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Device Grade Homoepitaxial Diamond Thin Films Grown by Step-Flow Mode

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High quality homoepitaxial diamond thin films were obtained with step-flow growth by microwave plasma chemical vapor deposition in the presence of CH_4 lower than 0.15 % diluted by H_2. These films showed atomically flat surface and excitonic emission (5.27 eV) at room temperature that was related to the wide band-gap of diamond (5.45 eV). The atomic force microscopy observation revealed that these films had bi-atomic layer steps without any unepitaxial crystallites in the whole area of 4 × 4 mm^2 Ib (001) synthetic diamond substrates, whose terrace width depended on the off-angle of each substrate. The hydrogenated atomically flat diamond thin films, which behaved as p-type semiconductors, realized ideal Schottky junction properties by means of Al deposition. These results indicated that device grade diamond thin films were grown by step-flow mode. The key to obtain such an ideal diamond thin films was growth rate lower than 30 nm/h, which was much lower than conventional one.
Key words: diamond, step-flow, atomically flat, excitonic emission, growth rate

1. INTRODUCTION

Diamond is generally recognized as an insulating material. Once successfully doped, however, it is a wide band-gap semiconductor with excellent potential due to the unique combination of its physical and electronic properties, such as high breakdown voltage, high thermal conductivity, small dielectric constant, and radiation hardness [1]. These diamond features are useful to high power, high temperature and high frequency, in short high stability in harsh environment, device applications. To achieve these goals, first, ideal diamond bulk or thin films are necessary.

In natural diamond the donor/acceptor concentration can be measured [2] but not controlled. The development of a high pressure, high temperature (HPHT) method of near-equilibrium diamond synthesis provided the first opportunity for control of diamond defects. However, impurities from the catalysts essential to the economic production of the synthetic crystals provide another source of compensation. Chemical vapor deposition (CVD) is used for the growth of many diamond films. However, normally trials of the CVD diamond growth were based on heteroepitaxy in which high amount of carbon source was necessary for the first nucleation. According to this tendency, the studies of diamond film growth by CVD concentrated to the high-growth rate even for the homoepitaxy. This results in including non-diamond phase, undesirable impurities and unepitaxial crystallites (UCs) in the grown diamond films as shown in Fig.1. To eliminate such UCs, another efforts by means of oxygen or boron incorporation into CVD process were performed, or vicinal diamond substrates were used. These kinds of approach realized to get wide smooth surface at the resolution of the optical microscopy and secondary electron microscopy (SEM), and to achieve Schottky diodes and field-emission transistors (FET) on hydrogenated CVD diamond surfaces, while optical and electrical properties could not achieve ideal diamond ones [3-5]. Because of such a wide band-gap of diamond as 5.45 eV, it is basically too difficult to reduce all undesirable defect levels.

Under these circumstances, we started growth and characterization of homoepitaxial diamond thin films with such a concept as obtaining ideal pure ones [6-9]. Recently, we reported the step-flow growth of diamond films on synthetic Ib diamond (001) substrates using microwave plasma CVD system under a concept of clean epitaxy [7,9] and with growth rate much lower than the conventional one [10]. The source gas was pure CH_4 diluted by H_2 because of simple chemical system for any discussion about both growth mechanism and electric properties. As a result, we succeeded to obtain atomically flat diamond thin films, and to show ideal diamond properties of both optical and electrical properties by means of cathodoluminescence (CL) and current-voltage (I-V) measurement of Schottky diode.

2. EXPERIMENTAL

The diamond growth experiments were carried out using a microwave plasma assisted CVD reactor equipped with a temperature-controllable substrate holder by a 60 kHz rf induction heating system. The system enables us to control the substrate temperature and the microwave power independently. Stainless chamber wall is used in this system to avoid Si contamination incorporated into deposited diamond films [6].

Table.1 Growth conditions for homoepitaxial diamond thin film growth. Deposition time was varied to obtain enough film thickness to investigate each measurement. They were in the range of from 0.17 to 2 μm.

Gas-flow rate [sccm]	400
CH_4 [%]	from 0.016 to 2.0
Pressure [Torr]	25
Background pressure [Torr]	$3x10^{-7}$
Substrate temperature [°C]	800
Microwave power [W]	750

The diamond films were deposited on HPHT Ib diamond (001) substrates with dimensions of 4×4×0.3 mm^3. Conditions for the diamond film growth are shown in Table 1. In the presence of 0.016% to 2.0% CH_4 diluted with H_2 gas, diamond thin films were synthesized. Gas pressure, total gas flow rate, substrate temperature, microwave power were 25 Torr, 400 sccm, 800 °C and 750 W, respectively. Deposition time was set to get enough thickness to measure CL and Schottky junction properties. All of the diamond substrates in this experiment have lower off-angles than 2°, which were measured by X-ray diffraction method with diamond (004) plane peak. According to previous reports ([4,11-14]), an effect of these off-angles on macroscopic morphology can be negligible at low CH_4 concentration growth in this paper.

After growing the homoepitaxial diamond thin films, optical microscopy and atomic force microscopy (AFM) were used to investigate the surface morphology, and the density of UCs. Transmission electron microscopy (TEM) was used to confirm origin and structure of UCs.

