Crack and defect formation in diamond films

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Abstract In this paper, mechanisms of defect and crack initiation in a diamond film prepared at substrate temperatures are investigated using direct current plasma chemical vapor deposition method. The study is by way of X ray diffraction (XRD), optical microscope (OM), and scanning electron microscopy (SEM) and reveals that initiation of defects and cracks during the growth of diamond films depends strongly on substrate temperature. The defects and impurities formed in high substrate temperatures include mainly residual stresses, and non-diamond phase such as graphite and amorphous carbon, which result in forming crack and microscopic hole in diamond film. X ray diffraction, optical microscope and SEM have been used to examine the temperature dependence of various defect inductions. It is found that cracks in diamond film are generally derived at grain boundary. In general, diamond films prepared in high temperature substrate will result in high residual stress at the interface between the diamond film and the substrate

Keywords Diamond film, Defect, Crack, Substrate temperature, Residual stress

1. Introduction

Due to its excellent physical and chemical properties, diamond film prepared using chemical vapor deposition (CVD) is becoming a popular material in many engineering applications such as infrared optical window, coating cutting tools, biomaterials, micromechanical, and thermal heat sink materials [1-3]. Diamond film can grow on hetero-epitaxial substrates, such as Si, Mo, Ti, and Ta substrates. It should be mentioned that diamond film deposited on the substrates mentioned above may induce some defects and impurity due to lattice mismatch and residual stress. Takeuchi et al. [4] analyzed surface defect status of diamond by photoelectron emission yield experiments; Ikeda et al. [5] investigated facture shape of polycrystalline diamond film through indentation test. Shames et al. [6] studied the localization and nature of defects for powder and compact diamond film samples. Stiegler et al. [7] investigated the impurity and defect incorporation in diamond films deposited from a carbon-hydrogen-oxygen gas system at substrate temperatures between 560 and 345 ^{o}C. Jeong et al. [8] explored mechanisms of cracking in the CVD films was investigated experimentally and theoretically. Qin and Kang et al [9, 10] investigated experimentally the effect of film thickness and size on fracture toughness. In the recent years, diamond films become popular and commercial diamond wafers are successfully used for some important fields. However, crack and defect problems reported in the literature are for large size diamond wafer only [11, 12]. For diamond film deposited on curved surface, (for example convex substrate), and it was very difficult to keep a uniform temperature on a convex substrate. It induces often cracks and defects due to non-uniform temperature distribution over the substrate surface. Crack problems for such a thin film seem not being reported in the literature. In this study, we select Mo as substrate material for depositing diamond film because of its low lattice mismatch between the diamond and the underlying Mo substrate. The mechanisms of crack and defect generation during the depositing process of the diamond film are investigated. It should be mentioned that a new substrate cooling system presented in [13] was used to ensure nearly uniform temperature over the substrate surface.

2. Experimental

The deposition system used in the present work for the growth of diamond films by direct current plasma jet CVD (DCPJCVD) is similar to that described in [14]. Using the deposition system, diamond films are prepared on convex molybdenum (Mo) substrate. The reaction gas employed is a mixture of methane (CH_4) and hydrogen (H_2), which are fed into a reaction chamber. Argon (Ar) gas is subsequently ignited by high frequency system to generate DC plasma. The anode and cathode are made of metal Mo and W, respectively. The substrate temperature is controlled by regulating the flow rate of the cooling water and the discharge current density. Typical experimental conditions for the growth of diamond film by DCPJCVD are given as follows: Source gases used are CH_4, H_2 and Ar; H_2 flow rate is 450 sccm, CH_4 flow rate is 3500 sccm; the total pressure of reaction chamber is approximately 43KPa, and CH_4 concentration is about 2.15 %. The substrate temperature is measured by an IR pyrometer and can be adjusted within the range of 830-1050℃. The diamond films are characterized by optical microscope, scanning electron microscopy, X ray diffraction with regard to surface morphology or defect, crack and their incorporation.CH_4

3. Results and discussion

As mentioned above, diamond films are prepared on Mo substrate by DCPCVD in this work. The substrate temperature is about 900-940 ℃ and the other growth conditions for the deposition process of the diamond films are kept constant or nearly constant. To illustrate the temperature distribution along radial direction, six points on the substrate surface labeled in O, A, B, C, D E as Fig. 1 and the temperatures at these points are measured on line using IR pyrometer.

