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Electrical characterization of phosphorus-doped n-type homoepitaxial diamond layers

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Abstract

Electrical properties of phosphorus (P)-related donors have been investigated for P-doped homoepitaxial diamond layers grown by microwave plasma CVD. Temperature-dependent current–voltage (*I–V*), capacitance–voltage (*C–V*) measurements and frequency-dependent *C–V* measurements have been carried out with lateral dot-and-plane (with ring-shaped gap) Schottky barrier diodes. N-type Schottky junction properties were obtained. The ideality factor and the rectification ratio of the Schottky junction were obtained to be 1.9 and 1.7×10^5 at ±10 V and 473 K, respectively. Frequency-dependent measurements on these Schottky barrier diodes have shown that the capacitance is reduced at high frequency, most likely due to the inability of deep centers to maintain an equilibrium ionization state under a high-frequency modulation. *C–V* measurements deduced that the net donor concentration was 6.2×10^{17} cm^{-3} and the corresponding built-in potential was 4.0 eV, when the P concentration was 8.3×10^{17} cm^{-3}. Phosphorus electrical activity was 0.75 in the P-doped diamond layer. The carrier thermal activation energy (the donor level) was evaluated to be 0.6 eV from the relation between the net donor concentration and the carrier concentration.

Keywords: Diamond film; Homoepitaxy; Electrical properties characterization; N-type doping

1. Introduction

Diamond has attracted much attention as a material for high-power devices, high-frequency devices and ultraviolet light-emitting devices. High-quality diamond and electrical conduction (p-type or n-type) control are desirable to realize these devices. It is still difficult to obtain n-type conduction for diamond because of deep donor states and/or difficulties in incorporation of donor dopants [1–6]. Recently, n-type conduction has been obtained in phosphorus (P)-doped diamond grown by microwave plasma chemical vapor deposition (CVD) [1,7,8]. The temperature-dependent Hall effect measurements have clearly shown n-type conductivity and have revealed a P-related thermal activation energy of 0.6 eV. Additionally, the realization of p–n junctions in diamond has been reported [9–11]. However, electrical characteristics are not well understood. This paper presents a report on n-type Schottky barrier diodes and on electrical properties measured by capacitance–voltage (*C–V*) measurements in P-doped n-type homoepitaxial diamond. *C–V* measurements are useful for investigating deep traps, which affect the free carrier densities [12]. Lateral dot-and-plane (with ring-shaped-gap) Schottky barrier diodes have been fabricated using Au/Ni for Schottky contacts and Au/Pt/Ti for ohmic contacts. Results of temperature-dependent current–voltage (*I–V*) measurements, *C–V* measurements and frequency-dependent capacitance measurements are shown. Net donor concentration has been evaluated from the results of *C–V* measurements. We have investigated the relation between P concentration [determined by secondary

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ion mass spectroscopy (SIMS)], net donor concentration (determined by C–V measurements) and carrier concentration (determined by Hall effect measurements). The phosphorus electrical activity (the ratio of donor concentration to incorporated P concentration) and the carrier thermal activation energy will be shown. We have tried to discuss the influence of residual impurities on n-type conduction.

