Control of electrical conductivity in diamond by boron implantation —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. Interestingly, 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, shows superconductivity in samples grown by high-pressure and high-temperature synthesis.[1)] Theoretically, the superconducting critical temperature T_c can be increased substantially by reducing the effects of 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, whereas a different method based on ion implantation is also worth investigating, since it enables selective ion doping in a controlled manner.

We attempted to control the electrical conductivity in diamond by means of the ion-implantation technique with the use of RILAC at RIKEN. In our study, for n- and p-type semiconductors (and possibly superconductors), nitrogen and boron ions are implanted into diamond, respectively. By changing the beam intensity and irradiation time, the concentration of nitrogen or boron was controlled. Note that achieving an n-type semiconductor, and needless to say an n-type superconductor, by the nitrogen-doping of diamond is challenging, since nitrogen behaves as a deep donor in diamond and does not contribute to conductivity.[3)] The electrical conductivity observed in the nitrogen-implanted diamonds (*e.g.*, at $n_{\mathrm{N}} \sim 7.5 \times 10^{21}$ N/cm^3) is, therefore, most likely explained in terms of the carbon atoms connected via the sp^2 bonding produced by radiation damage. The Raman spectra support this scenario.

In this fiscal year, we mainly investigated 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) using an ECR ion source.[4)] We prepared ten samples of different concentrations ranging from $n_{\mathrm{B}} \sim 4.9 \times 10^{20}$ to 6.8×10^{22} B/cm^3. Measurements of the magnetization and electrical resistivity show that the as-implanted diamond samples do not exhibit superconducting transitions, even though n_{B} values are nominally beyond the metal-to-insulator transition at 3×10^{20} B/cm^3. In order to reduce the lattice damage produced during the implantation, we attempted annealing treatments after implantation. As the phase diagram of carbon (Fig. 1) shows, diamond is not stable at low pressures; we annealed the samples at 800°C and 4 GPa (in the diamond-stable region) for one hour. The annealed samples, however, indicate no sign of superconductivity. Rather, the annealing treatment degraded the diamond crystals: the (222) peak at a higher angle in x-ray diffraction measurement disappeared after annealing, whereas the (111) peak remained. Figure 2 shows a typical change in the Raman spectra after annealing. The fluorescence emission due to NV$^-$ defect centers is clear, suggesting that the annealing treatment promotes the NV formation process, where nitrogen ions have been embedded in the Ib-type diamond as impurities. Hereafter, we must also consider the effect of the NV$^-$ centers on the electrical conductivity in the implanted diamonds.

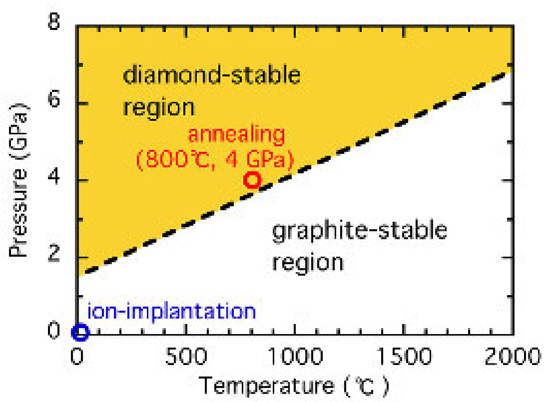

Fig. 1. Phase diagram of carbon. The annealing condition in this work is indicated by a red circle.

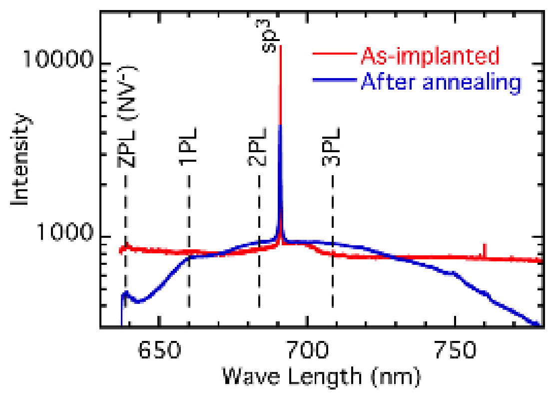

Fig. 2. Laser Raman spectra (632.8 nm excitation) of the as-implanted and annealed samples for $n_{\mathrm{B}} \sim 6.8 \times 10^{22}$ B/cm^3. The broken lines indicate the fluorescence emission of the zero-phonon line (ZPL) and n-phonon lines (nPLs; "phonon side band") due to negatively charged nitrogen-vacancy (NV$^-$) defect centers.

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