Control of Electronic Properties of Diamond by Boron / Nitrogen Injection Using High Energy Ion Source

Takaaki Minamidate[1], Hiroki Yamazaki[2], Masanori Kidera[3], Hiroshi Yamamoto[4], Hideki Ueno[2], and Reizo Kato[1]

[1]Condensed Molecular Materials Laboratory, RIKEN, [2] Nuclear Spectroscopy Laboratory, RIKEN, [3] Ion Source Team, RIKEN, [4]Institute for Molecular Science

Pure diamond is a good insulator with a wide bandgap of 5.5 eV, and it is known that it shows semiconducting properties when the boron or phosphorus is induced as the carrier donor. Then the doped-diamond is expected as a next generation semiconductor device. In addition, in 2004, it was discovered by E. A. Ekimov *et al*. that the superconductivity appears in the boron-doped diamonds in a high concentration region [1]. As long as it has been reported so far, with increasing the boron concentration, the superconducting transition temperature (T_C) rises [2]. According to the theoretical calculations by T. Shirakawa *et al*., we can increase T_C when diamond is properly implanted with boron ions at its specific lattice positions of carbon. Thus the research on ion-doped-diamond using MBE (molecular beam epitaxy) and CVD (Chemical Vapor Deposition) methods, which make subtle doping-control possible, has been actively carried out. At present, T_C exceeds 10 K for the CVD-grown diamond at the boron concentration of ~10^{22} cm^{-1} [2].

In the present study, instead of MBE or CVD, we tried to control the electronic states by the ion implantation using ECR (Electron Cyclotron Resonance) ion sources. This method provides extremely high-concentrations of ions, and various ion species can be injected. As is known in the commercial semiconductors such as Si and GaAs, the damage in the crystal and inhomogeneity of dopants are improved by the thermal annealing process. In the case of diamond, since the diamond is the high-pressure phase of carbon, the conversion of diamond to graphite can occur by simply heating the diamond. The thermal annealing treatment of diamond is still a hot research field. In this research, by suppressing extraction voltage, lattice damage is minimized.

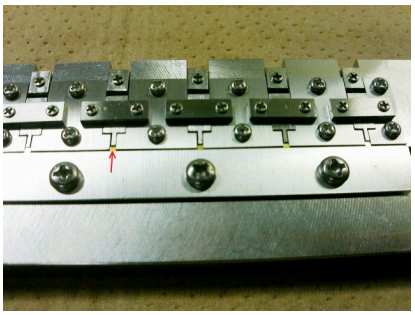

Fig. 1: Sample holder.

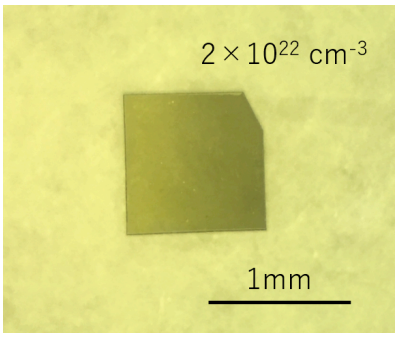

Fig. 2: Boron-doped diamond.

This year, the boron-doped diamonds were prepared for the hole-doped systems, and the experimental results were compared with the literature data. The expected ion concentration was calculated from the ion beam intensity and exposure time. The ion concentration was systematically varied among the samples by changing the exposure time. Figure 1 shows the samples placed on the sample holder. A typical doped diamond is shown in Fig. 2. The right-hand side of the sample, which was transparent before the irradiation, turned black.

First, in order to investigate the electric conductivity, we measured the electrical resistance by the conventional four-probe DC method. Figure 3 shows the electric resistivity for the samples with ion concentrations (ρ) of 2×10^{21}, 4×10^{21}, and 2×10^{22} cm^{-3}. The data of each sample is normalized with

respect to the room temperature value. The electrical conductivity systematically increases with increasing ρ. The data points are very scattered. This behavior can be seen when there is a problem in the electrode contact. We may improve the situation by increasing the doping density on the surface or by changing the method of the electrode preparation.

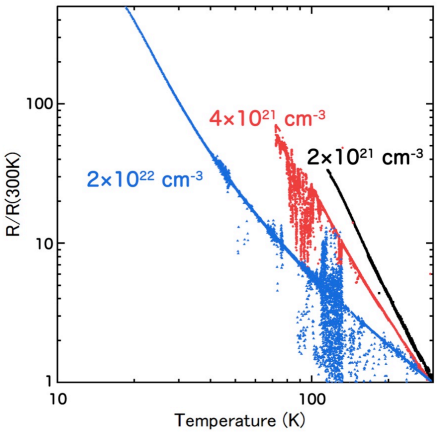

Fig. 3: Temperature dependence of the resistivity of B-doped diamond for each doping density.

Subsequently, in order to detect (a) the paramagnetic moment due to the formation of lattice defects and (b) the appearance of superconductivity, the static magnetization measurements were carried out using MPMS (Quantum Design). The temperature dependence of the magnetization at the magnetic field of 0.1 T for various ρ is shown in Fig. 4. In these measurements, no Meissner effect associated with the superconducting transition was observed. Each curve of the magnetic susceptibility is composed of the Curie component and a temperature-independent paramagnetic component. We see that, as ρ increases. The *T*-independent component apparently increases in the higher ion concentrations of 8×10^{21} and 2×10^{22} cm^{-3}. In general, the pure diamond shows diamagnetism; however a paramagnetic behavior is seen even in the sample without doping. The diamond used here contains 0.1% nitrogen intrinsically, so that the observed paramagnetic moment likely comes from the nitrogen-vacancy pairs, and/or the deterioration at the sections that were heated up in the laser-cutting process. We are now investigating the origins of these paramagnetic components.

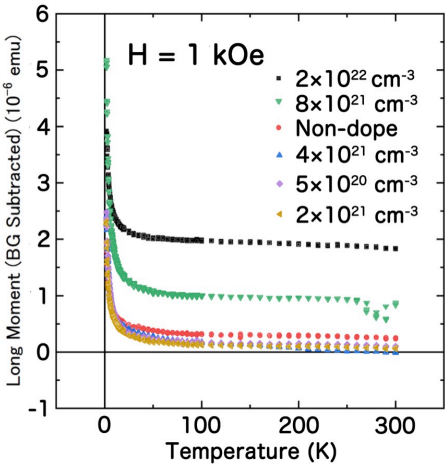

Fig. 4: Temperature dependence of the static magnetization of B-doped diamond for each doping density.

According to the previous research, the doping amount of 10^{21}~10^{22} cm^{-3} is enough to drive the electronic state of diamond into the metallic state and further into the superconducting state. Our results, however, show that the electric resistance exhibits the semiconducting behavior without any signs of superconductivity. It is probable that effective ion concentrations were smaller than the calculated ones. As shown in Fig. 2, the depth of black color varies across the specimen, suggesting that there is an inhomogeneous distribution of the dopants. Next year, we will attempt to carry out the thermal annealing to control the inhomogeneity of the ion concentration and prepare the sample with more boron concentration to examine the relation between the electronic state and ion-concentration.

Reference

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[2] H. Umezawa et al., arXiv:cond-mat/0503303 (unpublished).

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