2. Experiments

The materials investigated here were grown by microwave plasma CVD on Ib (111) diamond substrates, using methane (CH_4) [1,6]. The dopant source was phosphine (PH_3). The thickness of the P-doped layer was 1.5 μm. Lateral dot-and-plane (with ring-shaped gap) Schottky barrier diodes were fabricated on the P-doped homoepitaxial diamond layers. The electrode pattern has been shown in previous reports [13]. Before fabricating Schottky barrier diodes, the samples were kept in a mixture of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) at 200 °C for 15 min to remove any graphitic layer and/or surface contamination. Moreover, just before the evaporation of the Schottky contact metal, the P-doped diamond surface was exposed to an oxygen microwave plasma at 500 W for 5 min to remove surface contamination during the patterning process of metal contact pads. Each Schottky contact pad (Au/Ni) was surrounded by ohmic contacts (Au/Pt/Ti) with 20-μm gap. There were 18 Schottky contact pads on a 2-mm^2 sample. The three different areas of Schottky contact pads were 7.5×10^{-4}, 3.4×10^{-4} and 2.0×10^{-4} cm^2, respectively. The Au/Pt/Ti ohmic contacts were annealed at 700 °C for 10 min in N_2 ambient before fabricating Schottky contacts, and the area was 150 times greater than the area of the Schottky contact pads. I–V measurements were performed to investigate the Schottky properties in the temperature range from 300 to 573 K. C–V and frequency-dependent capacitance measurements were performed to investigate donor characteristics in the temperature range from 300 to 573 K, with a frequency ranging from 100 Hz to 1 MHz. The net donor concentration was evaluated by C–V measurements with dielectric constant ε=5.7. Temperature-dependent Hall effect measurements were carried out to investigate the carrier (electron) concentration for the same sample before fabricating the Schottky barrier diodes. The P concentration was determined by SIMS measurements.

3. Results and discussion

Fig. 1 shows the representative results of I–V measurements at 300, 373, 473 and 573 K in a P-doped homoepitaxial diamond layer. These I–V properties clearly

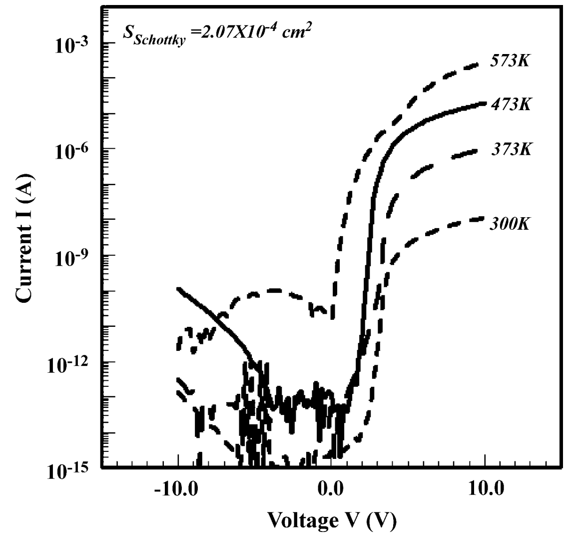

Fig. 1. Typical I–V curve at 300, 373, 473 and 573 K in P-doped homoepitaxial diamond.

show n-type conduction. The ideality factor (n-factor) of the Schottky junction in this sample was found to be 1.9, and the rectification ratio was 1.7×10^5 at $\pm$10 V at 473 K. The ideality factor decreased from 3.6 to 1.9 with increasing temperature from 300 to 473 K; however, at 573 K, it slightly increased to n=2.2. The most plausible reason for the improvement in the ideality factor is reduction in resistivity of the diamond layer with increasing temperature. The increase of ideality factor and the large leakage current in reverse bias at 573 K is attributed to the degradation of the Au/Ni contact or the interface between the Au/Ni contact and the diamond. The contact resistance may not be negligible in these I–V curves because it is difficult to obtain ideal ohmic contacts for n-type diamond, as shown in previous reports [14]. The details of the contact behavior are now under investigation. However, it is assumed that the contact resistance does not greatly influence the capacitance measurement. The measured capacitance can be attributed to the Au/Ni Schottky barrier because the Au/Ni contact area is considerably smaller than the Au/Pt/Ti contact area (<1%).

