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Hoshino, Yasushi / Seki, Yuhei / Nakata, Jyoji

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REALIZATION OF P-TYPE CONDUCTIVE LAYER ON TYPE IIA CVD DIAMOND BY B^+ ION IMPLANTATION AT ROOM TEMPERATURE FOLLOWED BY 1150 AND 1300°C ANNEALING

Yuhei Seki[1], Yasushi Hoshino[2#], and Jyoji Nakata[1,2]

[1] *Field of Physics, Graduate School of Science, Kanagawa University*

[2] *Department of Mathematics and Physics, Kanagawa University*

2946, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

We have investigated the electrical properties of heavily B-doped type IIa diamond introduced by ion implantation at room temperature with a flat impurity concentration of ~200 ppm, followed by thermal annealing at 1150 and 1300°C. We confirmed *p*-type conductivity and typical activation energy of acceptor B in diamond at wide temperatures range from 173 to 1073 K. The doping efficiency for the sample after the 1150°C annealing was realized to be 78%, which is the best value ever reported. The Hall mobility around room temperature was realized to be higher than 100 cm^2/Vs. It is consequently revealed that at least room temperature B-implantation followed by above 1150°C annealing is sufficiently effective for the electrical activation of B doped in high quality diamond.

I. Introduction

Effective impurity doping in diamond by ion implantation is one of the crucial topics to realize diamond electronic devices for decades. So far, the impurity doping has been usually performed during the synthesis process of diamond film using chemical vaper deposition (CVD). However, the impurity doping by ion implantation is quite superior to that during synthesis process in terms of the merits of high controllability, short process time, large doping area, and low financial costs. One can easily introduce any dopants in the desired area and depth with an accurate concentration; therefore, ion implantation is a common tool for fabricating Si-based semiconductor devices

According to previous reports, some research groups tried to dope various impurities of B, P, O, and S in type IIa diamond by ion implantation technique; however, the effective impurity doping using ion implantation technique has not yet been practically accomplished. [1-9] In the previous letter, we reported the great progress of the electrical properties for the B^+ ion implanted into the type-IIa diamond substrates at room temperature, followed by relatively low temperature annealing at 1150 and 1300°C [10]

yhoshino@kanagawa-u.ac.jp

II. Experiment

We performed B^+-ion implantation at room temperature (RT) into the type IIa diamond substrates synthesized by CVD method. The B^+ ions were implanted with 8 different energies of 5 to 60 keV to obtain a flat B concentration from the surface to the 130 nm depth. The total fluence was 4.6×10^{14} cm^{-2} and the B concentration at the plateau region was 3.6×10^{19} cm^{-3} estimated by secondary ion mass spectroscopy. The samples were then covered with a thin SiO_2 film with ~100 nm thick to prevent surface graphitization during the following annealing treatment. We finally annealed these samples at 1150 and 1300°C for 2 h in Ar ambient in a quartz furnace. After the annealing, the deposited SiO_2 film was completely removed by diluted HF solution.

The electrical properties such as specific resistance, carrier concentration, Hall mobility, and carrier type were analyzed by Hall effect measurement based on Van der Pauw method at the temperature range from 77 to 1073 K. We adopted the Ohmic electrodes consisting of Au/Pt/Ti multilayer.

III. Results and discussion

Figure 1 shows the sheet and specific resistances of the B^+-implanted samples at RT followed by 1150 and 1300°C annealing, as a function of the reciprocal measured absolute-temperature. For reference, we measured the sheet resistances of the sample-holder without mounting sample and the C^+-implanted diamond substrate under the same implantation condition as B implantation. Here, it should be noted that $^{12}C^+$ ion has almost the same atomic and mass number as $^{11}B^+$ ions, expecting the similar defect amounts created in the diamond substrate, but does not act as an acceptor in diamond. It is found in Fig. 1 that no significant electrical conduction was observed in the sample holder and the C^+-implanted sample, indicating that the electrical conduction via the induced defects by ion implantation was negligibly small. The sheet resistance of the B-implanted samples followed by 1150 and 1300°C annealing was significantly decreased and the activation energy was estimated to be ~0.3 eV, corresponding to the ionization energy of acceptor B. It

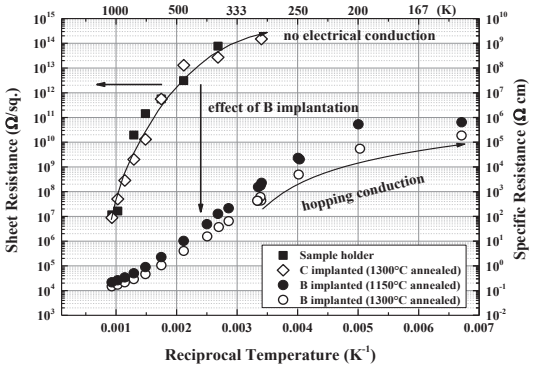

Fig. 1: Sheet and specific resistance for the B-implanted samples at RT followed by 1150 and 1300°C annealing. For reference, the sheet resistances of the sample holder and C-implanted sample after 1300°C annealing are shown.

