

ANALYSIS OF FRACTURE BEHAVIOR OF THIN POLYCRYSTALLINE DIAMOND FILMS

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The effect of the substrate temperature and CH₄ concentrations on the fracture behavior of thin polycrystalline diamond films was systematically investigated by X-ray diffraction and scanning electron microscopy. The results show that the fracture behavior of thin polycrystalline diamond films synthesized by direct current plasma jet chemical vapor deposition is closely related to the substrate temperature and CH₄ concentrations. A high substrate temperature, due to difference in the thermal expansion coefficients of the substrate and the diamond film, causes thin polycrystalline diamond films to generate high residual stresses, which usually exceed fracture strength of thin diamond film and even that of diamond. The fracture toughness is found to drop with the increasing ratio of CH₄ concentration. In case of high CH₄ concentrations, various defects and impurities, such as cracks, microscopic holes, graphite, and amorphous carbon were observed in the films. Thus, the substrate temperature and CH₄ concentrations should be strictly controlled within an appropriate range.

Keywords: thin polycrystalline diamond film, fracture, substrate temperature, CH₄ concentration, residual stress.

Introduction. Direct current plasma jet chemical vapor deposited (DCPJ-CVD) thin polycrystalline diamond films have been widely used in optical, electronic, mechanical, and thermal applications [1–3]. The fracture behavior of thin diamond films is of great importance. Residual stresses reduce the fracture toughness and mechanical strength of films. Understanding of their fracture behavior is essential for these applications. A diamond film is usually grown on the hetero-epitaxial substrates, such as Si, Mo, and Ti. The film deposited on the substrates can contain some defects and impurities due to the lattice mismatch and residual stresses. Takeuchi et al. [4] analyzed the surface defect status of diamond. Ikeda et al. [5] investigated the fracture behavior of a polycrystalline diamond film. Shames et al. [6] studied the localization and nature of the defects for powder and compact diamond films. Stiegler et al. [7] analyzed the impurity and defect incorporation in diamond films. Jeong et al. [8] explored the mechanisms of cracking in CVD films experimentally and theoretically. In recent years diamond films have become very popular, and commercial diamond wafers are successfully used. However, cracking and defect problems reported in the literature are observed for the large-sized diamond wafer only [9, 10]. For diamond films deposited on curved surfaces (e.g., convex substrates), it is very difficult to keep a uniform temperature over a heterogeneous substrate. Cracks and defects are easily formed due to non-uniform temperature distribution over the substrate surface. To the best of our knowledge, crack problems for such a thin film were not yet reported in the literature. In this study, we selected Mo as the substrate material for depositing diamond film because of a low lattice mismatch between diamond and the underlying Mo substrate. The mechanisms of generation of cracks and defects during the depositing process of the diamond film are investigated. It should be mentioned that a new substrate cooling system presented in [11] was used to ensure nearly uniform temperature over the substrate surface.

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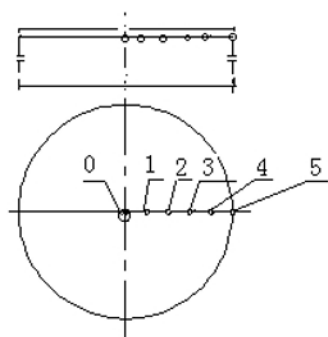


Fig. 1. Schematic diagram of the substrate radial direction.

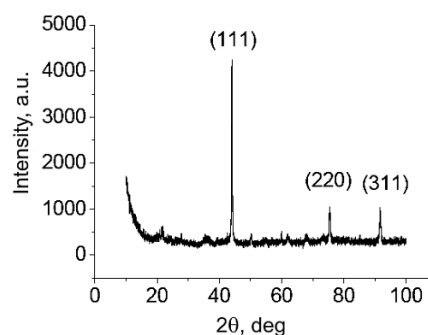


Fig. 2. XRD analysis of a diamond film.

