

Analysis of Fracture Behavior of Thin Polycrystalline Diamond Films

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Анализ поведения тонких поликристаллических алмазных пленок при разрушении

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С помощью рентгеновской дифракции и сканирующей электронной микроскопии исследовано влияние температуры подложки и показателя концентрации CH_4 на поведение тонких поликристаллических алмазных пленок при разрушении. Показано, что поведение при разрушении тонких поликристаллических алмазных пленок, синтезированных химическим осаждением покрытия с помощью плазменной струи при постоянном токе, зависит от температуры подложки и показателя концентрации CH_4 . Большая температура подложки приводит к возникновению высоких остаточных напряжений в тонких поликристаллических алмазных пленках вследствие различных значений коэффициента теплового расширения подложки и алмазной пленки, которые, как правило, оказываются выше значений сопротивления разрушению тонкой алмазной пленки и алмаза. Обнаружено, что вязкость разрушения уменьшается с увеличением показателя концентрации CH_4 . По достижении высоких показателей концентрации CH_4 в тонких пленках образуются такие дефекты и примеси, как трещины, микроскопические отверстия, углерод в форме графита и аморфный углерод. Температуру подложки и показатель концентрации CH_4 необходимо контролировать в надлежащем диапазоне.

Ключевые слова: тонкая поликристаллическая алмазная пленка, разрушение, температура подложки, концентрация CH_4 , остаточное напряжение.

Introduction. Direct current plasma jet chemical vapor deposited (DCPJ-CVD) polycrystalline diamond thin films have been widely used in optical, electronic, mechanical and thermal applications [1–3]. The fracture behavior of diamond thin films is of great importance. The residual stresses reduce the fracture toughness and mechanical strength of films. Understanding of their fracture behavior is essential to these applications. Diamond film is usually grown on the hetero-epitaxial substrates, such as Si, Mo, and Ti. The film deposited on the substrates may induce some defects and impurities due to 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 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 mechanisms of cracking in the CVD films experimentally and theoretically. In the recent years, diamond films 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 along 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 select Mo as the substrate material for depositing diamond film because of a low lattice mismatch between the 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.

Experimental. In this work, polycrystalline diamond thin films were deposited onto a molybdenum substrate with 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 carbon source for the growth of a diamond thin film. Argon (Ar) gas was subsequently ionized by CVD system to form the DC jet plasma. The anode and cathode were made of metal tungsten and copper, respectively.

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

With the growth of the polycrystalline diamond thin films, the temperature distribution along the radial direction is 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 diamond thin film is shown in Fig. 2.

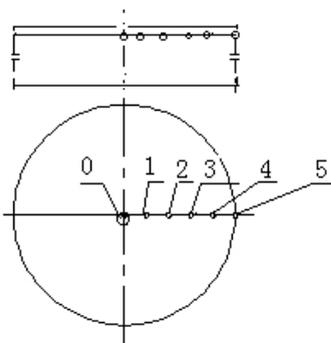


Fig. 1

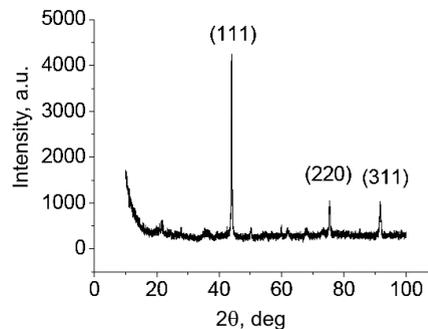


Fig. 2

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

Fig. 2. XRD analysis of a diamond film.

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 is polycrystalline, as (111) facet of the film is dominant. It should be noted that many properties of the diamond thin film are strongly influenced by its crystal orientation and grain size.

Figure 3 shows the relation of diamond thin film microstrain versus its radial direction for different CH₄ concentrations and crystal orientations. It can be seen that with the increase in CH₄ concentration, the film microstrain is substantially increased. Here, 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 formation of microcracks and even fracture of the diamond film. It has also been found that higher CH₄ concentrations induce higher microstrains and residual stresses. In this study, the diamond thin film exhibited a poor fracture resistance.

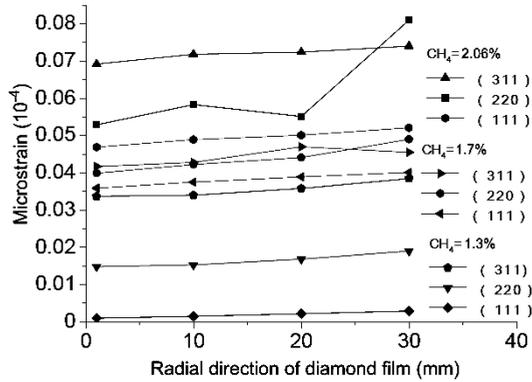


Fig. 3. Microcharacterization of a diamond film.

Figure 4 depicts variation of the substrate temperature at six various 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 – at edge (i.e., point 5). It is also seen from Fig. 4 that the substrate temperature increases with the increase in the deposition time. 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, the temperature fluctuation was about 3–6% of the mean value, so that its effect on the growth of diamond film was negligible.

