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Ultrapure diamond growth by chemical vapor deposition

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Abstract

Defect formation during diamond homoepitaxial growth was sufficiently inhibited by adding oxygen simultaneously in the growth ambient with high concentration of 2 %. A 30-μm thick homoepitaxial diamond film with surface roughness of <15 nm was obtained with reasonable growth rate of approx. 3 μm h^{-1} by optimizing the growth condition. Concentration of substitutional nitrogen in the homoepitaxial diamond (100) films was less than 1 ppb.

1. Introduction

In this decade, studies on semiconducting diamond for the power device application have intensively been conducted in several research groups. Here, a use of diamond crystals with low defect density is crucial for obtaining high blocking voltage. In addition, precise control of impurities especially in the lower concentration range is essential for *i*-layer formation of diamond pin structure. High crystalline quality and high purity of diamond crystals are also requested in the field of research on quantum information using diamond. Here, the number density of color centers has to be controlled in the range of <1 ppb to be single photon sources. For this reason, the impurity concentration of diamond should be much less than ppb range.

Although a lot of effort was devoted to improve the quality of diamond films [1], localized defects still remain in the crystals with the number density higher than 10^4 cm^{-2}. Some of the defects in the homoepitaxial layers originate from the surface defects of the substrates that were mainly introduced during a mechanical polishing process. These polishing defects can be removed by applying oxygen plasma etching. Etching rate at the defective area is faster compared to the surrounding area with better crystalline quality. Thus, drawback of this oxygen plasma etching is roughening of substrate surface due to its anisotropic etching.

Here, we propose advanced diamond growth condition that removes crystalline defects effectively during the growth process of homoepitaxial diamond films. Essential point of this condition is oxygen addition in the source gas with rather high concentration, which was 2 % to the total flow rate in the present case. Growth feature of the homoepitaxial diamond (100) films in the high oxygen concentration condition is discussed.

2. Experimental

(100)-oriented HPHT grown type-Ib crystals were used as substrates. Dimension of these substrates is 3.0×3.0×0.5 mm^3. Surfaces of the mirror-polished (100) substrate were tilted into the [110] crystallographic direction by 3 degree to obtain better surface flatness of homoepitaxial diamond films. Homoepitaxial diamond (100) films were deposited on these substrates using the homebuilt microwave plasma-assisted chemical-vapor-deposition (MPCVD) apparatus [2]. Configuration of the MPCVD apparatus has been described elsewhere.

In this study, two different source gas compositions, either oxygen addition during growth or not, were applied for homoepitaxial diamond (100) film growth. The diamond sample named S1 was grown on a type-Ib substrate under the following condition; total gas pressure, microwave power, methane concentration (flow ratio of CH_4 to the total gas flow), oxygen concentration (flow ratio of O_2 to the total gas flow), and substrate temperature were 120 Torr, 1.4 kW, 10 %, 2 %, and 1000±10 °C, respectively. Higher methane concentration of 10 % was necessary to obtain reasonably-high growth rate of >1 μm h^{-1} under the high oxygen concentration of 2 %. The diamond sample named S2 was grown on a type-Ib substrate under the following condition; the total gas pressure, microwave power, methane concentration, oxygen concentration and substrate temperature employed were 120 Torr, 1.4 kW, 4 %, 0 %, and 960±10 °C, respectively. Diamond film was grown for 10 hr. Microwave power density estimated from the injected microwave power divided by the plasma volume was ~50 W cm^{-3}.

3. Results and Discussion

Figures 1 (a) and (b) show optical microscope images of the diamond surfaces. Homoepitaxial diamond surface of the sample S1 was flat without any non-epitaxial crystallites even after the thicker diamond layer growth of ~30 μm. On the other hand, the polishing defects became obvious for the sample S2. In addition, non-epitaxial crystallites embedded in a homoepitaxial diamond film appeared on the surface of the sample S2 after the 10 hr growth. In this condition with no oxygen addition, top surface of molybdenum sample holder was covered by polycrystalline diamond through the long-time diamond growth process and part of the polycrystalline diamond layer on the holder was confirmed to be peeled. The formation process of non-epitaxial crystallites on the homoepitaxial film is de-

