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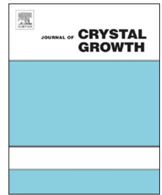

Substrate temperature optimization for heavily-phosphorus-doped diamond films grown on vicinal (001) surfaces using high-power-density microwave-plasma chemical-vapor-deposition

Osamu Maida*, Shuhei Tada, Haruki Nishio, Toshimichi Ito

Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

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A B S T R A C T

We have investigated the growth condition suitable for homoepitaxial diamond growth of phosphorus (P)-doped films on vicinal (001) substrates with a misorientation angle of 5° using the high-power-density microwave-plasma (MWP) chemical-vapor-deposition (CVD). The P-doped layers were grown with H_2-diluted (1%) CH_4 gas containing $P(CH_3)_3$ with P/C ratio of 0.99% at various substrate temperatures ranging from 960 to 1210 °C by using a conventional MWPCVD system with a quartz-tube chamber. It is found from exciton-related cathodoluminescence spectra taken at ≈80 K and secondary ion mass spectrometry profiles that reasonably-high-quality P-doped layers with containing a substantial amount of substitutional P donors were grown on vicinal (001) substrates only at substrate temperatures of ≈1160 °C although the sample surface completely lost the original flatness with a roughness of ≈0.3 nm. This indicates that the suitable process window should be rather narrow for the P-doped diamond homoepitaxial growth on the vicinal (001) substrate using the present MWPCVD with 1% CH_4 source gas and that the crystalline steps should play an important role on the growth process appropriate for the P atom incorporation to substitutional sites.

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1. Introduction

Since diamond has various interesting physical properties such as large bandgap, high carrier mobility, negative electron affinity for hydrogen terminated surfaces and so on, it is expected as a potential material for high-performance electronic devices such as highly sensitive ultraviolet (UV) light detectors [1], UV light emitting diodes [2] and highly efficient electron emitters [3,4]. One of the most important research subjects, before such diamond electronic devices are commercially available, is to develop a relevant doping process especially for *n*-type impurity since the *p*-type doping process with boron (B) atoms has been well developed.

Nowadays, only phosphorus (P) is recognized as the *n*-type dopant available for diamond although the activation energy of P donors (≈0.6 eV) is rather large, compared to the cases of the conventional semiconductors. On one hand, the reliable process for doping P to diamond was first developed for (111)-oriented surfaces which tended to most easily incorporate dopants of all the surface directions in the case of diamond [5]. On the other hand, the growth of *n*-type diamond films on (001) substrates is an essential requirement for actual technological applications [6]. This is because it is more difficult to mechanically polish (111) diamond surface than (001) one [7] while it is easier to obtain higher quality diamond with smoother (001) surfaces, compared to the (111) case. In the case of high-pressure/high-temperature-synthesized (HPHT) single-crystalline diamonds, which are often employed as substrates for homoepitaxial growth using chemical-vapor-deposition (CVD) methods, (111)-oriented substrates with a mirror-polished surface are more expensive than (001)-oriented ones. Furthermore, in the cases of undoped and B-doped diamond films, it is reported that the performance of metal/diamond junction properties as well as electrical and optical properties are indeed better for (001) surfaces than (111) ones [7]. These situations generate some significant technological problems with respect to photolithography, etching, metallization, and throughput. From these view points, therefore, there is a strong need for development of *n*-type doping on (001)-oriented diamond. In 2005, Kato et al. [6] overcame this difficulty in the P doping process by means of a microwave-plasma (MWP) CVD method with a stainless chamber by optimizing the growth conditions for the (001) substrates, which were resultantly quite different from those for the (111) growth. After that they have further improved their P doping process [7,8]. Furthermore, Pinault-Thaury *et al.* have reported advantages of high C/H ratios and high misorientation angles on P-doped diamond MWPCVD growth at 37.5 Torr and 850 °C with C/H mole ratios of 0.25–5 % and vicinal (001) substrates having misorientation angles of 0–5° [9].

* Corresponding author.
E-mail address: maida@eei.eng.osaka-u.ac.jp (O. Maida).

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So far, we have been studying homoepitaxial growth of (001)-oriented diamond films by means of a high-power-density MWPCVD method even with a conventional quartz-tube chamber by operating our growth system in a rather high pressure region of 70–85 Torr at high temperatures of 960–1210 °C, and have reported such effectiveness of employing vicinal (001) substrates as increases in both the growth rate and the B incorporation efficiency under the MWPCVD conditions of high power densities and high temperatures as well as improvement of the electronic quality [10–12]. This indicates that there are at least two suitable MWPCVD growth windows for high quality diamond growth. The two windows include the conventional one with low pressures below ≈ 40 Torr and low temperatures below ≈ 900 °C where most studies on the MWPCVD diamond growth have been performed as well as the high-power-density window that we have successfully developed [1,9,13]. In the case of the P-doped CVD diamond growth under similar high pressures and high temperatures, however, no clear advantages of employing vicinal (001) substrates have been attained yet. It seems that under such growth conditions uniformly heavily P-doped thick diamond films hardly grow without significant degradation of the quality. In the previous work, we found that employing vicinal (001) substrates leaded to an improvement in incorporating P atoms into diamond but that the emission intensity of cathodoluminescence (CL) related to excitons bound to P donors was too low to evaluate the electronic quality. Furthermore, very high electrical resistivities of the P-doped diamond grown at high pressures and high temperatures made it difficult to characterize their electrical property.

