Article

Basal plane bending of homoepitaxial MPCVD single-crystal diamond

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Abstract: We report herein high-resolution x-ray diffraction measurements of basal plane bending of homoepitaxial single-crystal diamond (SCD). The results reveal that growth parameters such as temperature, growth time and basal plane bending of the substrate affect the basal plane bending of SCD. First, the basal plane bending of SCD depends mainly on the substrate itself. The basal plane bending of SCD becomes more severe with increasing basal plane bending of the substrate and this type of basal plane bending cannot be recovered. The SCD growth experiments show that the basal plane bending increases at high temperature and with increasing growth time. Finally, to understand the mechanism behind basal plane bending, we investigate the substrate-surface temperature distribution as a function of basal plane bending of SCD fabricated by chemical vapour deposition (CVD). This allows us to propose a bending model and understand the origin of basal plane bending. The results indicate that an uneven temperature distribution on the substrate surface is the main cause of the CVD diamond base-plane bending.

Keywords: basal plane bending; homoepitaxial single-crystal diamond (SCD); high-resolution x-ray diffraction; growth temperature

1. Introduction

Single-crystal diamond (SCD) has a wide band gap, high thermal conductivity, high breakdown voltage, high carrier mobility and strong resistance to radiation, which earns it the name ‘the ultimate semiconductor’.[1-4] It can be used as a substrate material for deep ultraviolet detectors, particle detectors, high-power, high-voltage and high-frequency electronics, etc. Motivated by these promising applications, large-size, high-quality SCD growth using high, pressure high temperature (HTHP) and microwave plasma chemical vapour deposition (MPCVD) has become an important research topic.[5-6]

The MPCVD technique has now led to the fabrication of 2-inch mosaic SCDs. In parallel with these improvements, other research has focused on the quality of SCDs for use with other semiconductors such as SiC or GaN. In general, basal plane bending degrades the crystal quality by inducing dislocations and even cracks.[7-8] In addition, the relationship between basal plane bending and growth parameters has been studied. Hock et al.[9] investigated in situ lattice plane bending during crystal growth and demonstrated that lattice-plane bending and thermo-elastic stress vary with growth rate. Yang found that Conclusions substrate attachment strongly affects basal plane bending and plastic-deformation-induced dislocations.[10] Sumathi[11] used x-ray diffraction to measure a basal plane bending of 100 arcsec in AlN, which suggests a high structural homogeneity in the crystals. However, no reports yet exist on basal plane bending in SCD.

This work thus presents a detailed x-ray diffraction study of basal plane bending in homoepitaxial SCD deposited by MPCVD. The results indicate that spatial variations in basal plane bending are approximately spherical. In addition, we discuss how growth temperature, substrate quality and growth time affect the bending radius. Furthermore, we propose a mechanism whereby the temperature gradient affects basal plane bending in SCD.

2. Materials and Methods

Basal plane bending was measured by using a Bruker D8 Discover high-resolution x-ray diffractometer (HRXRD) operating with Cu Kα1 radiation with the anode at 40 kV and a current of 40 mA. The x-ray beam was scanned in 1 mm steps from one edge of the substrate to the other.

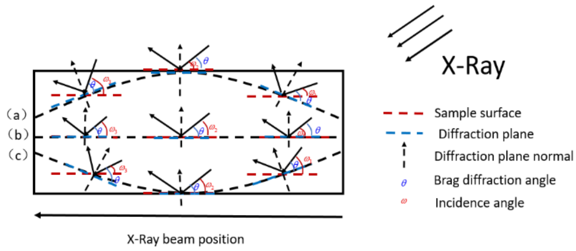

Figure 1. Schematic diagram of HRXRD measurement of lattice plane bending. Panels (a)–(c) show that the lattice plane is convex, flat and concave, respectively.