3. RESULTS AND DISCUSSION

Figure 1 shows one of the typical UCs that appears from very early stage of CVD growth in the presence of CH_4 higher than 0.15%. During the CVD deposition, these UCs grow and induce defects in the film as shown in Fig.2. When the presence of CH_4 became lower than 0.15%, such UCs disappeared and the surface smoothened. Especially when the presence of CH_4 became lower than 0.025%, the atomic level steps of diamond (001) plane could be observed by AFM as shown in Fig.3. Each terrace width in this figure corresponds to a relation between off-angle of 0.4° and step height of bi-atomic layer of (001) diamond plane. Surface roughness drastically decreased with a few hundred nano-meter thickness. These improvements of surface morphology could be controlled by the presence of CH_4, and we considered the growth rate was important.

When the presence of CH_4 became higher than 0.15%, some diamond films with more than 1 μm thickness showed bunching morphology on the substrate whose off-angles were lower than 3° [9,11-14]. In addition we got atomic smooth surface as shown in Fig.3 in the presence of CH_4 lower than 0.15%. These indicate that the diamond films were grown by step-flow mode.

The relation between CH_4 concentration and growth rate is shown in Fig.4. The inserted figure, enlarging of the low CH_4 concentration region, depicts that the

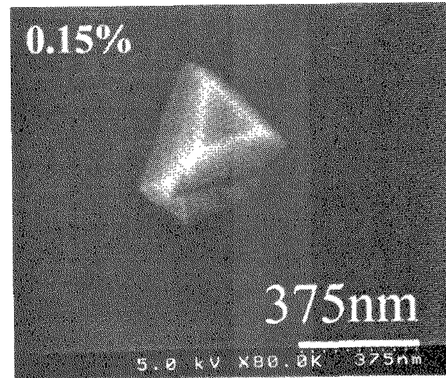

Fig.1 A field emission SEM image of one of the typical UCs that appear from very early stage of CVD growth in the presence of CH_4 higher than 0.15%.

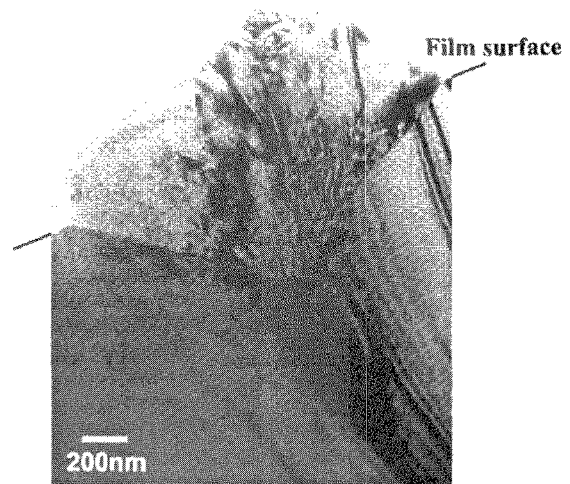

Fig.2 A cross sectional TEM image of one of the typical UCs. Boundaries between the UC and epitaxial film region include dislocations

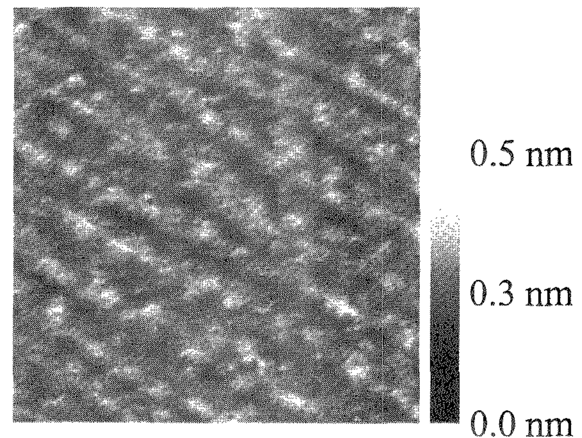

Fig.3 An AFM image of (001) plane of the CVD diamond thin film grown in the presence of 0.025% CH_4 for 42 hours.

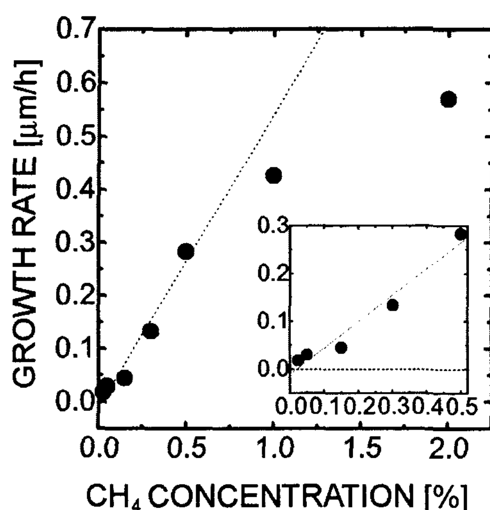

Fig.4 The relation between CH_4 concentration and growth rate. The inserted figure, enlarging of the low CH_4 concentration region, depicts the growth rate becomes negative at CH_4 concentration = 0, which indicates etching by H_2 plasma.

growth rate becomes negative at CH_4 concentration = 0, which indicates etching by H_2 plasma. Actually H_2 plasma etched diamond. The atomically flat diamond surface as shown in Fig.3 could be obtained with the growth late lower than a few tens nano-meter per hour (around CH_4/H_2<0.15%, the growth rate was about 30 nm/h), which was close to the one of molecular beam epitaxy (MBE). In addition, H_2 plasma has strong etching effect on graphic carbon phase [15,16]. Although the substrate temperature was too low with comparing the equilibrium condition of diamond phase, we believe that quasi-equilibrium diamond growth condition on diamond substrate was realized under such strict growth condition of diamond films.