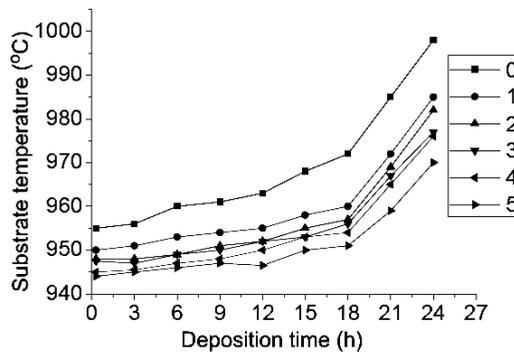


Fig. 4. Substrate temperature vs deposition time.

When diamond film is prepared onto a hetero-epitaxial substrate, some defects and impurities in diamond film may be inevitably induced due to the lattice mismatch and residual stresses. The residual stress is the main deteriorating factor of the diamond film, which strongly depends on the substrate temperature.

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

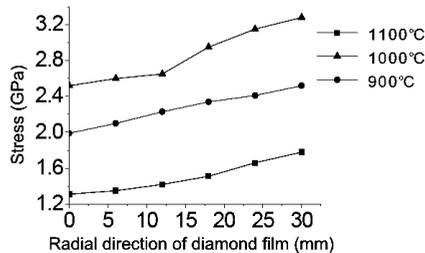


Fig. 5. Residual stress in radial direction of polycrystalline diamond thin films.

Figure 5 shows that the residual stress of the film increased along with the increase of the substrate temperature when the substrate temperature was 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 more numerous impurities in diamond films occurred when the substrate temperature was increased or high CH₄ concentration was used. Thus, the residual stress of the diamond film increased with the increasing 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 polycrystalline diamond thin film, which would provide relaxation of the residual stress 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 growth of other grains. As a consequence, the thin film will exhibit a low nucleation density and a large grain size. Noteworthy is that the coefficient of thermal expansion (CTE) of Mo substrate is higher than that of a diamond, which may induce a higher residual stress in the diamond thin 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. Polycrystalline diamond thin films exhibit a poor fracture resistance. Further investigation of the fracture behavior of polycrystalline diamond thin film 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 the diamond were found which covered the total surface and resulted in the local fracture of the diamond films. The SEM images of the film for the latter 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].

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 formation of some defects such as cracks, non-carbon impurities and microscopic holes due to inappropriate growth process. These 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.

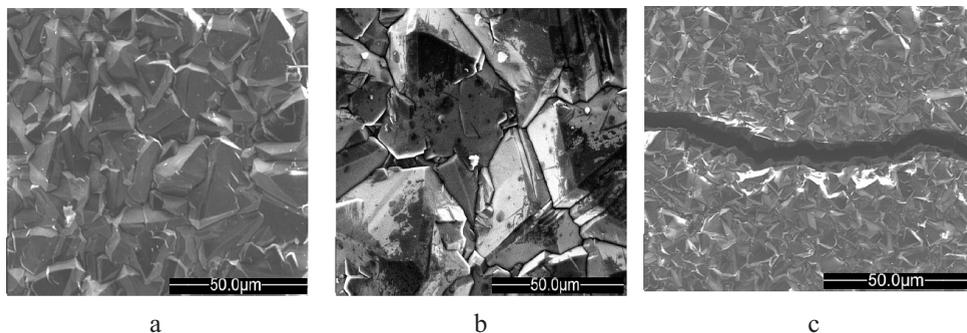


Fig. 6. SEM image of the diamond film: (a) uniform and integrated pattern; (b) microcrack; (c) local fracture.

In particular, some microcracks appeared in the diamond film due to improper growth processes, such as high or low substrate temperatures, high CH_4 concentration and high growth rate, as shown in Fig. 6b. When these microcracks get further converged and accumulated, the cracks became visible. The diamond film was deposited with 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 in Fig. 6b that microcracks in the diamond film generally appear at the grain boundaries. These defects may cause a sharp deterioration, in terms of physical and mechanical performance of the diamond film.

The DCPJ-CVD diamond film has undergone the process of nucleation and growth. During the nucleation stage, the carbon-containing gas source with the appropriate parameters of process 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 involved a certain thickness of the diamond film. While 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 the nucleation surface grain. Therefore, formation of the diamond film and the substrate are not entirely brought 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, the increased substrate temperatures or high CH_4 concentrations result in higher residual stresses or more numerous impurities in diamond films. The microvoids evolved into the polycrystalline diamond thin 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 and the substrate between the diamond interfaces. The properties and the crystal grains of the diamond film imply the initial crack formation and further fracture. Poor fracture resistance sharply decreases the mechanical property of the diamond films. Under external force, the initial crack is firstly caused by the stress concentration at the crack tip region, 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 carbon source and the substrate surface temperature could be uniformity 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 polycrystalline diamond thin films. In this work, a study on diamond film deposited at different substrate temperature and CH₄ concentrations was carried out, using the XRD and SEM techniques. The results obtained show that some defects rapidly grow with the increase in the substrate temperature. The XRD analysis testifies that high temperature results in high residual stresses in diamond film if the substrate temperature is less than 985°C. When the substrate temperature exceeds 1100°C, the prepared diamond film has very low residual stresses due to larger number of microcracks in the film, which provide relaxation of the residual stresses. The SEM results reveal that some radial cracks have penetrated the surface of the diamond film and extended to the center of diamond film. Coalescence and growth of these cracks may induce formation of microscopic holes and even cause the diamond film local fracture.