Experimental. In this study, thin polycrystalline diamond films were deposited onto the molybdenum substrate with a diameter of 60 mm using the DCPJ-CVD system [12]. In this process, a mixture of methane (CH_4) and hydrogen (H_2) gases was used as the carbon source for the growth of a thin diamond film. Argon (Ar) gas was subsequently ionized by the CVD system to form the DC jet plasma. The anode and cathode were made of tungsten and copper, respectively.

The Mo substrate was pretreated before growing films. The substrate temperature was varied by the cooling water flow and the system power variation. The typical experimental conditions for the growth of a diamond film by DCPJCVD are as follows. The methane content was 1.8–8.0%, with the hydrogen flow rate of 1000 ml/min. The total pressure in the reaction chamber was approximately 45–50 kPa. The substrate temperature was controlled within 850–1100°C by an on-line infrared (IR) pyrometer. The fracture behavior of the films was investigated by scanning electron microscopy (SEM) as well as X-ray diffraction (XRD) was used to analyze the surface morphology, defects, cracks, and fracture behavior.

During the growth of thin polycrystalline diamond films, the temperature distribution along the radial direction was labeled as 0, 1, 2, 3, 4, and 5 on the substrate. The schematic diagram is shown in Fig. 1.

Results and Discussion. The XRD pattern for the microstructure orientation of a thin diamond film is shown in Fig. 2.

It can be seen that the peaks were identified at diamond (111), (220), and (311) for evolution of the morphology of the diamond film. The results indicated that the diamond film was polycrystalline, as the (111) face of the film is dominant. It should be noted that many properties of the thin diamond film are strongly influenced by its crystal orientation and grain size.

Thin diamond film microstrain versus its radial direction for different CH_4 concentrations and crystal orientations is shown in Fig.3. It can be seen that with an increase in CH_4 concentrations, the film microstrain is substantially increased. Here, the microstrain value in the (111) face is small and is much higher in the (311) face. Thus, the corresponding macroscopic stress is also increased. The residual stress is so high, that it results in the formation of microcracks and even fracture of the diamond film. It has also been found that higher CH_4 concentrations give rise to higher microstrains and residual stresses. In this study, the thin diamond film exhibited a poor fracture resistance.

Figure 4 depicts substrate temperature variations at six different points versus the deposition time. The highest temperature of the film is observed at the central point (i.e., point 0) and the lowest temperature occurs at the edge (i.e., point 5). The substrate temperature increases with an increase in the deposition time (Fig. 3). The temperature difference along the radial direction does not exceed 20°C. The surface temperature of the film decreased along the outward radial direction. The temperature difference of the substrate may significantly affect the quality of the film. However, temperature fluctuations were about 3–6% of the mean value, so that its effect on the growth of the diamond film was negligible.

When the diamond film is deposited onto the hetero-epitaxial substrate, some defects and impurities in the diamond film may inevitably arise due to the lattice mismatch and residual stresses. The residual stress is the major deteriorating factor for the diamond film, which strongly depends on the substrate temperature.

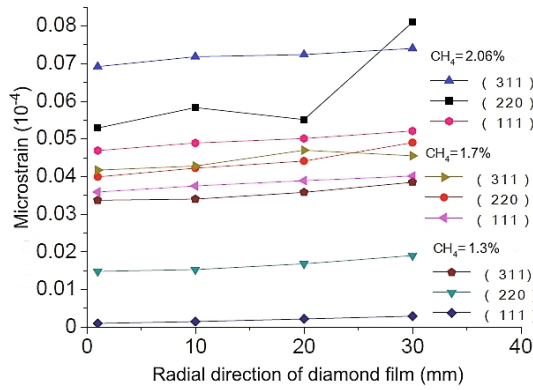


Fig. 3. Microstrain of a diamond film.