Figure 5 shows the dependence of normalized intensity of excitonic emission (5.27 eV) on CH_4 concentration. CL spectra from grown diamond films were measured at room temperature [17,18]. Normalization was performed with considering both film thickness and the volume activated by electron beam injection. The excitonic emission directly corresponds to the band-gap of diamond, and emission at room temperature indicates that there are no visible and invisible localized states between the band-gap. In short, this indicates the high quality diamond. As shown in Fig.5, the intensity of excitonic emission increased when CH_4 concentration decreased. Thus, synthetic diamond films with ultra-low growth rate have few amounts of defects.

When diamond was exposed to hydrogen plasma, hydrogen-accumulated layer was induced near its surface region [19-23]. It shows p-type semiconducting properties. As-grown diamond thin films have also such a p-type surface semiconductive layer so that Schottky junction is realized by metal deposition when the work function of metal is small enough than that of p-type layer of diamond surface region. Al films deposited on an as-grown diamond surface were used as Schottky electrodes.

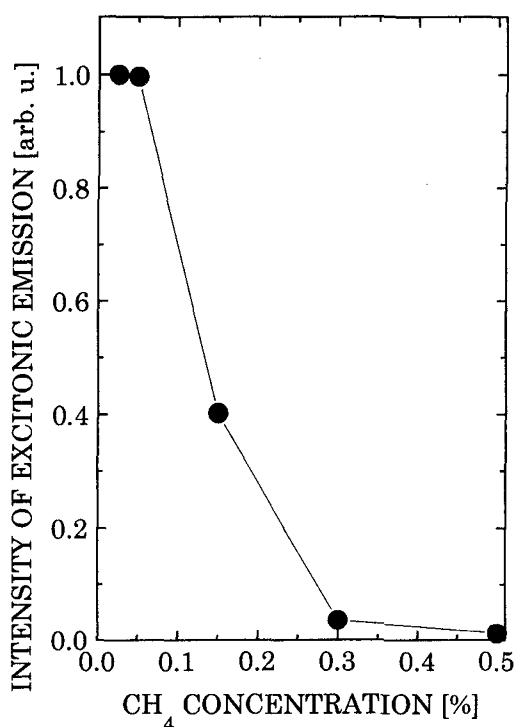

Fig.5 The dependence of normalized intensity of excitonic emission from grown diamond thin films at room temperature on CH_4 concentration.

Figure 6 shows the electrical properties of the Al-Schottky diodes on diamond films grown in the various presence of CH_4. All of them show non-symmetric I-V curves between forward and reverse biases, while the ideal factor of diode and reverse leakage current become well with lowering the CH_4 concentration. In addition, the diamond film grown in the presence of 0.016% CH_4, 42 electrodes in the 43 total ones on the film surface showed excellent Schottky properties as shown in this figure. This result well-corresponds to the ones of surface morphology and CL.

4. CONCLUSIONS

Homoepitaxial diamond thin films were grown by microwave plasma CVD with ultra-low growth rate. They showed atomically flat, unepitaxial crystallites (UCs) free surfaces, and strong ultraviolet excitonic emission at room temperature. These properties realized ideal Al Schottky contacts on hydrogenated diamond surfaces. The key parameter to obtain such an ideal diamond film was growth rate lower than several tens nano-meter per hour (< 30 nm/h), and this result in enhancing the step-flow growth mode.

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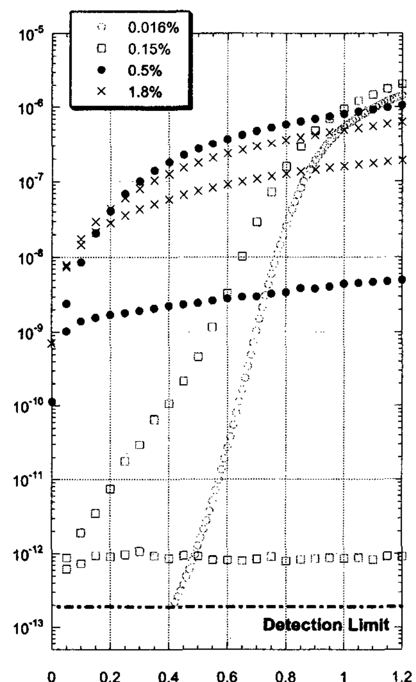

Fig.6 The electrical properties of the Al-Schottky diodes on diamond films grown in the various presence of CH_4.

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