High-density n-type doping of diamond by nitrogen beam implantation

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After the discovery of the superconductivity of boron-doped (p-type) diamond in 2004[1)], studies have been extensively conducted to raise the T_c of diamond superconductivity. These studies have indicated that a high doping concentration of boron is favorable for increasing the T_c of superconductivity. High doping concentration can be introduced by the chemical-vapor-deposition (CVD) method[2,3)]. Based on this technique, T_c has so far reached 11.4 K[4)] at doping concentration $\rho = 8.4\times10^{21}$ cm^{-3}. Theoretically, it has been predicted that a very high critical temperature $T_c \geq 100$ K is possible for doped diamond[5)], because the high phonon frequency of diamond is favorable for increasing the T_c of superconductivity.

Unfortunately, the doping concentration achievable by CVD is limited to less than $\rho = 10^{22}$ cm^{-3} for boron and, more seriously, $\rho = 10^{20}$ cm^{-3} for phosphorus (n-type). With higher concentration, the dopants are known to form dimers, causing localization of the doped carriers, and thus cannot be used for electric conduction. In view of electronic applications, both p-type and n-type dopings are necessary. From an analogy to other superconductors such as high-T_c cuprates, it is natural to expect n-type superconductivity in diamond. To date, however, high-density doping of n-type carrier has not been achieved.

A new approach expected to realize high-density doping is heavy-ion implantation, because i) a sharp fall-off at the distal edge in the stopping range (i.e., Bragg peak), which becomes remarkable for heavy-ion beams, is favorable for the purpose of high doping concentration, and ii) dopant dimerization should not occur very frequently because of the high randomness of the implanted atoms. Taking these advantages, we have been conducting doped-diamond studies in order to realize an n-type diamond superconductivity with T_c as high as possible. Furthermore, it is also important to reproduce the increase in T_c in boron-doped p-type region, in particular, outside the CVD limit, under the scheme of heavy-ion implantation utilizing the high beam current of various heavy ions available at the RIBF facility. In parallel, the optimization of conditions for heavy-ion implantation including an annealing process to make the diamond lattice as clean as possible should be also investigated.

In the present work, we report on the first nitrogen-ion implantation experiment at RIBF[a)] to investigate a possible onset of n-type superconductivity of diamond. A beam of $^{14}N^{3+}$ delivered at energy $E/A = 450$ keV from the RILAC accelerator at RIBF was implanted into (100)-faceted single crystals of type Ib diamond[6)]. This beam energy was set to be much lower than the Coulomb barrier to avoid the radioactivaion of samples. The crystals were prepared in the form of 4 mm × 4 mm × 0.3 mm(t), and mounted on a Cu ladder placed in the center of the GARIS target chamber. The implantation was carried out at room temperature at beam current $I = 3 \sim 10\ \mu$A.

The density $\rho(^{14}N)$ of the implanted ^{14}N particles was simply calculated by

$$\rho(^{14}\mathrm{N}) = \frac{I \cdot T}{q \cdot S \cdot \Delta R}, \quad (1)$$

where I is the beam current, T is the irradiation time, $q = 3^+$ is the charge state of the beam, $S \simeq \pi\times4$ mm$\times6.5$ mm is the beam spot size, and ΔR is the stopping-range distribution of the beam in the crystal. Taking a value of $\Delta R \simeq 0.2\ \mu$m at the mean stopping range $R \simeq 2.5\ \mu$m, calculated with the simulation code SRIM[7)], we determined $\rho(^{14}N)$ of five nitrogen-implanted diamond crystals, ranging from $\rho = 7.8 \times 10^{20}$ to 1.9×10^{22} cm^{-3}. These densities are approximately the same as the reported CVD-doped boron densities at which superconductivity of diamond has been observed[1,4,8)]. Offline resistivity measurements of the obtained nitrogen-doped crystals as a function of temperature are in progress.

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a) The experiment was performed under the Experimental Program ML1006-LINAC29.