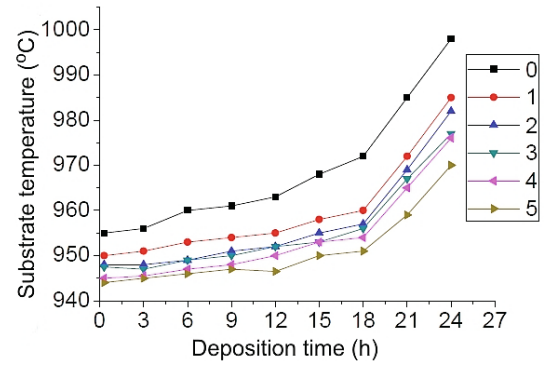


Fig. 4. Substrate temperature vs deposition time.

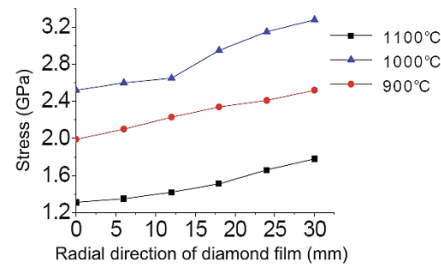


Fig. 5. Residual stress in radial direction of thin polycrystalline diamond films.

Diamond film specimens were prepared and tested at 900, 1000, and 1100°C, respectively. Other growth parameters were kept constant in the experiment. The residual stress in the diamond film was measured with the XRD technique, and the respective results are shown in Fig. 5.

Figure 5 shows that the residual stress of the film increased along the radial direction with an increase in the substrate temperature when the substrate temperature varied in the range of 900–1000°C. Tensile stresses varied in the range of 1.5–3.2 GPa. However, it was found that the residual stress decreased significantly when the substrate temperature was equal to 1100°C. The possible reason is that much higher residual stresses or numerous impurities in diamond films occurred when the substrate temperature increased or high CH₄ concentrations were used. Thus, the residual stress of the diamond film increased with temperature. However, when the substrate temperature is too high, say, 1100°C, high residual stresses may result in formation of microcracks in the diamond film. Those microcracks and microvoids will develop and eventually result in the cracking and fracturing of the thin polycrystalline diamond film, which would provide the relaxation of residual stresses to a smaller value at 1100°C.

This implies that at high substrate temperatures a partial nucleation process of the original diamond film would rapidly occur, which would inhibit the growth of other grains. As a consequence, the thin film will exhibit a low nucleation density and large grain sizes. Noteworthy is that the coefficient of thermal expansion (CTE) of Mo substrate is higher than that of diamond, which may induce higher residual stresses in the thin diamond film when the film is cooled down from a relatively high temperature, thus deteriorating its mechanical strength [13]. If the internal stress of the diamond film is higher than the ultimate (fracture) strength, microcracks and even fracture may occur. Thin polycrystalline diamond films exhibit poor fracture resistance. Further investigation of the fracture behavior of thin polycrystalline diamond films was made using the diamond film SEM image shown in Fig. 6.

Figure 6a shows that, for a reasonable substrate temperature (880°C) and CH₄ concentration (1.3%), the diamond crystal is approximately uniform and has clear grain boundaries. However, at the substrate temperatures of 970 and 1040°C, microcracks in diamond were found which covered the total surface and resulted in the local fracture of diamond films. The SEM images of the film for the last two temperatures are shown in Fig. 6b and 6c, respectively. Cracks and fracture had a negative influence on physical and mechanical properties of the film such as mechanical stiffness, optical properties, and thermal conductivity [14].

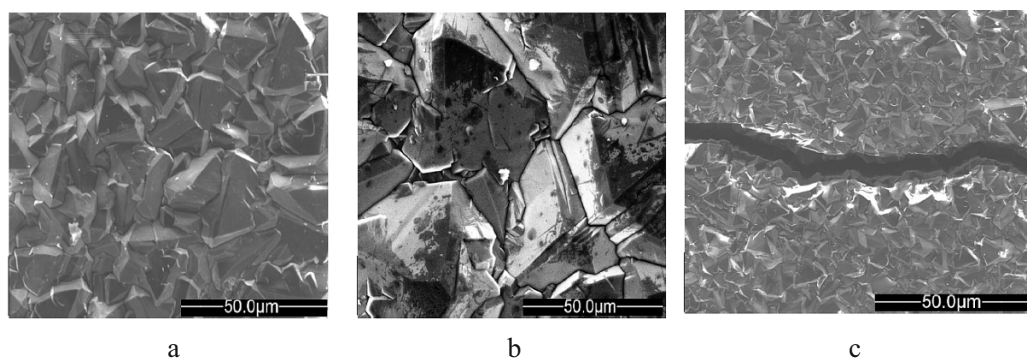


Fig. 6. SEM images of the diamond film: (a) uniform and integrated pattern; (b) microcrack; (c) local fracture.