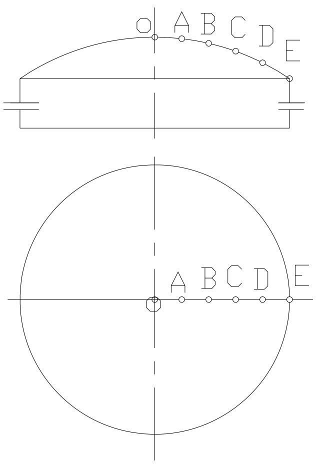

Fig. 1 Schematic diagram of radial direction of substrate

Fig. 2 shows the variation of temperature at the six points with deposition time. As expected, Fig. 2 shows that the highest temperature of the diamond film occurs at central point O and the lowest temperature presents at edge point E.

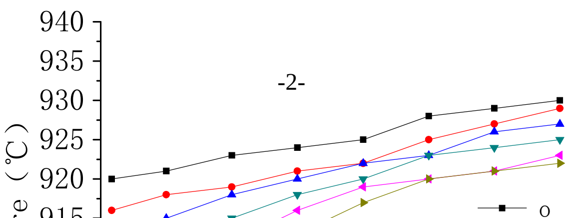

Fig. 2 Temperature distribution of diamond films at different deposition time: from 3 to 21 hours

It is also found from Fig. 2 that diamond temperature increases with the increase in deposition time. Temperature difference along the radial direction is not obvious and the maximum is about 15 ^{o}C only as Fig. 2. It is also found that surface temperature of the diamond film decreases along the outward radial direction. The temperature difference (or temperature fluctuation) on surface of substrate may significantly affect the quality of the diamond film. It is found that, when temperature difference was under 1-2% of the maximum, it has a negligible negative effect on the growth of diamond film.

When diamond film was prepared on a hetero-epitaxial substrate, some defects and impurity in diamond film may be inevitably induced due to lattice mismatch and residual stress. It is observed from the experiment that the residual stress is the main defect in diamond film, which depends strongly on the substrate temperature.

In this paper, four diamond film samples had been prepared and tested under substrate temperatures of 870, 940, 980 and 1050 ^{o}C respectively. The other growth parameters are kept the same in all experiments. The residual stress in diamond film is measured using X-ray diffraction (XRD), and the corresponding results are listed in Fig. 3.

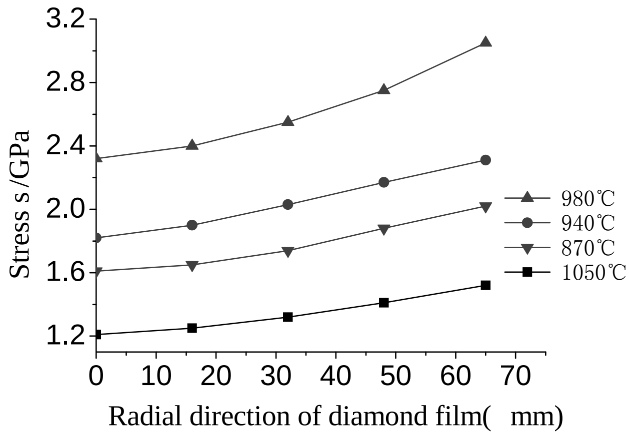

Fig. 3 Residual stress of diamond film

It is observed from Fig. 3 that the residual stress of the diamond film increases along with an increase in the substrate temperature when substrate temperature varied in the range 870-980 ^{o}C, Tensile stresses vary in range of 1.4 GPa - 3.0 GPa. It is interesting to note that the residual stress decreases significantly when the substrate temperature reaches 1050 ^{o}C. The mechanism for inducing this phenomenon should be further investigated.

