Characterization of Phosphorus-doped Diamond Prepared by Microwave Plasma CVD

M. Kamo, S. Koizumi, S. Mita*, A. Sawabe* and R. Kalish**

National Institute for Research in Inorganic Materials
1-1 Namiki, Tsukuba, Ibaraki 305, Japan
* Department of Electrical Engineering and Electronics, Aoyama Gakuin University
6-16-1 Chitosedai, Setagaya, Tokyo 157, Japan
Technion, Technion City, Haifa 32000, Israel

INTRODUCTION

Preparation of n-type semiconducting diamond is one of the problems to be solved for the development of electronic devices made with diamond. Although efforts have been made to dope diamond with phosphorus, no successful results of n-type semiconductor doping with good reproducibility have been reported. In a previous paper on SIMS analysis of phosphorus-doped diamond[1],it has been suggested that phosphorus atoms in the diamond are terminated by hydrogen atoms. Therefore, the phosphorus atoms may not be donors. Moreover, it has been pointed out that phosphorus atoms are not substitutionally, but interstitially doped in diamond because the radius of a phosphorus atom is too large compared with that of a carbon atom[2]. Areport on ESR measurements of phosphorus-doped diamond indicates that phosphorus atoms are able to be substitutionally doped into diamond to a concentration on the order of $10^{17}cm^{-3}$ [3].

In this paper, 1)the growth conditions for phosphorus doping were investigated in order to avoid hydrogen termination of phosphorus atoms, 2) a SIMS instrument was used for analysis of the grown diamond, and 3) Hall effect and resistivity were measured for the estimation of the electrical properties of the phosphorus-doped diamond.

EXPERIMENTAL

Diamond was deposited by a microwave plasma-assisted CVD system which is essentially the same as that reported previously[4]. Mechanically polished (111) surfaces of type Ib high-temperature and high-pressure synthesized diamond were used as substrate. Deposition was carried out by passing a mixture of hydrogen, methane and phosphine through the chamber and then applying microwave power to induce a glow discharge under the following conditions: methane concentration(CH_4/H_2); 0.15%, phosphine concentration(PH_3/CH_4); 800-20000ppm, total pressure; 10.7kPa, total gas flow rate; 200sccm, substrate temperature; 950°C, duration time; 2 hours. The substrate temperature was monitered using a single-color optical pyrometer through the plasma. The growth layer was characterized by scannning electron microscopy(SEM), reflection high-energy electron diffraction(RHEED), secondary ion mass spectroscopy(SIMS) and Raman spectroscopy. For SIMS analysis, O_2^+ion was used as the primary ion beam and positive secondary ions were measured. Raman spectra of growth layes were measured using Raman instrument with a confocal microscopy. Hall measurements were carried out using a van der Pauw method, in which Titanium was used as electrodes.

RESULTS AND DISCUSSION

The homoepitaxial growth conditions for phosphorus-doped diamond on (111) surface shown above were determined by preliminary experiments. The growth rate has been enhanced by the addition of phosphine gas in the source gas mixture. Under the growth conditions, the growth rate was about 0.15μm/h. The streakes in the RHEED pattern of the layer grown at 1000ppm of PH_3 indicate that the surface is smooth and flat, although a little bit of pits are observed in an SEM picture. Raman spectrum of the layer indicates that no existence of graphitic carbon in the layer is detected. These results confirm that the growth layer is high quality diamond. A depth profile of SIMS analysis of the layer is shown in Fig.1. In the figure, values 1, 12 and 31 of m/e indicate hydrogen, carbon and phosphorus, respectively. Existence of phosphorus atoms in the layer is obviously confirmed with the figure. As reported previously, hydrogen atoms intended to be easily doped into homoepitaxially grown diamond with phosphorus doping under the conditions studied previously. But, Fig.1 indicates that no remarkable increase of hydrogen is observed in the growth layer, though hydrogen is detected at the interface between the growth layer and the substrate. The result means that the growth has been performed under the conditions optimised for excluding hydrogen from the growth layer. Higher substrate temperature and higher total pressure have been applied in this study compared with those in the previous study. It is supposed that the higher temperature accellerates removal of hydrogen atoms from growing diamond surface, and that the higher pressure enhances dissociation of P-H bonds of PH_3 molecules in the microwave plasma, because of higher power density for plasma. These effects are considered to contribute decreasing hydrogen content in the growth layer.

