マイクロ波プラズマによるダイヤモンド膜の合成と応用

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Diamond films were synthesized by microwave plasma-assisted chemical vapor deposition (CVD) to investigate the possibility of controlling the film morphology by changing the CVD conditions and the CVD reactors. It was found that the film morphology was strongly influenced by the CVD conditions and reactors. In terms of the film area, it is now possible to deposit diamond films over a 6-inch area using a 60-kW, 915-MHz reactor. There are a number of applications for diamond films, and particularly, heteroepitaxial films were found to be very useful for practical applications such as UV sensors.

1. Introduction

The diamond film technology has advanced significantly during the past 5 years or so, partly because of the use of semi-production type CVD reactors that can generate a large plasma using the 915 MHz microwave with the input power of 60 -100 kW. As a result, a uniform diamond film deposition over a 6-inch area became possible. This is a remarkable advancement from the past technology where 2.45-GHz, ≤ 8 -kW reactors were use to coat diamond films over 2 - 3 inch areas. For diamond film production, it is necessary to investigate to what degree the film morphology can be controlled by the large reactor to synthesize the best film for a specific application. As a topic for such applications, a recent development of UV sensors will be presented.

2. CVD Reactor and Film Morphology

The reactor used is shown in Fig. 1. It is normally operated under conditions of (source gas: c) 1-5% CH₄/H₂, (gas flow rate) 2000 sccm, (gas pressure: *P*) 60 – 200 Torr, and (substrate temperature: T_s) 800 - 1200 °C. The growth rate is 1 – 10 µm/h, but generally, the film quality is better for a low growth rate. Under standard CVD conditions with a standard substrate pretreatment, a polycrystalline diamond film was deposited on the substrate, where the orientations of the diamond grains in the film are random. The grain size depends on the growth time and the input power P_m , and normally 5 – 10 µm.

To investigate the film morphology, CH_4+CO_2 / H_2 was used as the source gas. The reason for the addition of CO_2 is that in a precedent study using CH₄/H₂ as the source gas, the film morphology was not satisfactorily controlled. Note that the film morphology is expressed by the α -parameter that is defined by $\alpha = \sqrt{3} (v_{111}/v_{100})$, [1] where v_{111} and v_{100} are the growth rate of (111) and (100) faces of diamond along the direction normal to each face, respectively. The α -parameter normally takes a value between 1 and 3, and Fig. 2 shows the correspondence between the α -values and the diamond crystal shapes.



Fig. 1. 915-MHz microwave plasma CVD reactor for diamond film synthesis. It can coat a film over a 6-inch substrate.



Fig. 2. The α -parameter and the crystal shape. [1]

Figure 3 shows the film morphology achieved by using the source gas, CH_4+CO_2/H_2 , [2] and the numbers in the figure are the α -values. The SEM images, a - d, correspond to the surfaces of the films synthesized under conditions indicated by a d in the figure, respectively. To express the "effective" carbon concentration, C^* , it is defined by $C^* = [c(CH_4) - c(CO_2)]/[c(CH_4) - c(CO_2) +$ $c(H_2)$], where c(X) is the vol% of molecule X in the source gas. For $C^* < 0$, no diamond was deposited. It was thus found that by using CH_4+CO_2/H_2 as the source gas, the α -values was attained not only between 1 and 3 but also beyond this range by changing C^* and T_s . Based on the data, it was possible to grow uniaxially <100>-oriented diamond film over a 6-inch substrate.



Fig. 3. Morphology of the films synthesized by the reactor shown in Fig. 1. [2]

3. Diamond UV sensors

Diamond has a large bandgap of 5.45 eV so that it exhibits a photoconductivity to the light with the wavelength $\lambda \leq 220$ nm, deep ultraviolet (UV). Recently, a UV sensor was made using a highly oriented diamond (HOD) film, in which (100) faces of diamond are parallel to the film surface and azimuthally aligned in the same direction. [3] On the surface of the HOD film, interdigited electrodes of Pt was fabricated with the gap length of 5 - 10µm. Figure 4 shows the photoresponse of the fabricated UV sensor to the laser irradiation. The UV sensor was operational only for the laser light with $\lambda \leq 220$ nm, insensitive to the solar light, and could follow the laser pulse with ns time scale. There was no significant damage on the sensor even by the direct irradiation of the laser light. Figure 5 shows the packaged sensors. The solar-insensitive, robust UV sensors are expected to be widely used to monitor the UV lights from lumps and lasers in the coming years.

4. Conclusion

It seems that for commercial production of diamond films, it is necessary to construct even a larger CVD reactor than that shown in Fig.1. The new reactor must have a capability of coating diamond uniformly over a 40-cm substrate with a biasing capability. Generation and control of such a large plasma at a pressure of 100 - 200 Torr is a big challenge. To this end, further research of science and technology of microwave plasma will be important.



Fig. 4. Photoresponses of the diamond UV sensor for ArF (193 nm) and dye (313nm) laser irradiations. The response to the former is approximately 100 times more intense than that to the latter. Note that the laser peak width is ~ 5 ns. [3]



Fig. 5. Packaged diamond UV sensors.

References

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