N-type doping on (001)-oriented diamond

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Abstract

Growth of (001) *n*-type diamond by phosphorus doping using microwave plasma-enhanced chemical vapor deposition has been achieved. The detailed growth conditions and procedures are described. The doping efficiency is discussed by secondary ion mass spectroscopy (SIMS) and *n*-type conduction is confirmed using Hall-effect measurement with an AC magnetic field. The crystallinity of (001) *n*-type diamond is evaluated by X-ray diffraction, Raman spectroscopy, reflection high-energy electron diffraction, and cathodoluminescence analysis, indicating that the crystalline perfection is relatively fine. The spatial distribution of impurity incorporation is also discussed using a SIMS mapping technique. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

N-type doping on (001)-oriented diamond has been one of the major issues for the development of diamond-based electronic applications in *p*–*n* junctions such as light-emitting diodes, high-frequency high-power devices, and in unipolar devices such as cold cathode electron-emitters [1–5]. Phosphorus (P) has been considered to be the most promising element, because the fabrication of *n*-type diamond has already been achieved on (111)-oriented diamond by gas-phase P doping during a plasma-enhanced chemical vapor deposition (CVD) process [6]. However, it has been experimentally shown that P incorporation and *n*-type control cannot be achieved when (001)-oriented diamond is used for CVD growth, owing to the lower incorporation efficiency of P atoms and/or hydrogen incorporation as killer centers for P donors.

Generally, a (001)-oriented substrate is desirable for electronic device applications. The (111) surface is known to be quite difficult to polish mechanically, whereas with the (001)

surface it is relatively easy to get a smooth surface. The HTHP (111)-oriented diamond substrates are difficult to produce which makes them expensive and their size is limited to typically $2 \times 2 \times 0.5$ mm^3 at present, causing significant technological problems regarding photolithography, etching, metallization, and throughput. Moreover, the electrical and optical properties of diamond films on (001) substrates are better than those on (111) substrates, e.g. the atomically flat surface and the strong UV emission in non-doped CVD diamond, the Schottky junction property with the ideality-factor of 1.01 in a hydrogen terminated surface, and the highest mobility of 1840 cm^2/V s in B-doped CVD diamond were already achieved in diamond films on (001) substrates [7–9], but not yet in (111) substrates.

From these viewpoints, there has been a strong need for the development of the *n*-type doping technique on (001)-oriented diamond. In 2005, we successfully overcame this difficulty by P doping under well optimized conditions during CVD growth [10], which are quite different conditions for (111) growth. This paper describes our recent achievements in detail, including the procedures and conditions during the CVD growth and the characteristic electrical properties. The crystal perfection of (001) *n*-type diamond has been evaluated using X-ray diffraction (XRD), Raman spectroscopy, reflection high-energy electron diffraction (RHEED), and cathodoluminescence (CL) analysis. The uniformity of impurity incorporation,

especially in hydrogen atoms, is discussed using a SIMS mapping technique.

2. Experimental setup

Homoepitaxial diamond films were grown using a microwave plasma-enhanced CVD reactor consisting of a 6-in. stainless-steel chamber produced by ASTex. The maximum output microwave power was 1.5 kW and the base pressure of the system can be raised to $\sim 5 \times 10^{-9}$ Torr by a turbomolecular pump with an oil-free screw pump. The source gases used were CH_4 (purity: 6 N) diluted with H_2 (9 N) and PH_3 (6 N) diluted with H_2 ($PH_3/H_2 = 5.0\%$, 6 N). The gas flow rate was controlled independently by mass flow controllers. Substrates used were commercially available type-IIa and -Ib diamond crystals with (001)-oriented surface, which were grown by a high-temperature high-pressure synthesis (HTHP) method. The substrate size was $3.0 \times 3.0 \times 0.5$ mm^3 and $2.5 \times 2.5 \times 0.5$ mm^3 for Ib and IIa crystals, respectively. The misorientation angle of all diamond substrates used in this experiment was measured by XRD of the diamond (004) plane peak. The substrate was set on a graphite susceptor with a molybdenum sample holder and heated inductively by a 60 kHz rf generator. Its temperature was controlled by a thermocouple attached to the backside of the susceptor and was kept constant during the CVD growth. The substrate temperature was monitored by an optical pyrometer from the top window through the plasma and was confirmed to be stable. The plasma condition observed by optical emission spectroscopy was also stable during the growth.

