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Selective growth of diamond thin film employing yttria-stabilized zirconia thin film mask

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Selectively grown polycrystalline and homoepitaxial diamond thin films were fabricated by using a novel process employing yttria-stabilized zirconia (YSZ) as a thin film mask. The diamond deposition was carried out by electron-cyclotron resonance microwave plasma-assisted chemical vapor deposition with (CO, B_2H_6)/H_2 as the gas source. Spatial distribution of the morphology of the selectively grown diamond films was observed and it indicates migration of the growth species on YSZ film mask. By making full use of the selective growth technique, selectively grown trilayered epitaxial diamond film, which consist of boron-doped (entirely), undoped (selectively) and boron-doped (selectively) layers, has been accomplished. Visible luminescence from each of the layers grown on the same substrate has been investigated for the first time by cathodoluminescence.

1. INTRODUCTION

To deposit diamond selectively in a pattern is an essential technique to make diamond electronic devices, and its realization itself is concerned with the mechanism of diamond nucleation, so it is of importance to study the selective growth method and to evaluate the selectively grown films. Meanwhile, considering that it is hard to product n-type semiconducting diamond with good electrical conductivity at present, it is also important to investigate multi-layered structures consisting of boron-doped and undoped diamond films for realization of diamond unipolar-devices [1]. In this paper, we show diamond can grow selectively by using a new selective growth technique employing a yttria-stabilized zirconia (YSZ) film mask and evaluate the selectively grown polycrystalline and homoepitaxial diamond films. In order to make further investigations into the multi-layered structure, a selectively grown p-i-p epitaxial trilayered structure has been made and its crystallinity was examined.

2. EXPERIMENTAL

In this present study, we adopted YSZ material as the selective film mask, since from our research, diamond cannot nucleate on a YSZ crystal [2]. The procedure of making a YSZ thin film mask for diamond selective growth is as follows. As the substrates, Si (100) and synthetic type-Ib diamond single crystals (100) were used. For the Si substrate, the surface was scratched beforehand by diamond powder using an ultrasonic method. A Photoresist was patterned on the substrates by a photolithographic method. YSZ was then deposited using an rf-diode sputtering deposition technique in an atmosphere of Ar at a pressure of 7.5×10^{-2} Torr. As a target, 6 mol % Y_2O_3 and 94 mol % ZrO_2 of YSZ ceramic powder was used. The substrate temperature was about 60 °C, where YSZ film was formed as an amorphous phase, during sputtering. Then the YSZ thin film was lifted off in acetone.

Diamond deposition on the substrates patterned by YSZ thin film was carried out using electron-cyclotron resonance microwave plasma assisted chemical vapor deposition (CVD) apparatus [3]. The CVD gas, which was a mixture of H_2, CO and B_2H_6 was introduced into the system. The flow rates of H_2, CO and B_2H_6 (100 ppm, diluted by H_2) were 220 sccm, 12 sccm and 0 or 48 sccm (B/C=800 ppm), respectively. The total pressure during the deposition was 0.6 Torr. The input microwave (2.45 GHz) power was 2.1 kW. The sample was heated to a temperature of ~800 °C and electrically biased at 70 V. Deposition was carried out for 3-7 h (1-3 μm thickness).

The surface morphology of the selectively grown diamond thin films were studied by scanning electron microscope (SEM). The selectively grown homoepitaxial films were characterized by reflection high-energy electron diffraction (RHEED) technique and cathodeluminescence (CL) measurement.

3. RESULTS AND DISCUSSION

Figure 1 shows an SEM image of a selectively grown polycrystalline diamond film. The selectivity of the diamond deposition is very high, that is, the YSZ films offered a good masking effect. Its masking effect may be caused by the etching of the YSZ film by the plasma during diamond CVD.

Figure 2 shows an SEM image of a selectively grown homoepitaxial diamond film. Its RHEED pattern (Fig.3) indicates that the film has good crystallinity. However, surface roughness, which may be caused by polishing traces of the substrate,

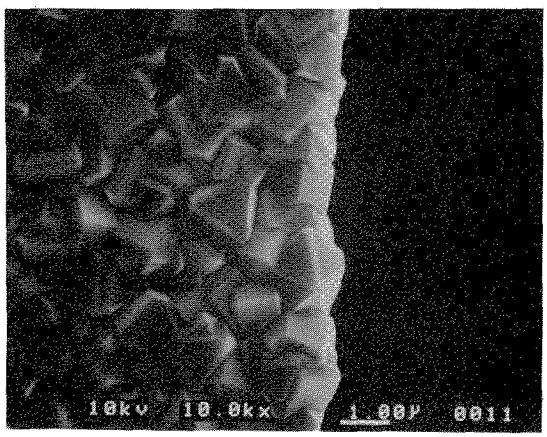

Figure 1. SEM image of selectively grown polycrystalline diamond film.