We applied the basic principle of x-ray diffraction to detect lattice-plane bending.[12-13] When the lattice plane is not bent, the normal orientation of the diffraction plane remains the same regardless of the beam position. As a result, the angle of incidence is independent of the beam position (ω1 = ω2 = ω3; where ω is the angle between the incident beam and the sample surface), as

shown in Fig. 1(b). However, when the lattice plane is bent, the normal orientation of the diffraction plane will vary with x-ray position. For a convex (concave) lattice plane, as shown in Fig. 1(a) [1(c)], the angle of incidence increases (decreases) monotonically as the x-ray beam is scanned over the sample surface, so ω1 < ω2 < ω3 (ω1 > ω2 > ω3). Upon scanning in a given direction from one edge of the wafer to the other, ω gradually changes and the bent lattice plane forms an approximately spherical surface. From the slope of ω as a function of scanning distance x, the radius R of the bending plane is Upon scanning in a given direction from one edge of the wafer to the other, ω gradually changes and the bent lattice plane forms an approximately spherical surface. From the slope of ω as a function of scanning distance x, the radius R of the bending plane is

$$, \quad R=\left(\frac{d\omega}{dx}\right)^{-1}$$

where R[14] is the radius of lattice curvature in the plane of diffraction and ω is measured in radians. The geometrical chamber system and the deposition reaction system is described in detail by Whang.[15]

Three groups of experiments were undertaken. Tables I–III summarize the growth conditions. To compare how the substrate affects basal plane bending, we used (100)-oriented HTHP and MPCVD SCD as substrates for samples H and M. The substrates were purchased from Jinan Zhongwu New Material Co. Ltd. (China). For SCD growth, the concentration ratio of methane to hydrogen was 3%, the pressure was 275 torr and the growth time was 4 h. The samples labelled H1–H4 were grown separately at 900, 1000, 1100, and 1150 °C, respectively. Table II details the growth conditions. Table III is for sample H3, which was grown in three cycles. After each growth period of 4 h, HRXRD was used to evaluate how growth time affects basal plane bending.

Table 1.

ID	Substrate	Growth time (h)	Pressure (torr)	Methane/hydrogen	Substrate temperature (°C)
H1	HTHP diamond	4	275	3.00%	900
M1	MPCVD diamond	4	275	3.00%	900

Table 2.

ID	Substrate	Growth time	Pressure (torr)	Methane/hydrogen	Substrate temperature (°C)
H1	HTHP diamond	4hf	275	3.00%	900
H2	HTHP diamond	4h	275	3.00%	1000
H3	HTHP diamond	4h	275	3.00%	1100
H4	HTHP diamond	4h	275	3.00%	1150

Table 3.

ID	Substrate	Total growth time	Pressure (torr)	Methane/hydrogen	Substrate temperature (°C)
H3	HTHP diamond	4h	275	3.00%	1100
	HTHP diamond	8h	275	3.00%	1100
	HTHP diamond	16h	275	3.00%	1100

3. Results and discussion

For sample H1 and M, the basal plane bending was measured before MPCVD growth and after growth. Figure 2 shows the relative ω (Δω400) peak positions as a function of beam 3.1. Subsection position.As the beam moves from one edge of the substrate to the other, the relative ω (Δω400) peak positions decrease linearly, which indicates spherical bending of the basal plane. The shift in peak position before and after the MPCVD growth of the H1 sample was 14.76 and 2.88 arcsec and the corresponding radii of the lattice curvature were 55.93 and 358.17 m.

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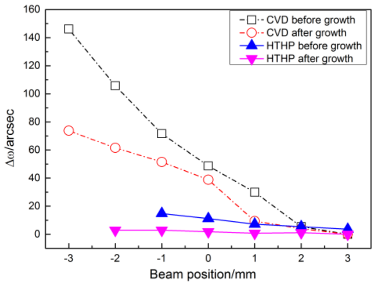

(a)

Figure 2. Peak position of ω(Δω400) as a function of beam position on diamond plane.