The amount of impurities incorporated in the diamond films and the spatial distribution of P atoms were evaluated using secondary-ion mass spectroscopy (SIMS) by MST (Foundation for Promotion of Material Science and Technology of Japan). As a primary ion, Cs^+ accelerated at 14.5 keV was used for P, N, B, and Si atoms, and O_2^+ accelerated at 8.0 keV was used for Cu, Fe, Mo, and W atoms. The concentrations of P, N, and B atoms were quantified using each implanted standard sample. The spatial distribution of hydrogen atoms was determined by a SIMS mapping technique. The scanning ion beam area was 30×30 μm^2 and its resolution was ~ 1 μm^2.

The electrical properties were investigated by Hall-effect measurements (TOYO Co., ResiTest 8300) using the van der Pauw method as a function of temperature from 260 to 1000 K under an AC magnetic field of 0.6 T. As-grown diamond films were treated by an acid mixture (H_2SO_4/HNO_3, 3:1) at ~ 220 °C for 30 min. The electrodes with Ti (30 nm)/Pt (30 nm)/Au (100 nm) were evaporated through a mask with four symmetrically located holes and then annealed at 420 °C for 30 min in Ar atmosphere in order to achieve stable contacts.

The XRD rocking curve measurements were done by a Bede D1 diffractometer system using pure $CuK_{\alpha 1}$ radiation. The two germanium monochromator crystals were operated with the Ge (004) reflection which provides a primary X-ray beam. During the rocking curve measurements the detector with open aperture was set to the diamond (004) Bragg angle. Raman spectra were measured by a conventional system with excitation by the 633 nm line of an He–Ne laser. Cathodoluminescence analyses

were also performed using an experimental setup of a scanning electron microscope with an optical system comprising an ellipsoidal mirror, an optical fiber, and a monochromator equipped with a charge-coupled device array. CL observation was performed with an electron beam of 13 kV and 3 μA, the penetration length of which was estimated to be ~ 1 μm.

Diamond films were grown on Ib substrate with ~ 2 μm for SIMS, electrical, CL, and RHEED measurements and on IIa substrate with large thickness of ~ 15 μm for XRD, Raman, and Electron spin resonance (ESR). The discussion of ESR results will be published elsewhere.

3. Epitaxial growth procedures and growth conditions

Before the CVD growth, all substrates were re-polished to remove the mechanical polishing patterns observed by optical microscope with Nomarski prism, and then cleaned by the following chemical treatments. First, the substrate was boiled in an acid mixture ($H_2SO_4/H_2O_2/H_2O$, 3:1:1) at 220 °C for 15 min to remove organic and metallic contaminations on the surface followed by HF treatment for 5 min to remove SiO_2 and metallic contaminations, and then the substrate was boiled again in SC1 ($NH_4OH/H_2O_2/H_2O$, 1:1:5) at 75 °C for 15 min to remove the particles and organic contaminations. After each chemical treatment, the substrate was rinsed by flowing deionized pure water. The cleaned substrate was then set on a molybdenum holder coated by a diamond layer and put in the CVD system. The chamber was evacuated to below 2×10^{-8} Torr.

For the CVD growth, the three-step growth method was carried out as shown in Table 1. The first step is for surface cleaning and stabilization of the CVD environment (plasma, pressure, temperature, etc.). The second step is for improving the surface of the initial substrate by means of ultra-low CH_4 concentration growth [11]. The third step is the actual CVD diamond growth. This method is useful for obtaining a relatively smooth surface and high quality films with reproducibility. The growth conditions for (001) and (111) *n*-type doping are summarized in Table 1. The main differences between (001) and (111) *n*-type doping are: i) dilution ratio of methane in H_2 (CH_4/H_2 ratio) and ii) gas-phase concentration of P in CH_4/H_2 (PH_3/CH_4 ratio). To achieve (001) impurity doping, it is also important to optimize the $[CH_4]/[H_2]$ ratio, in addition to the dopant gas ratio. It has already been reported that growing on

Table 1
Details of growth conditions and the three-step growth method

	(001) P doping			(111) P doping
	Step 1	Step 2	Step 3	
Substrate temperature [°C]	900	900	900	900
Pressure [Torr]	25	25	25	25
Microwave power [W]	750	750	750	750
Total gas flow [sccm]	400	400	400	400
CH_4/H_2 [%]	0	0.05	0.4	0.05
PH_3/CH_4 [%]	0	0	5.0	0.05
Duration [h]	0.5	0.5	5–30	