It should be mentioned that, when the substrate temperature is in a higher, value, the nucleation process of some microcrystals of the original diamond film will speed up which causes the other microcrystals to slow down their emerging and growing process. As a consequence, in the thin film will be in low nucleation density and larger grain size. Noted that the coefficient of thermal expansion (CTE) of Mo substrate is higher than that of diamond, It may induce significant residual stress in diamond film when the film is cooling from a relatively high temperature, which will degrade its mechanical property [15]. If the internal stress of diamond film is greater and more than fracture strength of the diamond film, it may induce microcracks and even fracture.

To investigate further the formation mechanism of microcracks in diamond film, experimental testing using Optical microscope (OM) has been conducted. The OM photograph of diamond film is shown in Fig. 4.

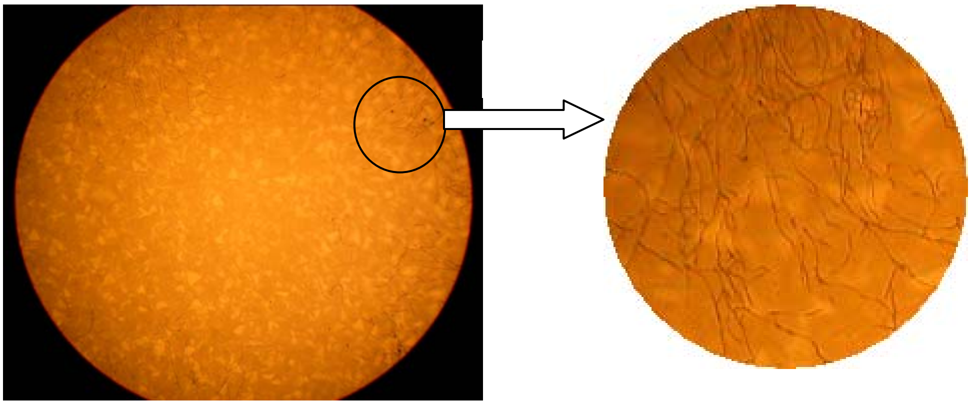

Fig.4. Optical microscope photograph of diamond film, (a) whole (30×), (b) an enlarged scale (100×)

It can be seen from Fig. 4 (a) that, in a low amplification, the size of the diamond crystals is approximately uniform and clear grain boundary appears. Fig. 4b shows an enlargement of microstructures of the diamond film. It is found that some radial microcracks penetrates the surface of diamond film and extends to the center area of the diamond film. Thus, when the substrate temperature is as high as 1050 ℃, some radial microcracks are created in the diamond and extend to the whole surface. Partial residual stress in diamond film is released with the creation of microcracks which is in agreement with the results shown in Fig. 3. Crack and defects cause significantly damage of physical and mechanical properties of the diamond film, including dimensional stability, mechanical stiffness, optical properties, and thermal conductivity.

The mechanism of defect formation in the thin diamond can also be explained as follows. Diamond film prepared on the substrate with curve surface usually accompanies some defects such as crack, non-diamond impurity, and microscopic hole due to inappropriate growth process. These defects like microcracks can extend to the surface of diamond film from somewhere inside. This is the major factor to cause diamond rupture. Fig. 5 shows a diamond film with some microcracks and non-microcrack.

