beam implantation.



Fig. 1. Phase diagram of carbon.²⁾

As a continuation to the study in the last fiscal year, to decrease the density of $N-V^-$ defects observed in the HTHP annealed Ib-type diamond (see Fig. 2), we used single-crystals of IIa-type diamond

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Fig. 2. Structure of the N-V⁻ center [left] and typical Raman spectra before (red) and after (blue) annealing [right]. The fluorescence emission spectrum for N-V⁻ defect centers is also indicated (black) for comparison.

(EDP, Japan) with a nitrogen concentration of less than 8 ppm. We further investigated the dependence of boron-implantation yield on the crystallographic orientation of diamond surface; we prepared two series of IIa-type diamonds with their crystal surfaces of (100) and (111). With an ECR ion source,³⁾ a boron beam (B¹⁺) was implanted into the diamonds at 5 keV, which corresponded to an implantation depth of approximately 10 nm from the surface. In this study, we used decaborane (B₁₀H₁₄) as an ion source. The area of a beam spot was 0.071 cm². Implantation was conducted with a total concentration of $n_{\rm B} \sim 5 \times 10^{20}$, 4×10^{21} ,

 8×10^{21} , or 2×10^{22} B/cm³. Several samples were annealed at 800°C and 4 GPa for one hour with cubicanvil high-pressure apparatus. For comparison, the boron-implanted samples without annealing were also prepared. Thus, we obtained the samples with all the different combinations of the following conditions: (a) four different $n_{\rm B}$'s, (b) two types of the crystal surface: (100) and (111), and (c) with/without the annealing treatment following the implantation. Measurements of resistivity and magnetization suggest that, regardless of the annealing of HTHP after implantation, all these samples exhibited no superconductivity and their electrical conductivities indicated no particular difference from those for Ib-type diamonds.

Our trials to obtain boron-doped diamond by ionimplantation technique do not show signs of success

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so far. Therefore, for doping by ion-implantation, it is highly required to remove the residual defects in the ion-implanted diamonds in a certain manner. Closer cooperation between ion-beam technique and solid state physics will be extremely essential to solve the problem in the future.

References

- 1) E. A. Ekimov et al., Nature 428, 542 (2004).
- 2) F. P. Bunday et al., J. Chem. Phys. 35, 383 (1961).
- 3) M. Kidera et al., Eur. J. Mass Spectrom. 13, 239 (2007).