The mechanism of fracture formation in the film can be explained as follows. Diamond films were deposited onto the heterogeneous substrate, which was usually accompanied by the origin of some defects, such as cracks, non-carbon impurities and microscopic holes due to inadequate growth process. Such defects like microcracks extended from inside to the diamond film surface. This is the major factor controlling the diamond film fracture. Figure 6 depicts the diamond film containing some defects, microcracks and a fractured zone.

In particular, some microcracks appeared in the diamond film due to improper growth processes, such as high or low substrate temperatures, high CH_4 concentrations, and high growth rates, as shown in Fig. 6b. When these microcracks get further converged and accumulated, the cracks became visible. The diamond film was deposited acquiring a relatively columnar pattern, but it also contained some microstructural defects, including amorphous carbon and graphite, as well as a microvoid, which propagated and turned into a macrocrack with the eventual fracture of the film, as shown in Fig. 6c. It can also be observed that microcracks in the diamond film generally appear at the grain boundaries (Fig. 6b). These defects may cause a marked deterioration, in terms of physical and mechanical performance of the diamond film.

The DCPJ-CVD diamond film underwent the process of nucleation and growth. During the nucleation stage, the carbon-containing gas source with the appropriate process parameters has formed a certain number of isolated diamond nucleation sources on the deposition substrate. Diamond nucleation sources continued to expand, then covered the entire surface of the substrate, and eventually grew along the vertical direction of the substrate. Finally, this process produced a certain thickness of the diamond film. Since the nucleation density is usually less than 10^{12} cm^{-2} on the non-diamond substrate [14, 15], it results in a gap between the grain and its nucleation surface. Therefore, the diamond film and the substrate do not get into a close contact. The presence of these tiny non-contact areas in the diamond film may be observed even for the entire surface of the substrate, leaving microvoids in the film-based interface. In particular, growing substrate temperatures or high CH_4 concentrations result in higher residual stresses or numerous impurities in diamond films. The microvoids evolved into the thin polycrystalline diamond film also contribute to its cracking and fracturing, which can be seen in Fig. 6. The presence of microvoids and microcracks weakened the binding of the diamond film-substrate interfaces. The properties of the diamond film and the crystal grains imply the initial crack formation and further fracture. Poor fracture resistance sharply decreases the mechanical properties of the diamond films. Under external force, the initial crack is first nucleated by the stress concentration at the crack tip, then this crack propagates and eventually triggers the coating to break off. However, through the control of the growth temperature of the diamond film, the concentration of the carbon source and the substrate surface temperature could be uniformly optimized. These made it possible to prepare a high-quality diamond film without microcracks, as shown in Fig. 6a.

Conclusions. The formation of cracks and fracture represent an intrinsic problem in fabricating thin polycrystalline diamond films. In this study, the diamond film deposited at different substrate temperatures and CH_4 concentrations was investigated using the XRD and SEM techniques. The results obtained show that some defects grow rapidly with the substrate temperature. The XRD analysis testifies that high temperatures result in high residual stresses in the diamond film at the substrate temperatures less than 985°C . When the substrate temperature exceeds

1100°C, the diamond film is subjected to very low residual stresses due to a larger number of microcracks in the film, which cause the relaxation of residual stresses. The SEM results reveal that some radial cracks penetrate through the surface of the diamond film and extend to its center. Coalescence and growth of these cracks can bring about the formation of microscopic holes and even induce the local fracture of the diamond film.

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