Control of electrical conductivity in diamond by boron-implantation using an ECR ion source—application of high-temperature and high-pressure annealing

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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). Ekimov *et al.* reported that B-doped diamond, when doped beyond the metal-to-insulator transition at $n_\mathrm{B} \sim 3 \times 10^{20}$ B/cm^3, exhibits superconductivity in samples grown by the high-pressure and high-temperature synthesis.[1)] Theoretically, the superconducting critical temperature T_c can be significantly increased by reducing the effects of the disorder in the B-doping processes.[2)] For a higher T_c, more subtle control of doping using CVD and/or MBE methods is required. However, a different method based on ion implantation is also worth investigating, since it enables selective ion-doping in a controlled manner. This has great potential for future device applications.

We attempted to control the electrical conductivity in diamond by using the ion-implantation technique, utilizing RILAC at the RIBF facility. For n- and p-type semiconductors (and possibly superconductors), nitrogen and boron ions were implanted into diamonds, respectively. By varying the beam intensity and irradiation time, the concentration of nitrogen or boron was controlled. Note that it is challenging to obtain the n-type semiconductor, as well as the n-type superconductor, by nitrogen-doping of diamond, since nitrogen behaves as a deep donor in diamond and does not contribute to conductivity.[3)]

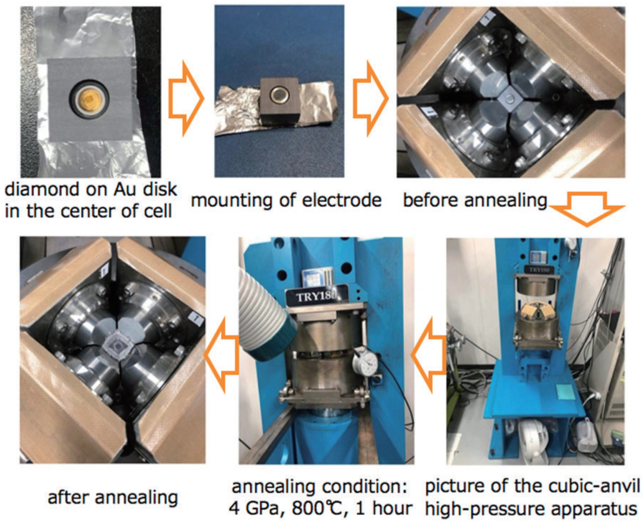

Fig. 1. The process of high-temperature and high-pressure annealing.

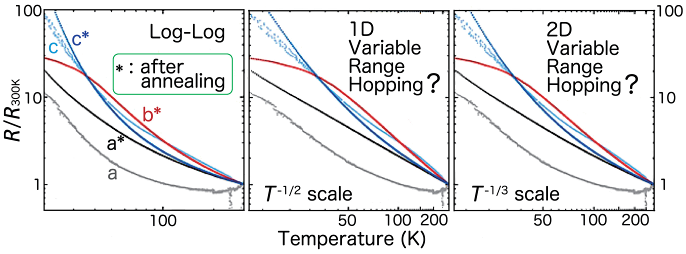

Fig. 2. Temperature dependence of electrical resistivity before and after annealing for B concentrations of (a) 1.8×10^{21}, (b) 1.3×10^{22}, and (c) 6.8×10^{22} B/cm^3. The possibility of the hopping conductivity in carrier-doped semiconductor cannot be denied for these samples.

Fig. 3. Typical appearance of Ib- and IIa-type diamonds.

In this fiscal year, we continued studying boron-implanted diamonds. Boron ions were implanted into diamond crystals (each size is $1 \times 1 \times 0.3$ mm^3) at 5 keV (implantation depth: ~10 nm) by using an ECR ion source.[4)] Ten samples of different concentrations from $n_\mathrm{B} \sim 4.9 \times 10^{20}$ to 6.8×10^{22} B/cm^3 were studied. The magnetization and electrical resistivity measurements showed that the as-implanted diamonds do not exhibit superconducting transitions, even though n_B's are nominally beyond the metal-to-insulator transition at 3×10^{20} B/cm^3. To reduce the lattice damage produced during the implantation, we performed annealing treatments after implantation. The phase diagram of carbon shows that diamond is not stable at low pressures; we annealed the samples at 800°C and 4 GPa for 1 hour. The process of the annealing is shown in Fig. 1. Contrary to our expectations, the annealed samples exhibited no sign of superconductivity (see Fig. 2).

The laser Raman spectra with 632.8 nm excitation indicated that the annealing promoted the NV$^-$ center formation in diamond. To reduce this effect, we are preparing for the boron implantation of IIa-type diamonds (Fig. 3) with nitrogen concentration less than 8 ppm.

References

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