Lightly phosphorus-doped homoepitaxial diamond films grown by chemical vapor deposition

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Lightly phosphorus-doped {111} homoepitaxial diamond films have been grown by microwave plasma-assisted chemical vapor deposition under optimized growth conditions. The Phosphorus concentration in the film can be controlled at a low doping level of the order of 10^{16} cm^{-3}. *N*-type conductivity of the films with phosphorus concentrations above 1×10^{16} cm^{-3} is reproducibly confirmed by Hall-effect measurements in the temperature range from 300 to 873 K. The highest value of the Hall mobility at room temperature is 660 cm^2/V s obtained for a film with a phosphorus concentration of 7×10^{16} cm^{-3}. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1840119]

Diamond is a wide-band-gap semiconductor for application to high-power, high-temperature, and high-frequency electronic devices and/or optoelectronic devices due to its excellent properties.

N-type doping of diamond is one of the fundamental issues to be resolved for development of diamond-based devices. Phosphorus (P) is expected to be a promising candidate for *n*-type dopant of diamond. We have successfully synthesized P-doped diamond films on {111} diamond substrates by microwave plasma-assisted chemical vapor deposition (CVD) using phosphine (PH_3) as a dopant source.[1,2] The temperature-dependent Hall-effect measurements revealed *n*-type conductivity of the P-doped diamond films with an activation energy of 0.6 eV.[2] Cathodoluminescence spectroscopy,[3] photoconductivity measurements,[4] and infrared absorption spectroscopy[5] supported the P donor level that is located at 0.6 eV below the bottom of the conduction band. These results demonstrated that P acts as a donor in diamond. Combining both P and boron (*p*-type) doping, therefore, has been shown to give diode characteristics with good properties.[6]

In order to achieve higher performance of a diamond *pn* junction, it is necessary to improve the electrical properties of the boron- and P-doped layers. Recently, a drift mobility of 4500 cm^2/V s for electrons in undoped homoepitaxial CVD diamond[7] and a Hall mobility of 1840 cm^2/V s for holes in a boron-doped {100} homoepitaxial diamond film[8] at room temperature (RT) have been reported. On the other hand, the maximum Hall mobility in a P-doped {111} film with a P concentration of 3×10^{18} cm^{-3} has been detected to be 240 cm^2/V s at RT.[2] It is expected that with decreasing doping concentration, the mobility will become higher. However, up to now, such lightly doped films with high Hall mobilities have not been obtained. A possible reason may be attributed to compensation of donors by defects or residual impurities. The improvement of electrical properties is strongly related to the improvement of crystalline perfection. In order to obtain P-doped films with high crystalline perfection, optimized growth conditions such as lower methane concentration and higher substrate temperature were applied. In addition, an ultrahigh-vacuum chamber and high-pure reactant gases were used in the present study.

In this letter, we report on the growth of lightly P-doped diamond films with high crystalline perfection by microwave plasma-assisted CVD. These films have been characterized by secondary ion mass spectroscopy (SIMS) and Hall-effect measurements.

The growth of diamond is performed by a stainless-steel-type microwave plasma-assisted CVD system with the capability of precisely controlling growth conditions. The vacuum chamber can be evacuated to below 5×10^{-8} Torr. The P concentration of an unintentionally doped film was of the order of 10^{15} cm^{-3} due to the residual P compounds in the chamber.

Lightly P-doped diamond films were epitaxially grown on synthetic type Ib diamond {111} substrates with dimensions of $2\times2\times0.5$ mm^3. The source gas was 0.05% CH_4 (6N) diluted with H_2 (9N). Doping with P was carried out by adding PH_3 (6N) to the source gas. The PH_3/CH_4 ratio in the source gas was varied from 10 to 1000 ppm. The gas pressure, the total gas flow rate, the substrate temperature, and the growth duration were 100 Torr, 1000 sccm, 900 °C, and 3 h, respectively. The resultant film thickness was approximately 1 μm.

Heavily P-doped diamond layers were selectively grown on a lightly P-doped film to form ohmic contacts. The detailed process of selective doping has been described in the previous paper.[9]

Before forming electrodes, the surface of diamond films was chemically oxidized to remove the surface conductive layer using a solution of $NaClO_3$ in HNO_3 at 200 °C for 3 h. Ohmic electrodes composed of Ti capped with Au were formed on heavily P-doped diamond layers by vacuum evaporation.

Hall-effect measurements using the van der Pauw method were carried out in the temperature range between

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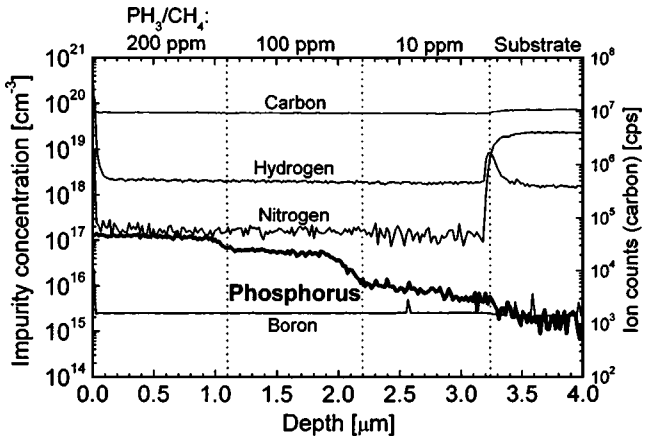

FIG. 1. SIMS depth profile of impurities in a P-doped diamond film consecutively grown at 10, 100, and 200 ppm in the PH_3/CH_4 ratio.

300 and 873 K at an ac magnetic field of 0.6 T with a frequency of 0.1 Hz.