Fig. 2 shows a typical result of the capacitance (C) at zero dc bias voltage as a function of frequency (f) for the P-doped diamond layer at 300, 373, 473 and 573 K. It is found that the capacitance strongly depends on the frequency. The observed variation in capacitance could be due to the high resistivity of the diamond and/or the well-known dispersion effect, which occurs when a deep level is unable to follow the high-frequency voltage modulation and contribute to the net space charge in the depletion region [15]. In most semiconducting materials, the former effect is relatively unimportant since the capacitance values were obtained from the series mode measurement of the inductance–capacitance–resistance (LCR) meter, in which the capacitance is determined independently of any series resistance. However, the considerable high resistivity of the P-doped diamond can also contribute to the decrease in capacitance

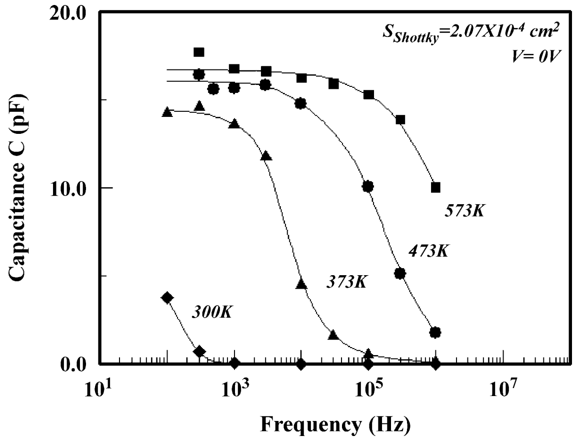

Fig. 2. Capacitance (C) at zero-bias voltage as a function of frequency at 300, 373, 473 and 573 K in P-doped homoepitaxial diamond.

at higher frequency. Further investigation is currently in progress to reveal the above-mentioned frequency dependence of capacitance. Generally, C–V measurements to evaluate net donor concentration should be carried out at adequately low frequency. The value of the capacitance increased in proportion to the Schottky contact area. This result indicates that the whole area of each Schottky (Au/Ni) contact pad is effective in the C–V and I–V measurements.

A representative result of C–V measurements at low frequency, 1 kHz, for the P-doped diamond layer at 473 K is shown in Fig. 3. The built-in potential (V_{bi}) was deduced to be 4.0 V from the correlation of $1/C^2$ with the applied voltage. This value of V_{bi} agrees reasonably with the calculated value of V_{bicalc}=4.3 V, which was calculated with the simple equation, $V_{\mathrm{bicalc}}=\phi_{\mathrm{m}}-\chi-V_{\mathrm{n}}$, using reported values, namely, the electron affinity of (111) diamond of χ=0.5 eV and the work function of Ni ϕ_{m}=5.15 eV [16,17]. V_{n} means the difference between the Fermi level and the bottom of the conduction band. From the C–V measurements, we calculate the net donor concentration ($N_{\mathrm{D}}-N_{\mathrm{A}}$), or the net ionized impurity concentration, to be 6.2×10^{17} cm^{-3}.

Fig. 4 shows the depth profiles of impurity concentrations for the sample determined by SIMS. The P concentration, N_{P}, was 8.3×10^{17} cm^{-3} for the P-doped layer. The nitrogen concentration was 1.1×10^{19} cm^{-3} for the substrate, but that is lower than the detection limit (~2×10^{17} cm^{-3}). The other residual impurities, boron, hydrogen and oxygen, were not detected for both the substrate and the P-doped epitaxial layer. At the interface of the substrate and the P-doped layer, hydrogen was detected. The P electrical activity, η, which denotes the ratio of the net donor concentration to the incorporated P concentration [$\eta=(N_{\mathrm{D}}-N_{\mathrm{A}})/N_{\mathrm{P}}$], is 0.75. A relatively high ratio of the incorporated P atoms is ionized. One of the reasons of decreased P electrical activity is the electrical compensation of P donors by background acceptors. Although boron is thought to be one of the background acceptors, the boron concentration was less than 5×10^{15} cm^{-3} in the P-doped layer, and it is therefore almost negligible with respect to the donor concentration of 6.2×10^{17} cm^{-3}. This indicates that other residual impurities and/or defects may reduce the P electrical activity.