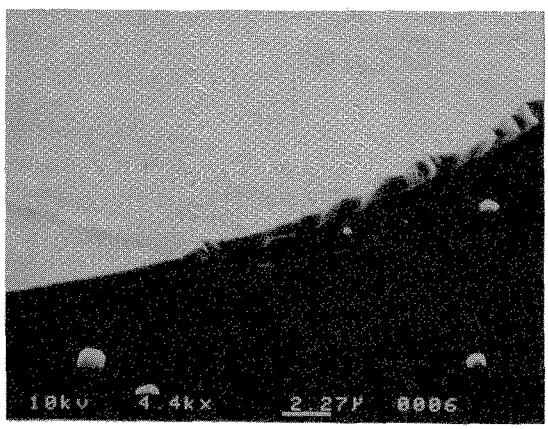

Figure 2. SEM image of selectively grown homoepitaxial diamond film.

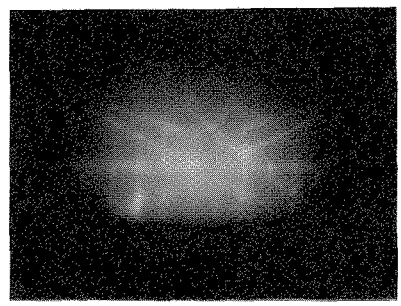

Figure 3. RHEED pattern of selectively grown homoepitaxial diamond film. 25 keV.

was observed and it also affected the edge face morphologies of selectively grown diamond film (Fig.2).

In these well-faceted samples, the morphology of the edge part and that of the center part are similar. But in the sample having poorer morphology, differences were revealed. In Fig.4, the edge part grain size of the selectively grown polycrystalline diamond film is rather large and its morphology significantly degraded as compared with the center part. The spatial distribution can also be seen in the selectively grown homoepitaxial diamond films. Figure 5(a) shows an SEM image of a selectively grown homoepitaxial diamond film which has secondary nucleations on the surface. (The grain growth on the surface of epitaxial diamond (100) films was occasionally observed at lower source gas

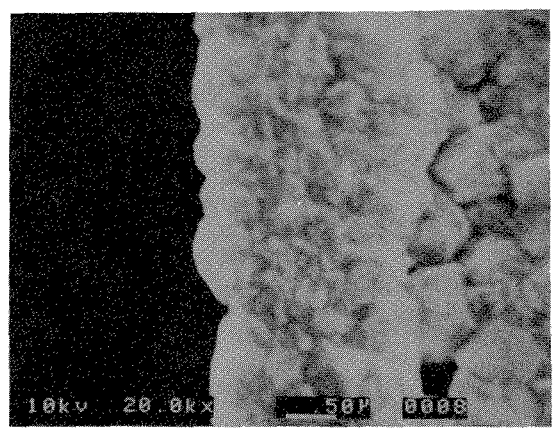

Figure 4. SEM image of selectively grown polycrystalline diamond film.

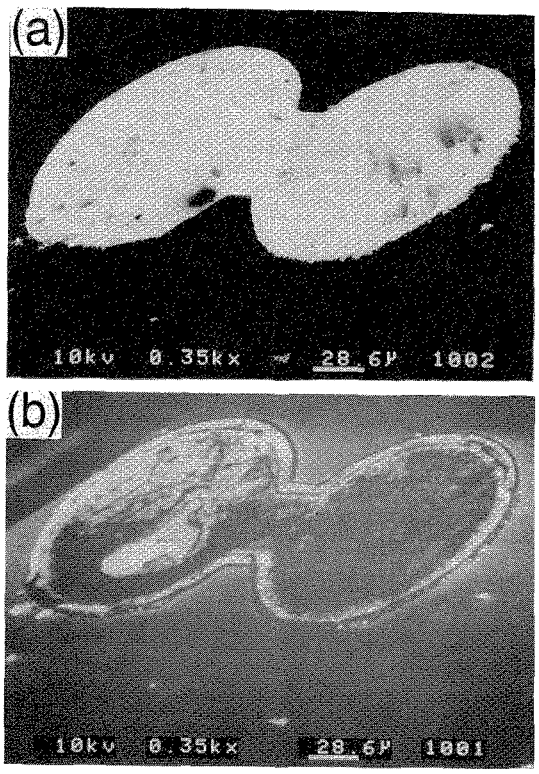

Figure 5. (a) SEM image of selectively grown homoepitaxial diamond film. (b) CL image corresponding to (a). 10 keV.

content than the optimum one [4].) Figure 5(b) shows the corresponding CL image, which is formed by the total emission signal from the sample. The CL image represents nonuniformity [5] of its emission pattern and the emission is relatively bright at the edge part.

The spatial distribution in the morphology and the nonuniformity of the CL image can be well explained if we postulate the migration of the growth species on YSZ film mask during deposition: If the migration on the mask film occurs during deposition, it follows that the source gas content of the edge part becomes effectively higher than that of the center part. In the former case, considering this supposition in connection with the well-known relationship between the CVD diamond film morphology and reactant source gas content [6], at higher source gas content than the optimum one, the facet shape of the diamond disappears, resulting in ball-shaped grain growth. In the latter case, although a number of nonradiative recombination centers were caused by defects in the film since the film was grown at lower source gas content, they are reduced at the edge part where the source gas content is relatively higher due to the migration of the growth species.