The peak positions before and after the growth of sample M were 146.16 and 73.80 arcsec, respectively, which correspond to lattice curvature radii of 8.47 and 16.78 m. The results show that (1) the curvature radius of SCD after MPCVD growth is closely related with the substrate curvature,(2) the curvature radius of SCD grown on a HTHP substrate is much greater than that of SCD grown on a MPCVD substrate. The plane bending of SCD is inherited from the substrate, which indicates that the substrate plays an important role in determining the SCD plane bending. This mechanism is similar to having dislocations propagate from the substrate. Reducing basal plane bending thus requires the use of a high-quality substrate with no basal plane bending.

(a) (b)

Figure 3. (a) Peak position of ω(Δω400) as a function of beam position and at several temperatures. (b) Radius of curvature as a function of temperature.

For SCD grown on the HTHP substrate, the basal plane bending radius exceeds 50 m. We investigated how growth temperature and growth time affects the basal plane bending. Figure 3(a) shows relative ω (Δω400) peak positions as a function of beam position for samples H1 to H4. The slope of the curve increases with growth temperature, which translates into a reduced radius of curvature of the SCD base plane. As shown in Fig. 3(b), the radius of the SCD lattice curvature decreases monotonically with increasing growth temperature. At a growth temperature of 1150 °C, the radius of the lattice curvature reaches its minimum of 23.40 m.

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(a) (b)

Figure 4. (a) Relative position ω(Δω400) as a function of x-ray beam position on diamond plane for different growth times. (b) Radius of curvature as a function of growth time.

For sample H3, the relative ω (Δω400) peak positions do not decrease linearly. However, with increasing growth time at a given growth temperature, the slope of the curve gradually increases [see Fig. 4(a)]. As shown in Fig. 4(b), the radius of lattice curvature is 10.20 m for a total growth time of 16 h. Thus, longer growth time leads to more severe basal plane bending.

These results all indicate that the SCD basal plane bending is affected by temperature, growth time and substrate. They further demonstrate that basal plane bending is related to the temperature gradient and the substrate attachment. Ha et al.[16] used the finite-element method and ANSYS software to simulate the stress distribution during the growth of free and solid seeds and proposed that negative shear stress generates base dislocations in the crystal. By conducting a symmetric Laue geometry transmission test on a primary single crystal containing nitrogen-doped stripes obtained under different growth conditions, Seitz et al.[17] found that the basal plane bending of the single-crystal front end was consistent with the isotherm of the single crystal. In MPCVD growth, the SCD substrate uses open backside attachment, so substrate attachment is not the source of the bending. Based on the model proposed by Harris and Goodwin,[18-19] Silva et al.[20] simulated the temperature distribution in the SCD growth chamber and found a large temperature difference between the centre and the edges of the chamber. We thus consider herein the effects of temperature gradients.

In the MPCVD, the substrate is heated by the thermal radiation and conduction of the plasma ball itself to achieve a suitable SCD deposition temperature (see Fig. 5).

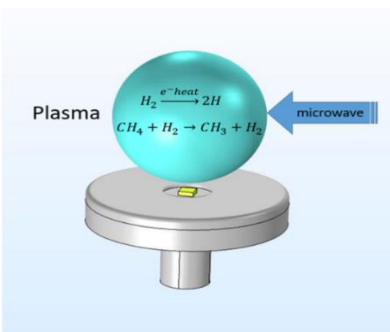

Figure 5. Schematic diagram of synthetic diamond grown by MPCVD.

Therefore, the deposition temperature of the substrate surface is related to the distance from the surface of the substrate crystal to the plasma. Because the plasma is spherical, the centre of the plasma ball is closer to the surface of the substrate crystal; that is, the temperature of the surface of the substrate crystal is highest near the centre of the plasma ball and lower near the periphery of the plasma ball.

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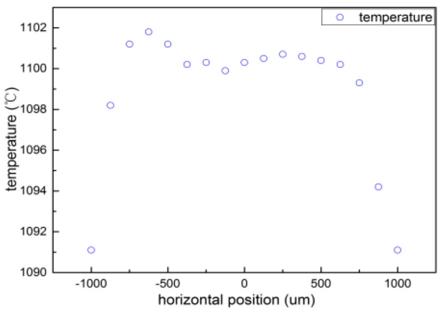

Figure 6. Distribution of sample surface temperature at 1100 ℃.