The carrier thermal activation energy, ΔE_{D}, is ~0.6 eV as deduced from the relation between the net donor concentration and the carrier concentration which will be discussed in the following. For the calculation based on the calculated charge neutrality equation, we assumed the effective mass of electron m_{e}*=0.57m_0, the compensating acceptor concentration $N_{\mathrm{A}}=1\times10^{15}$ cm^{-3} and the degeneracy factor g=2 [18]. The result, ΔE_{D}=0.6 eV is consistent with the activation energy that has been measured by Hall effect experiments, as shown in the previous reports [1]. The results, namely, high uncompensated phosphorus density and the large carrier thermal activation energy, reveal that the low carrier concentration in P-doped n-type diamond is not mainly caused by the inactivation of P atoms, but by the large carrier thermal activation energy.

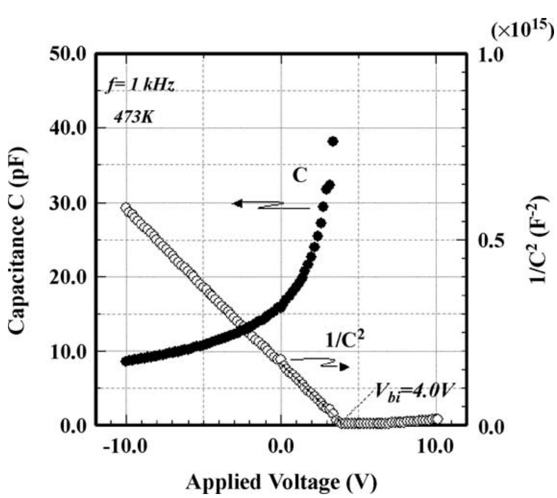

Fig. 3. Typical C–V curve at 473 K in P-doped homoepitaxial diamond. The applied frequency was 1 kHz.

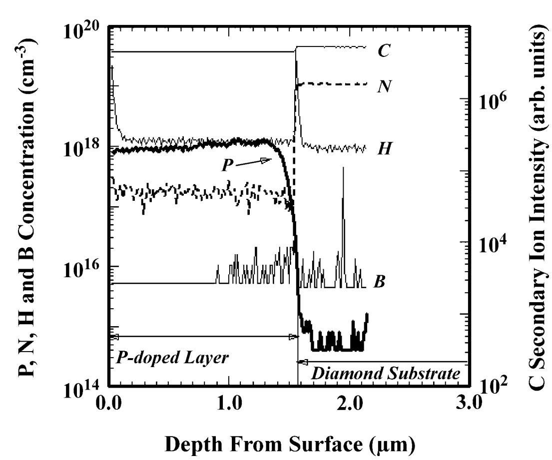

Fig. 4. Depth profiles of P concentration and residual impurities in the P-doped homoepitaxial diamond layer and the diamond substrate.

The existence of shallow donor states was not evaluated in this study because the capacitance was quite low and independent from applied voltage in the higher frequency region.

4. Summary

I–V and *C–V* measurements were carried out to investigate the electrical properties of P-related donors in P-doped homoepitaxial diamond with lateral dot-and-plane (with ring-shaped gap) Schottky barrier diodes. We obtained n-type Schottky junction properties. The frequency-dependent capacitance measurements revealed the existence of deep donor states. The net donor concentration was calculated to be 6.2×10^{17} cm^{-3}, the corresponding built-in potential (V_{bi}) is 4.0 V and the total P concentration was 8.3×10^{17} cm^{-3}. Phosphorus electrical activity was found to be relatively high (0.75). The electron thermal activation energy, or the donor level, was calculated to be 0.6 eV from the relation between the net donor concentration and the carrier concentration. These results reveal that the low carrier concentration in P-doped n-type diamond is not mainly caused by the inactivation of incorporated phosphorus, but by the large electron thermal activation energy.

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