

n-type conductivity of phosphorus-doped homoepitaxial single crystal diamond on (001) substrate

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Abstract

The macroscopic surface morphology and crystallinity of (001) *n*-type diamond films, which have been quite recently achieved by P-doping using plasma-enhanced chemical vapor deposition technique, were studied. The observation of diffraction spots, streaks, and Kikuchi patterns in reflection high energy electron diffraction analysis indicated that the surface smoothness and the crystallinity were fine. Regarding the electrical properties of (001) *n*-type diamond films, Hall-effect measurements over a wide temperature range from 260 to 1000 K were investigated. The conduction band transport without the effect of hopping transport was confirmed within this experimental temperature range.

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1. Introduction

The interest in valency control to realize *n*-type homoepitaxial diamond has increased rapidly in the past several years, due to the possibility to use diamond in light-emitting diodes, cold cathode electron emitters, high-frequency and high-power devices, etc. In 1997, *n*-type diamond films have been first succeeded by Koizumi et al. on (111) substrate using microwave plasma-enhanced chemical vapor deposition technique (MPCVD) with phosphorus, P, doping [1]. After their success, many efforts have been devoted to grow high-quality P-doped *n*-type diamond film [2–7], and nowadays the highest mobility has been reported to be ~ 660 cm²/V s by lightly P-doped (111) diamond film [7].

It has been experimentally recognized that P incorporation and *n*-type control can only be achieved when (111)-oriented diamond is used for growth. This restriction of substrate orientation is considered to bring disadvantages for device

applications. It is well known that the (111) diamond surface is difficult to polish mechanically, whereas on (001) surfaces it is relatively easy to achieve smooth surfaces. In addition, (111) substrates are difficult to produce which limits the size to typically $2 \times 2 \times 0.5$ mm³ and makes them expensive. This situation generates significant technological problems with respect to photolithography, etching, metallization, and throughput.

To bring diamond electronic applications closer to real markets and to manufacture bipolar devices for a wide range of applications, it is compulsory to control *n*-type doping using phosphorus on (001)-oriented crystals. Quite recently we have successfully achieved homoepitaxial growth of (001) *n*-type diamond by P-doping using a MPCVD technique with special deposition conditions which was not tried before and with a precise control of deposition conditions [8]. The *n*-type conductivity and the incorporation of P atoms into (001) diamond films were already confirmed using Hall-effect measurements and secondary-ion mass spectroscopy (SIMS), respectively.

In this paper, the difference of impurity-doping behavior in (001) and (111) diamond films, the macroscopic surface morphology and crystallinity, and electrical properties of (001) P-doped *n*-type diamond films are described.

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2. Experimental procedures

Homoepitaxial diamond films were grown on high-pressure and high-temperature synthetic Ib diamond (001) crystal with dimensions of $3 \times 3 \times 0.5 \text{ mm}^3$ by MPCVD. The main source gas was CH_4 diluted with H_2 , and P-doping was carried out using PH_3 diluted with H_2 . The $[\text{CH}_4]/[\text{H}_2]$ and $[\text{PH}_3]/[\text{CH}_4]$ ratios were controlled by mass-flow controllers. The gas pressure, total gas flow rate, and microwave power were fixed with 25 Torr, 400 sccm, and 750 W, respectively. The substrate temperature, measured by an optical pyrometer, was maintained at $900 \text{ }^\circ\text{C}$ during the diamond growth. The dilution ratio of methane, $[\text{CH}_4]/[\text{H}_2]$ ratio, and gas-phase P concentration, $[\text{PH}_3]/[\text{CH}_4]$ ratio, are 0.4% and 5.0%, respectively. The conditions are summarized in Table 1 and all films tested in this paper were grown using these conditions. The deposition duration was 5 h and the resulting film thickness was approximately $1.8 \text{ }\mu\text{m}$. The thickness of the film was confirmed by secondary-ion mass spectroscopy (SIMS) analysis and the interface between film and Ib substrate was decided by the depth profile of nitrogen.

The amounts of impurities incorporated in diamond films were estimated by SIMS. The concentration of P, N, and B atoms was quantified by using each implanted standard. The surface morphology was observed using a differential interference microscope with a Nomarski prism. To characterize the crystallinity, reflection high energy electron diffraction (RHEED) analyses were performed with electron beam energy of 15 keV .

Electrical properties were investigated by Hall-effect measurements (TOYO Co., ResiTest 8300) as a function of temperature from 260 to 1000 K applying AC magnetic fields of 0.6 T and using van der Pauw contact configurations. Before these experiments, the as-grown diamond films were chemically cleaned in H_2SO_4 and HNO_3 acid at $220 \text{ }^\circ\text{C}$ for 30 min. Electrodes (Ti (30 nm)/Pt (30 nm)/Au (100 nm)) were evaporated through a shadow mask with four symmetrically located holes and then annealed at $400 \text{ }^\circ\text{C}$ for 30 min in Ar atmosphere.