There are two ways to change the temperature gradient of the substrate surface: One way is to change the growth temperature of the substrate surface, and the other way is to change the distance between diamond and plasma. Figure 6 shows the distribution of surface temperature over the substrate crystal. The temperature gradient on the surface was 40 °C/mm at 1100 °C. Wang reports that the temperature gradient increases with the increasing growth temperature, which in turn increases the thermal stress, causing the SCD basal plane to bend. Higher temperatures lead to more severe base plane bending.

Figure 7 illustrates the bending model of the basal plane at different growth temperatures.Substrate holders are reported to play an important role in the deposition of SCD.[21-23]

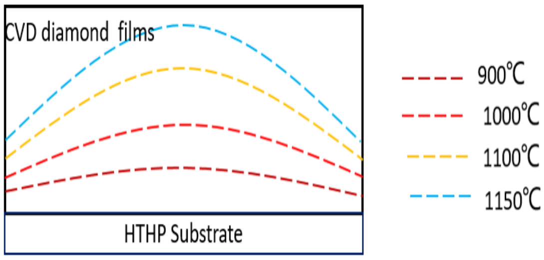

Figure 7. Results of proposed basal plane bending model for different growth temperatures.

Figure 8 shows the pocket holder design; in this design, the holder height d significantly affects the temperature gradient of the sample surface. Figure 9 shows the temperature gradient as a function of position on the substrate surface and for different holder heights. The results show that, for d = 1.3 mm, the temperature gradient at the surface of the substrate crystal fluctuates significantly. As the thickness of the CVD diamond film increases with growth time, the SCD surface approaches the plasma, and the fluctuations in surface temperature increase. In other words, the internal stress increases, which increases the SCD basal plane bending.

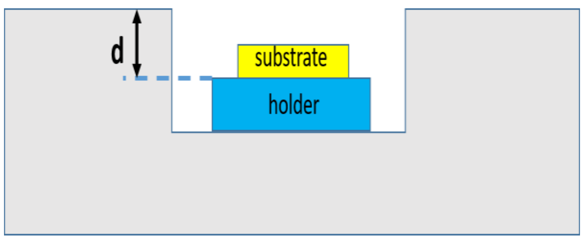

Figure 8. Pocket holder design for SCD synthesis.

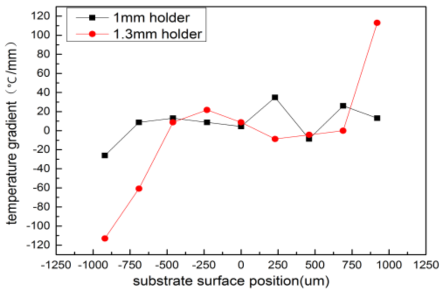

Figure 9. Temperature gradient as function of substrate surface position for different holder heights.

4. Conclusions

In summary, the substrate is the dominant factor determining basal plane bending in SCD. An effective method to alleviate basal plane bending is to use high-quality substrates with flat basal planes.

Growth temperature also strongly affects basal plane bending in SCD. A higher growth temperature increases the temperature gradient at the sample surface, which bends the basal plane. At 900 and 1150 °C growth temperatures, the radii of curvature of the lattice plane of CVD-grown diamond are 358.17 and 23.40 m, respectively. Increasing growth time also leads to increased basal plane bending. For 16 h growth time, the radius of curvature of the lattice plane is 10.20 m.

Finally, increasing the temperature gradient at the sample surface also increases basal plane bending. To describe this **phenomenon**, we propose a model of basal plane bending. The model indicates that the spherical distribution of the plasma and the distance between the plasma ball and the SCD surface is the main cause for basal plane bending in SCD.

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Conflicts of Interest: There are no conflicts of interest to declare.

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