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Резюме

За допомогою рентгенівської дифракції і скануючої електронної мікроскопії досліджено вплив температури підкладки і показника концентрації CH₄ на поведінку тонких полікристалічних алмазних плівок під час руйнування. Показано, що поведінка при руйнуванні тонких полікристалічних алмазних плівок, синтезованих хімічним осадженням покриття за допомогою плазмового струменя на основі постійного струму, залежить від температури підкладки і показника концентрації CH₄. Велика температура підкладки призводить до виникнення в тонких полікристалічних алмазних плівках високих залишкових напружень внаслідок різних значень коефіцієнта теплового розширення підкладки й алмазної плівки, які, як правило, вищі за значення опору руйнуванню тонкої алмазної плівки й алмаза. Виявлено, що в'язкість руйнування зменшується зі збільшенням показника концентрації CH₄. Після досягнення високих показників концентрації CH₄ у тонких плівках мають місце такі дефекти і домішки, як тріщини, макроскопічні отвори, вуглець у формі графіту і аморфний вуглець. Температуру підкладки і показник концентрації потрібно контролювати в необхідних межах.

1. D. Li, D. Zuo, W. Lu, et al., "Effects of methane concentration on diamond spherical shell films prepared by DC-plasma jet CVD," *Solid State Ionics*, **179**, 1263–1267 (2008).
2. D. M. Trucchi, C. Scilletta, E. Cappelli, et al., "Optimization of the performance of CVD diamond electron multipliers," *Diamond Rel. Mater.*, **15**, 827–832 (2006).
3. N. Jiang, S. Kujime, I. Ota, et al., "Growth and structural analysis of nano-diamond films deposited on Si substrates pretreated by various methods," *J. Crystal Growth*, **218**, 265–271 (2000).
4. D. Takeuchi, C. E. Nebel, and S. Yamasaki, "Surface defect states analysis on diamond by photoelectron emission yield experiments," *Diamond Rel. Mater.*, **16**, 823–825 (2007).
5. R. Ikeda, M. Hayashi, A. Yonezu, et al., "Fracture observation of polycrystalline diamond film under indentation test," *Diamond Rel. Mater.*, **13**, 2024–2030 (2004).

6. A. I. Shames, A. M. Panich, S. Porro, et al., "Defects localization and nature in bulk and thin film ultrananocrystalline diamond," *Diamond Rel. Mater.*, **16**, 1806–1812 (2007).
7. J. Stiegler, A. Bergmaier, J. Michler, et al., "Impurity and defect incorporation in diamond films deposited at low substrate temperatures," *Diamond Rel. Mater.*, **7**, 193–199 (1998).
8. J. H. Jeong, S. Y. Lee, W. S. Lee, et al., "Mechanical analysis for crack-free release of chemical-vapor-deposited diamond wafers," *Diamond Rel. Mater.*, **11**, 1597–1605 (2002).
9. Y. J. Baik, J. K. Lee, W. S. Lee, and K. Y. Eun, "Large area deposition of thick diamond film by direct-current PACVD," *Thin Solid Films*, **341**, 202–206 (1999).
10. C. S. J. Pickles, "The fracture stress of chemical vapour deposited diamond," *Diamond Rel. Mater.*, **11**, 1913–1922 (2002).
11. D. Zuo, D. Li, W. Lu, et al., *Methods and Devices of Uniform Substrate Temperature in Preparing Spherical Diamond Film*, Chinese Patent No. 200810024384.5 (2010).
12. D. Li, D. Zuo, R. Chen, et al., "Growth of high quality spherical diamond film by DC plasma jet CVD," *Synth. Reactiv. Inorg. Metal-Organic Nano-Metal Chem.*, **38**, 325–328 (2008).
13. O. Durand, R. Bisaro, C. J. Brierley, et al., "Residual stresses in chemical vapor deposition free-standing diamond films by X-ray diffraction analyses," *Mater. Sci. Eng. A*, **288**, 217–222 (2000).
14. C. Li, H. Li, D. Niu, et al., "Effects of residual stress distribution on the cracking of thick freestanding diamond films produced by DC arc jet plasma chemical vapor deposition operated at gas recycling mode," *Surf. Coat. Technol.*, **201**, 6553–6556 (2007).
15. D. Dai and K. Zhou, *Diamond Film Deposition Preparation Process and Application*, Metallurgical Industry Press, Beijing (2001).

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