Figure 1 shows the SIMS depth profiles of impurities in a P-doped film consecutively grown at 10, 100, and 200 ppm of PH_3 in CH_4. We confirmed control of the P concentration at low doping levels. The P concentrations were estimated to be approximately 1×10^{16} cm^{-3} for 10 ppm, 7×10^{16} cm^{-3} for 100 ppm, and 1×10^{17} cm^{-3} for 200 ppm while boron, nitrogen, and hydrogen concentrations were below the detection limits.

P-doped films with phosphorus concentrations above 1×10^{16} cm^{-3} show negative Hall coefficients in the temperature range from 300 to 873 K, which indicates *n*-type conduction of the films. In the case of films with a P concentration of 1×10^{16} cm^{-3} or less, although *n*-type conductivity of the films is observed at higher temperatures, negative Hall coefficients around RT have not been necessarily detected due to the high resistivity of the films. Figure 2 shows the temperature dependence of the carrier concentrations of P-doped diamond films with various P concentrations. The carrier concentrations are directly proportional to the P concentrations. The carrier concentration and resistivity of a film with a P concentration of 7×10^{16} cm^{-3} were 5×10^{10} cm^{-3} and $2\times10^{5}\ \Omega$ cm at RT, 6×10^{16} cm^{-3} and $2\ \Omega$ cm at 873 K, respectively. For a nondegenerate semiconductor, the activation energy and the compensation ratio can be calculated using the following equation:

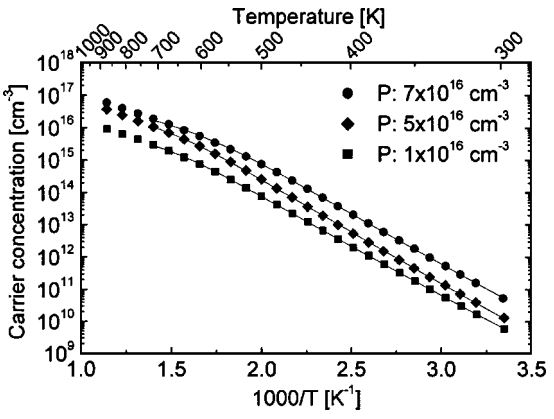

FIG. 2. Temperature dependence of carrier concentration for P-doped diamond films with various P concentrations. Solid curves indicate the theoretical calculations using Eq. (1).

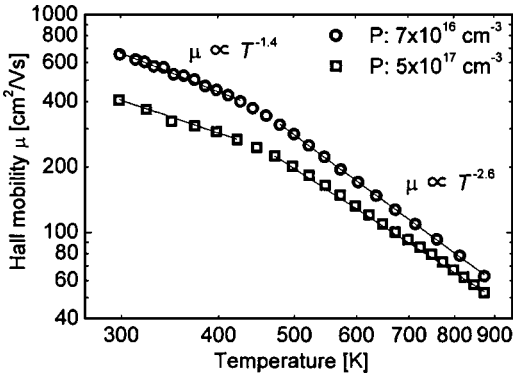

FIG. 3. Temperature dependence of Hall mobility for P-doped diamond films with P concentrations of 7×10^{16} and 5×10^{17} cm^{-3}.

$$\frac{n(n+N_A)}{N_D-N_A-n}=\frac{N_C}{g_d}\exp\left(-\frac{E_D}{kT}\right), \tag{1}$$

where n is the carrier concentration, N_D and N_A are the donor and accepter concentrations, N_C is the effective density of states in the conduction band, g_d is the degeneracy factor for the donor, E_D is the activation energy of the donor, k is the Boltzmann constant, and T is the temperature. For the films with a P concentration of 7×10^{16} cm^{-3}, we obtained $E_D=0.57$ eV, $N_D=6.8\times10^{16}$ cm^{-3}, $N_A=8.8\times10^{15}$ cm^{-3}, and the compensation ratio $N_A/N_D=0.13$. In a film with a P concentration of 1×10^{16} cm^{-3}, N_A was 6.4×10^{15} cm^{-3}. With decreasing P concentration below 1×10^{16} cm^{-3}, P-doped films become fully compensated and highly resistive. These results suggest that in the present study, the concentration of compensating defects that exist naturally in the {111} CVD film is of the order of 10^{15} cm^{-3}.

Figure 3 shows the Hall mobility of P-doped films as a function of temperature. The Hall mobility at RT increases from 410 to 660 cm^2/V s with decreasing P concentrations from 5×10^{17} to 7×10^{16} cm^{-3}. The value of 660 cm^2/V s is the highest ever reported for *n*-type diamond films. For films with P concentrations below 7×10^{16} cm^{-3}, however, no improvement of the Hall mobility has been achieved. This may be ascribed to the existence of compensating defects. The Hall mobility for the film with a P concentration of 7×10^{16} cm^{-3} decreases with increasing temperature as $T^{-1.4}$ up to 450 K. This indicates that acoustic phonon scattering dominates.[10] At temperatures above 450 K, the Hall mobility is proportional to $T^{-2.6}$. We assume that the Hall mobility at higher temperatures is dominated by various scattering mechanisms such as intervalley scattering, as well as acoustic phonon scattering. This is similar to that of what has been detected by drift mobility experiments in high-quality natural diamond.[11] These results indicate the high crystalline perfection of the lightly P-doped diamond films.

In summary, lightly P-doped {111} homoepitaxial diamond films have been grown by microwave plasma-assisted CVD. We demonstrate that controlled P doping with concentrations as low as 10^{16} cm^{-3} can be achieved. Hall-effect measurements reveal *n*-type conductivity of the films. The highest value of the Hall mobility at RT is 660 cm^2/V s obtained for a film with a phosphorus concentration of 7×10^{16} cm^{-3}. We conclude that the lightly P-doped diamond films with high crystalline perfection can be successfully obtained.

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