Control of the electrical conductivity in diamond by ion implantation

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Although diamond is an insulator with a large bandgap of 5.5 eV, it becomes a semiconductor when doped with a small amount of boron (for p-type) or phosphorus (for n-type). Doped diamonds hold promise as the material for next-generation devices in place of the existing Si- and GaAs-based semiconductors. In line with this research trend, Ekimov et al. reported that B-doped diamond, when doped beyond the metal-to-insulator transition at \( n_B \sim 3 \times 10^{20} \text{ cm}^{-3} \), shows superconductivity in the samples grown by high-pressure—high-temperature synthesis.\(^1\) Using inelastic X-ray scattering from a CVD (chemical vapor deposition) grown sample, strong softening of the optical-phonon modes was admittedly observed in superconducting B-doped diamond near the Brillouin-zone center.\(^2\) Theoretically, the superconducting critical temperature \( T_c \) can be raised substantially by reducing the effects of disorder in the B-doping processes.\(^3\) For a higher \( T_c \), more subtle control of doping using CVD and/or MBE (molecular beam epitaxy) methods is highly required, whereas a different method based on ion implantation is also worth investigating since it enables selective ion-doping in a controlled manner.

In this study, we try to control the electrical conductivity in diamond by means of the ion implantation technique, utilizing the beam facilities in RIKEN. For \( n \)- and \( p \)-type semiconductors (and possibly superconductors), nitrogen and boron ions are implanted into diamond, respectively. To create an \( n \)-type semiconductor by N-doping is a challenging work, since nitrogen behaves as a deep donor in diamond and does not contribute to conductivity.\(^4\) By changing the beam intensity and irradiation time, the concentration of the dopants in diamond was controlled. The electrical conductivity of the doped diamonds was measured using a four-probe configuration. Magnetization measurements were carried out to elucidate the effect of paramagnetic moments (due to lattice defects) and the emergence of superconductivity. Raman spectroscopy and X-ray diffraction (XRD) studies were also performed.

Figure 1 shows the temperature dependence of the electrical resistance \( R \) normalized to \( R \) (300 K) for B-doped diamonds. Their doping concentrations are indicated in the figure. The fairly high dispersion of data is supposedly due to bad electrical contact between the conductive paste and the diamond surface. A model of thermally-assisted hopping can provide a good fit to the experimental data. We are currently examining the physical significance of the fitting parameters. The results of the magnetization measurements (Fig. 2) show that our B-doped diamonds do not exhibit superconducting transitions at low temperatures, even though the doping concentrations are nominally beyond the metal-to-insulator transition at \( n_B \sim 3 \times 10^{20} \text{ cm}^{-3} \). Annealing treatment after the irradiation may be necessary for the samples to show superconductivity. The temperature dependence of the magnetization can be represented as the sum of the Curie and temperature-independent components. The correlation between each component and the doping concentration will be clarified by preparing the samples at higher concentrations.

As for the N-doped diamonds (\( e.g. \) at \( n_N \sim 7.5 \times 10^{21} \text{ cm}^{-3} \)), the results obtained by Raman spectroscopy and XRD show that they were fully converted into amorphous carbon in the as-implanted state as well as after annealing at 1000 K, likely due to radiation damage. We have to further consider the implantation/annealing process in order to minimize the lattice damage in diamonds.

**References**