3. Results and discussion

3.1. Crystal growth

Table 1 shows the optimized growth conditions for (001) P-doping as compared with the (111) P-doping conditions [9]. The main differences between (001) and (111) conditions are the dilution ratio of methane, $[\text{CH}_4]/[\text{H}_2]$, and gas-phase P concentration, $[\text{PH}_3]/[\text{CH}_4]$. The other conditions are identical between each other. In order to understand the behavior of

Table 1
Growth conditions for (001) and (111) P-doping

Surface orientation	(001)	(111)
Substrate temperature	$900 \text{ }^\circ\text{C}$	$900 \text{ }^\circ\text{C}$
CH_4/H_2 ratio	0.4%	0.05%
PH_3/CH_4 ratio	5%	500 ppm
Gas pressure	25 Torr	25 Torr
Microwave power	750 W	750 W

Table 2

Differences of impurity concentrations between (001) and (111) diamond films grown by same conditions optimized for (111) P-doping

Surface orientation	Impurity concentration [cm^{-3}]		
	P	B	N
(111)	$\sim 2 \times 10^{18}$	$\sim 1 \times 10^{16}$	$\sim 2 \times 10^{17}$
(001)	$< 2 \times 10^{15}$	$< 2 \times 10^{15}$	$< 1 \times 10^{17}$

impurity-doping, P-doping was performed on both (001) and (111) substrates using the (111) growth conditions and each impurity concentration was detected by SIMS analysis as shown in Table 2. On (111) substrate case, P atoms were incorporated to be $\sim 2 \times 10^{18} \text{ cm}^{-3}$, whereas on (001) substrate case P atoms were below the detection limit in SIMS analysis. The other impurities, boron and nitrogen, were also below the detection limit, indicating that growing on (001) diamond with parameters optimized for (111) doping does not result in any detectable incorporation of impurities. Moreover, just increase in $[\text{PH}_3]/[\text{CH}_4]$ ratio under (111) P-doping conditions did not bring (001) P-doping. The process window of P-doping is quite different between (001) and (111) diamond growth.

In case of (001) B-doped diamond [10], it has been reported that the B incorporation ratio strongly depends on $[\text{CH}_4]/[\text{H}_2]$ ratio as well as dopant gas ratio. B incorporation ratio increases with an increase in $[\text{CH}_4]/[\text{H}_2]$ ratio, indicating that the increase is effective in impurity incorporation. On the other hand, the numbers of carbon dangling bonds have been reported to increase with an increase in $[\text{CH}_4]/[\text{H}_2]$ ratio [11]. Since such dangling bonds have been considered to act as compensators of donor atoms [12], they must be suppressed in order to realize the *n*-type control, meaning the decrease in $[\text{CH}_4]/[\text{H}_2]$ ratio. Therefore, the optimization of $[\text{CH}_4]/[\text{H}_2]$ ratio is also important for *n*-type control by P-doping, not only the dopant gas ratio. Based on these phenomena, (001) P-doping conditions have been obtained as shown in Table 1.

From SIMS analysis, P concentration was estimated to be $\sim 2 \times 10^{18} \text{ cm}^{-3}$ on typical (001) P-doped diamond film. The incorporation ratio ($[\text{P}]/[\text{C}]/([\text{PH}_3]/[\text{CH}_4])$) was estimated to be 0.02% for (001) P-doping and was two-orders of magnitude smaller than that for (111) [9], indicating the difficulty of P-doping on (001) surface.

Fig. 1 shows the typical surface morphology of a (001) P-doped diamond film. The step bunching along a specific crystal orientation is clearly observed and the entire surface is covered with the steps. The height of these steps was estimated by atomic force microscopy to be $\sim 60 \text{ nm}$ and the average roughness of each terrace was $\sim 4.8 \text{ nm}$. Partially, the non-epitaxial crystallites and pyramidal hillocks can be found.

The macroscopic crystallinity and surface smoothness were determined by RHEED analysis. The RHEED patterns of hydrogen-terminated surface in the incident electron beam direction of [100] and [110] are shown in Fig. 2(a) and (b), respectively. Both in the [100] and [110] directions, sharp Kikuchi patterns with low back-ground were observed as bulk diffraction effects due to inelastically scattered electrons from the bulk [13]. If the surface is rough, these inelastically scattered electrons can barely pass through to the vacuum from

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