Table I : Electrical properties obtained by Hall effect measurements

Postaneal Temp. (°C)	Doping concent. (cm^{-3})	Acceptor concent. (cm^{-3})	Donor concent. (cm^{-3})	Compensation ratio (%)	Doping efficiency (%)	Ionization energy (eV)
1150	3.6×10^{19}	2.8×10^{19}	4.7×10^{18}	18.5	78	0.335
1300	3.3×10^{19}	1.7×10^{19}	2.9×10^{18}	19.5	52	0.302

is clearly indicated that the implanted B atoms occupied in the substitutional sites in the diamond lattice and were effectively activated.

Figure 2 shows the carrier concentration (a) and Hall mobility (b) as a function of reciprocal absolute-temperature and absolute temperature itself, respectively, obtained by Hall effect measurements. The circles and squares shown in Fig. 2(a) indicate the experimentally obtained carrier concentrations. Here, we performed the same electrical measurements for two different substrates with the same doping process, as shown in the figure with open and closed symbols, to confirm the experimental reproducibility. The solid lines indicate the theoretically calculated carrier concentration derived from charge neutrality condition and Fermi-Dirac distribution function by assuming specific parameters of acceptor concentration (N_A), compensation ratio (N_D/N_A), and ionization energy (E_A) of acceptor B so as to best-fit the experimentally observed results. The obtained results are summarized in Table I.

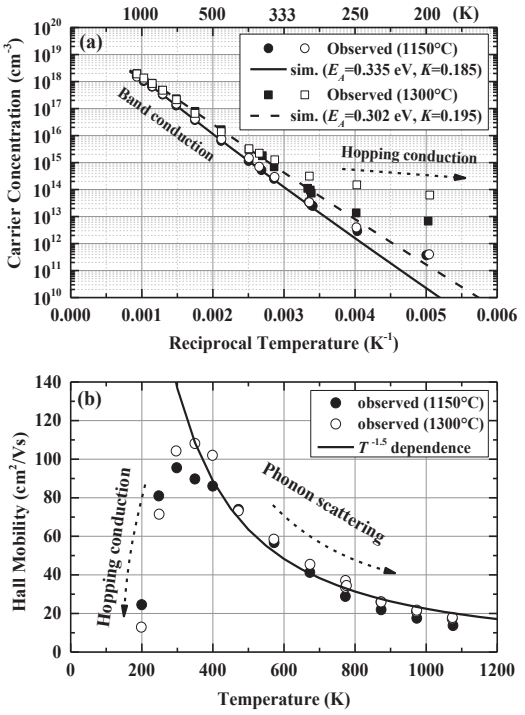

Fig. 2: Experimental and best-fitted carrier concentrations (a), and Hall mobility (b) for the B-implanted sample at RT followed by subsequent annealing at 1150 and 1300°C.

The most probable compensation ratio for the samples post-annealed at 1150 and 1300°C was estimated to be 0.185 and 0.195, respectively, being independent of the post-annealing temperature within experimental errors. The activation energies for the 1150°C- and 1300°C-postannealed samples were estimated be 0.335 and 0.302 eV, which correspond to the typical ionization energy of acceptor B for heavily B-doped diamond. As

also clearly shown in Fig. 2(b) that the experimentally obtained Hall mobility fitted very well to the theoretically expected temperature dependence ($T^{-1.5}$) above RT region and took the maximum value of 108 cm^2/Vs at RT for the 1300°C-postannealed sample. This obtained Hall mobility is almost the best value for B-doped diamond with the acceptor concentration of ~10^{19} cm^{-3}. By best-fitting the observed carrier concentration to the theoretical relation, we obtained the acceptor concentrations of 2.8×10^{19} and 1.7×10^{19} cm^{-3} for the 1150°C- and 1300°C-annealed samples, respectively. Thus, the doping efficiency, which is defined as the ratio of acceptor concentration to implanted B concentration was estimated to be 78 and 52 % for the 1150 and 1300°C-annealed samples, respectively. These doping efficiencies are 8.7 and 5.2 times higher than the previous results for the similar doping concentration reported by Vogel *et al*. and Tsubouchi *et al*., respectively. [6,7)]

IV. Conclusions

We investigated electrical properties such as carrier concentration, mobility, doping efficiency, and compensation ratio for the B-doped diamond by ion implantation at RT followed by annealing at relatively low temperatures of 1150 and 1300°C. We showed a significant improvement of the doping efficiency (~80%) for the heavily B-implanted diamond. Consequently, at least RT B-implantation followed by above 1150°C annealing is sufficiently effective for the electrical activation of implanted B. The Hall mobility observed in this study is comparable to the best value expected in the B-doped diamond with the same B concentration. The great progress in the doping efficiency of acceptor B should be the breakthrough for power device applications.

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