In this work, we have successfully optimized the CVD condition employed for the high-power-density MWPCVD process with a quartz-tube chamber to attain advantages of employing vicinal (001) substrates with a rather large misorientaion angle of 5° for homoepitaxial growth of rather heavily P-doped films.

2. Experiments

HPHT Ib vicinal (001) substrates with an approximate size of $3 \times 3 \times 0.3$ mm^3 were used in the present study. The misorientation angle from the [001] direction was $5° \pm 0.3°$ along [110] direction. For comparison, a HPHT Ib (001) substrate (with a misorientation angle $< 0.3°$) was also studied. After a series of cleaning processes [10], an undoped diamond layer with a thickness of ≈ 20 μm was homoepitaxially grown as a buffer layer on the substrate thus cleaned in a stainless steel chamber using a high-power-density MWPCVD method with a source gas of the C/H ratio $= 4.0\%$ [10]. Thereafter, only the vicinal substrate thus grown was divided into nine parts with an approximate size of $1 \times 1 \times 0.3$ mm^3 by means of a laser cut technique in order that the influence of crystalline quality of the HPHT Ib substrate employed on the quality of subsequently deposited film was as identical as possible. Then, the homoepitaxial growth of P-doped layers was performed on one of the cut substrates with a source gas containing P/C mole ratio=0.99% for 3 h at a various substrate temperature, T_s, ranging from 960 to 1210 °C by using a conventional MWPCVD system with a quartz-tube chamber having an inner diameter of 36 mm [10]. In the case of the high-power-density process window for the present apparatus, the T_s variation described above needed changes in both the gas pressure and the input MW power. The source gases used for depositions of undoped buffer and P-doped layers were composed of 7N-purity CH_4 and a 500 ppm hydrogen-diluted $P(CH_3)_3$. The other growth parameters used in the present study are summarized in Table 1.

Table 1
MWPCVD growth conditions employed for homoepitaxial diamond (001) films of an undoped buffer layer grown on a HPHT Ib substrate and P-doped layers grown on the buffer layer.

	Buffer layer	P-doped layer
Growth temperature (°C)	1010	960–1210
Microwave power (W)	3800	220–500
Gas pressure (Torr)	120	70–85
Deposition period (h)	5	3
CH_4/total (%)	4.0	1.0
P/C mole ratio (%)		0.99

A scanning electron microscope with a CL measurement apparatus was employed to measure secondary electron images of the samples, from which the electronic quality of the diamond samples was roughly estimated for their negative electron affinity surfaces [14]. CL spectra were taken at room temperature and low temperatures (≈ 80 K) to characterize the P-doped samples grown. Their surface morphology was characterized by means of a Nomarski-type optical microscope (OM) and an atomic force microscope (AFM) in the air. In order to estimate the amounts of impurities incorporated in the diamond films thus grown, depth profiles of incorporated atoms were obtained using secondary ion mass spectrometry (SIMS) from a specially fabricated homoepitaxial sample composed of P-doped, undoped and P-doped layers which were grown on an undoped buffer layer first at ≈ 1160 °C for 6 h (in total), then at ≈ 1010 °C for 20 min, and finally at ≈ 1010 °C for 3 h, respectively, under the otherwise conditions listed in Table 1.

3. Results and discussion

Fig. 1(a) shows a typical OM image taken after the homoepitaxial growth of P-doped layers at the growth temperature of 1010 °C on a "just" (001) substrate having no substantial misorientation angle ($< \approx 0.3°$). There were innumerable pyramid-like hillocks with various sizes, which were often observed in the case of heavily P-doped CVD samples grown on "just" (001) substrates and which

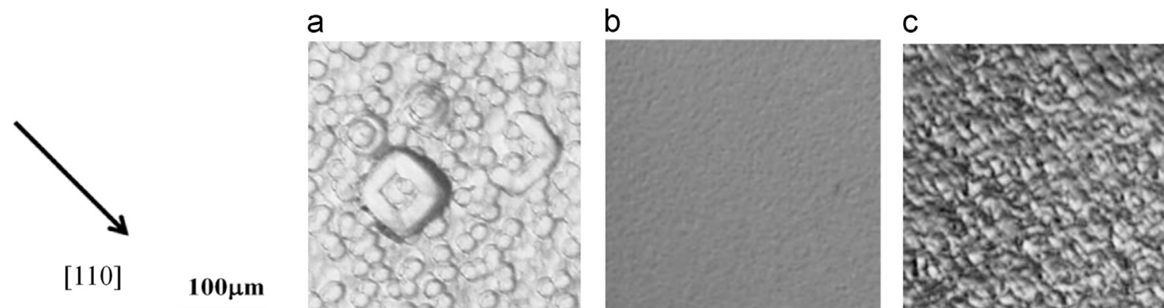

Fig. 1. Typical optical microscope images taken for P-doped layers homoepitaxially grown on a HPHT Ib (001) substrate (a) with no substantial misorientation angle and (b) and (c) with a vicinal (001) surface having an off-angle of 5° along [110] direction. The growth temperatures were (a) 1010 °C, (b) 1010 °C and (c) 1160 °C. In all the cases, an undoped buffer layer was homoepitaxially grown for 5 h before the P-doped layer growth. The arrow denotes the [110] direction of each sample.

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