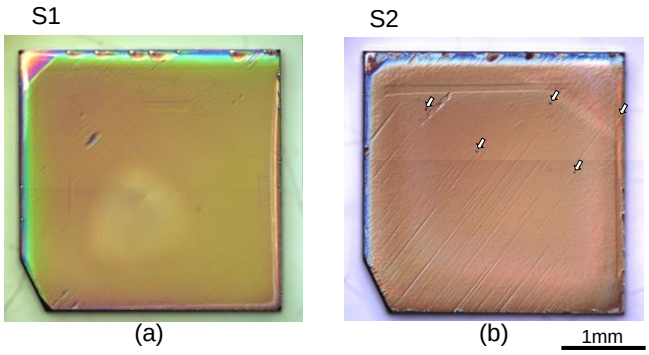

Fig. 1 Optical microscope images of homoepitaxial diamond film samples S1 and S2

duced as follows; at first diamond micro crystal grains are created on the molybdenum holder. Some of them are peeled from the holder and then jumped on the homoepitaxial layer during diamond growth process. Finally, they become a seed of non-epitaxial crystallites on the homoepitaxial diamond film and continue to grow until growth process finish. In contrast to the case of the sample S2 growth with no oxygen addition, polycrystalline diamond growth on the holder was negligibly small after the sample S1 growth with oxygen addition. This fact indicates that oxygen addition is effective to suppress the nucleation of diamond particles on the molybdenum holder.

Figures 2(a) and 2(b) show CL images for the sample S1 and S2 respectively taken at the monochromator wavelength of 235 nm. This luminescence originates from the free exciton (FE) recombination. As shown in Fig. 2(b), characteristic line-shape non-emission pattern was observed from the sample S2. This pattern resembles the linear morphology shown in Fig. 1(b), meaning that defects are formed along the polishing lines. This line-shape luminescence pattern was not observed from the sample S1, which is consistent with flat homoepitaxial film surface.

Since Ib (100) substrates used for the samples S1 and S2 were processed with equivalent polishing conditions, this result indicate an oxygen addition with high concentration is effective to remove defects localized near the surface such as polishing defects. Oxygen plasma etching or hydrogen/oxygen mixture plasma etching are basically anisotropic etching process. It means that substrate surfaces after these etching processes become much rougher than the original ones. As a result, it is not easy to obtain homoepitaxial diamond films with better flatness when surfaces of diamond substrates are processed by the oxygen-plasma etching, especially in the case of longtime process.

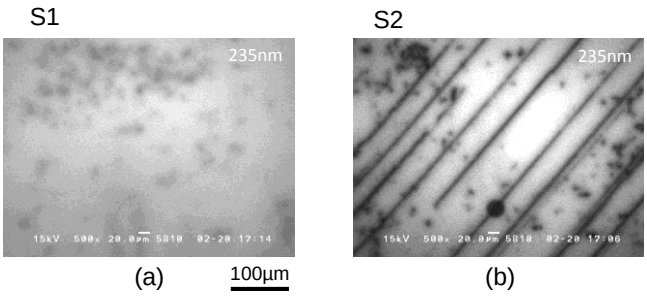

Fig. 2 Cathodoluminescence images of samples S1 and S2 taken at 300 K. The wavelength of 235 nm corresponds to the free-exciton recombination luminescence.

The results shown above indicate the homoepitaxial diamond growth with oxygen addition in high concentration under high microwave power condition shows unique growth mode combining both removal of substrate originating defects and lateral growth for flat homoepitaxial film formation. Optimization of methane concentration is indispensable, 10 % in the case of this study, for enhancing lateral growth. By utilizing this process, process systems for diamond growth and for diamond etching are not required to equip independently.

Secondary ion mass spectrometry (SIMS) measurement reveals that amount of hydrogen, nitrogen, boron and silicon was below detection limit. Concentration of nitrogen in substitutional site in diamond lattice was estimated to be less than 1 ppb by electron spin resonance [3]. Observation of NV centers in the homoepitaxial film of the sample S1 was carried out by using a confocal photoluminescence set-up, no NV centers were detected. These results indicated that the nitrogen concentration in diamond films were extremely lower level.

4. Conclusions

Homoepitaxial diamond (100) films were grown under the oxygen additive condition with high concentration of 2 %. Growth rate of 3 μm h^{-1} was achieved by increasing methane concentration up to 10 % and applied higher microwave power density condition of approx. 50 W cm^{-3}. Due to a simultaneous process of growth and etching, defect formation in the diamond films was minimized and flat diamond surface was obtained after 30 μm growth. Diamond films have high chemical purity, as evidenced by no detection of impurity elements by SIMS. High quality and high purity diamond films will open up new possibility for diamond-based optical and electronic devices.

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References

[1] T. Teraji, Phys. Stat. Sol. (a) **203** (2006) 3324.
[2] T. Teraji et al, Jpn. J. Appl. Phys. **51** (2012) 090104.
[3] T. Teraji et al, Appl. Phys. Exp. **6** (2013) 055601.