For further investigation into the selectively grown diamond films and the multi-layered structure, we tried to make a selectively grown p-i-p epitaxial trilayered structure by making full use of the selective growth technique. A schematic drawing of the structure is shown in Fig.6. The unique feature of this specimen is that it has the hybrid structure, which consists of boron-doped: B/C=800 ppm (entirely), undoped (selectively) and boron-doped: B/C=800 ppm (selectively) layers, on the same substrate: type-Ib diamond single crystals (100). (Each layer was deposited for 3 h, which corresponds

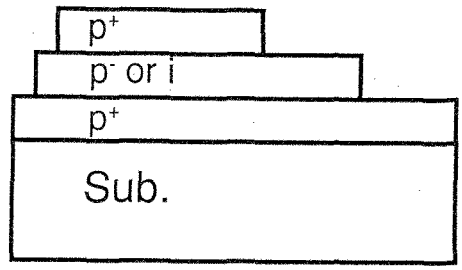

Figure 6. Schematic drawing of selectively grown p-i-p epitaxial trilayered structure.

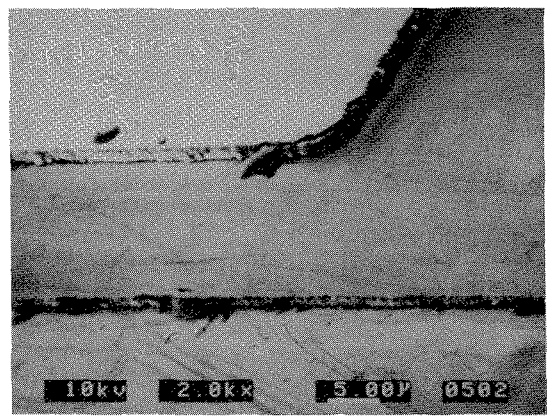

Figure 7. SEM image of selectively grown p-i-p epitaxial diamond trilayered structure.

to approximately 1.0 μm thickness.) Its structure is quite useful to evaluate the homoepitaxial diamond multi-layered structure by using the CL measurements, because the information of the inner layer can be obtained directly.

An SEM image of the trilayered structure is shown in Fig.7. The figure shows a good selectivity of the trilayered structure and that the surface of each selectively grown epitaxial layer was flat and smooth. Figure 8 shows the CL spectra of boron-doped (entirely), undoped (selectively) and boron-doped (selectively) epitaxial films grown on the one substrate. In the entirely deposited p^+-layer, the emission peak appears at 550 nm, but in the selectively grown p^+-layer, the emission spectrum becomes broader at low energy side. In the selectively deposited i-layer, another luminescent peak appears around 480 nm in addition. These spectra shown in Fig.8 are the spectra which are usually interpreted as "band-A" luminescence [7].

Kawarada et al. reported the CL spectra from polycrystalline CVD diamond. They found that in the undoped sample where the content of nitrogen and boron was greatly reduced the CL peak occurred at ~440 nm, whereas in the boron-doped sample another peak appeared at ~530 nm in addition [8].

According to the above findings, our observed spectra, relatively lower energy emission, suggests

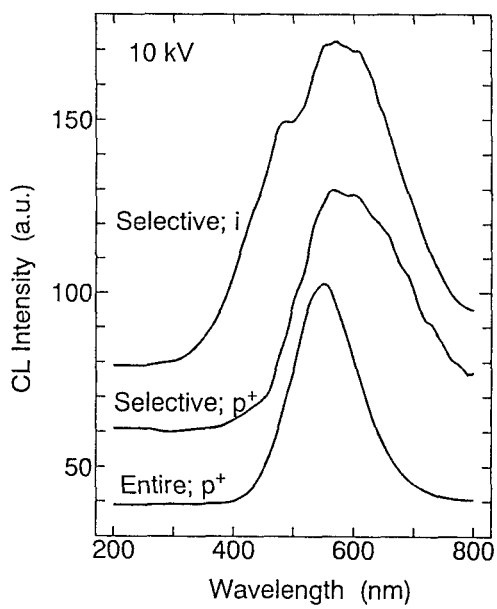

Figure 8. CL spectra of each of the layers on the specimen in Fig. 7. 10 keV.

nitrogen incorporation in the diamond film [9]. The broadening of the spectrum at low energy side in the selectively grown p^+-layer indicates the films suffers from local stress created by structural defects. The spectrum of the inner layer of undoped diamond may be influenced by the boron-doped layers which pinch it.

4. CONCLUSIONS

We have fabricated selectively grown polycrystalline and homoepitaxial diamond thin films by using a novel process employing YSZ as a thin film mask. The YSZ films showed a good masking effect. The spatial distribution of the morphology of the polycrystalline diamond films and the nonuniformity of CL image of the homoepitaxial diamond films were observed. They were an indication of the migration effect of the growth species on YSZ film mask during diamond growth. CL spectra of boron-doped (entirely), undoped (selectively) and boron-doped (selectively) epitaxial films grown on the one substrate were investigated for the first time owing to full use of the selective growth technique.

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