Electrical resistivities of the phosphorus-doped diamond(1000ppm) is shown in Fig.2. It is cleary that the resistivities decrease with increasing of temperature. The result means that the layer is semiconducting.

The linear dependence of the resistivity on measurement temperature for several P-doped samples with about the same slope has proved that the conduction mechanism is temperature activated with an activation energy of about 0.47eV. Negative Hall constants for the samples were found proving that the conductivity is due to electrons, i.e. n-type doping has been achieved by the presence of P in the samples. Results on the dependence of carrier concentration on inverse temperature have indicated that an activation energy is 0.43eV for the higher temperature than about 400K. However, the mobility is very low, - $23cm^2/V{\bullet}s$.

The data in this study prove that n-type diamond can be obtained by doping with phosphorus. But, these are preliminary results and impractical for device applications. Further studies are necessary for the applications.

SUMMARY

Phosphorus atoms were doped in diamond using a microwave plasma CVD method. From a depth profile of the SIMS analysis, the phosphorus atoms are found to be incorporated independently of hydrogen. Hall effect measurements prove that the diamond is n-type semiconducting.

REFERENCE

1) M. Kamo et al., Proc. 2nd Int. Conf. on New Diamond Science and Technology, 1991, p637.
2) A.T. Collins, Semicond. Sci. Technol., 4, 605(1989).
3) M.E. Zvanut et al., Appl. Phys. Lett., 65, 2287(1994).
4) M.Kamo et al., J Cryst. Growth, 62, 642(1983).

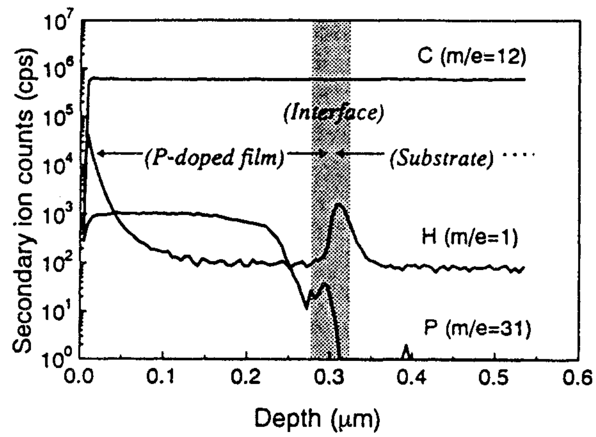

Fig.1 Depth profile of SIMS analysis of 1000ppm phosphorus-doped diamond.

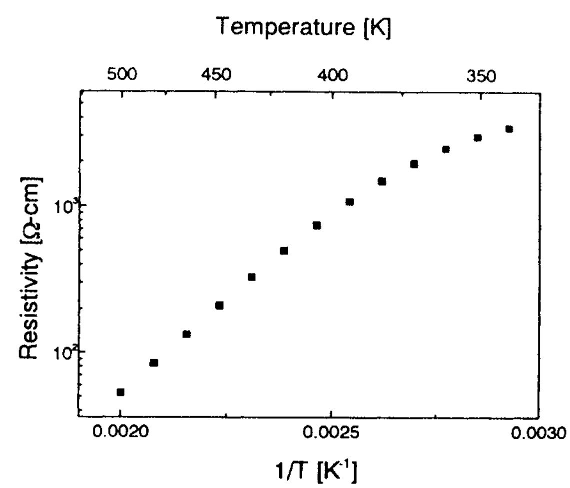

Fig.2 Temperature dependence of the resistivity of 1000ppm phosphorus-doped diamond.