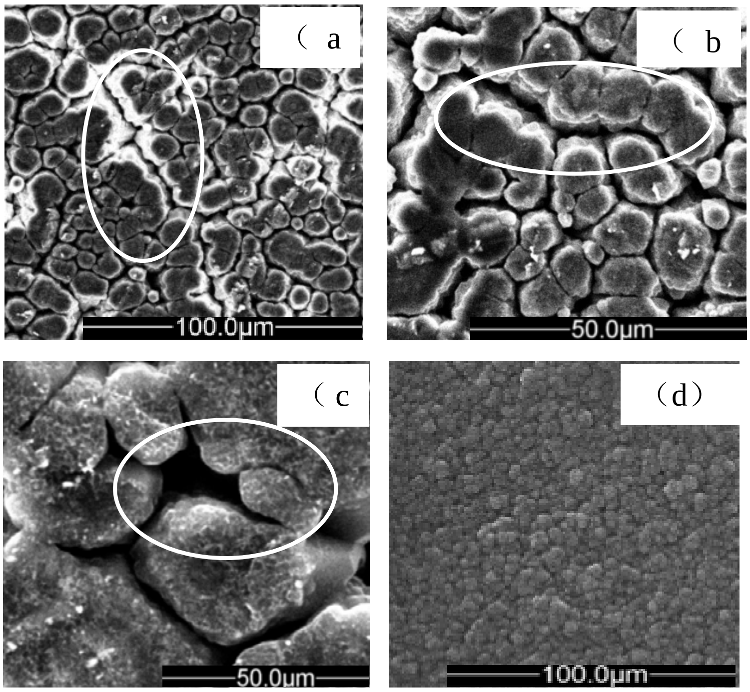

Fig.5. SEM photograph of diamond film, (a) little microcrack, (b) microcrack extending, (c) microscopic hole, (d) non-microscopic,

It is observed from Fig.5 that there exist some defects in the diamond film. In particular, some microcracks appeared in diamond film as shown in Fig. 5(a). When these microcracks further converge and accumulate, it may become a visible crack as shown in Fig. 5(b). Due to improper growth processes such as high or low substrate temperature, high CH_4 concentration and high growth rate, diamond film deposited with competitively columnar way, diamond film deposited may also contain some microstructure defects including amorphous carbon, graphite and microscopic hole as Fig.5c. It is also found from Fig. 5 that microcracks in diamond film generally appearing at grain boundary. These defects may cause sharply degrading in terms of physical and mechanical performance of diamond film.

CVD method, the process of synthetic diamond film has undergone the course of nucleation and growth. During the nucleation stage, the carbon-containing gas source under appropriate process parameters on the deposition substrate to form a certain number of isolated diamond nucleation. Growth stages of diamond nucleation continue to grow and even become one, to cover the entire surface of the substrate, and then grew along the vertical direction of the substrate; at last, it grew a certain thickness of the diamond film. While the nucleation density is usually less than 10^{12} cm^{-2} on the non-diamond substrate [16], which probably lead to a gap between the grain and the grain of the nucleation surface, so that the formation of the diamond film and the substrate are not entirely brought into close contact, and the presence of tiny non-contact area, these tiny non-contact area in the diamond film into an even cover the entire surface of the substrate still exists, leaving microvoids in the film based interface. Especially when the substrate temperature increases or high CH_4 concentration, this phenomenon is more obvious last microvoids evolved into micro-cracks as Fig. 5(a)-(c). The presence of micro-voids and microcracks weakening the binding of the diamond film and the substrate, between the interface of the diamond and the properties of diamond film, the crystal grains of the diamond film is formed the initial crack. Under external force, where the initial crack first cause stress concentration at the crack tip region caused by crack propagation, triggered coating breaking off. However, through the control of the diamond film growth temperature, the concentration of carbon source and the substrate surface temperature uniformity optimization, we are able to prepare a high-quality, without micro-cracks diamond film, as shown in Fig.5 (d).

4. Results and discussion

The formation of defects and crack represents an intrinsic problem in fabricating diamond film structures. In this work, of the study on diamond film deposited at different substrate temperature, through combination use of XRD, OM and SEM shows that some defects rapidly increases along with an increase in the substrate temperature. XRD analysis testifies that high temperature result in high residual stress in diamond film when the substrate temperature is less than 980 ℃. When the substrate temperature exceeds 1050 ℃, diamond film prepared has very low residual stress due to having more cracks in the film and most residual stress being released. OM and SEM results reveal that some radial cracks penetrates surface of diamond film and extends to center of diamond film. When those cracks gathered and grow up, they may induce microscopic hole and even cause local fracture in diamond film.

Acknowledgements

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References

[1] D. Li, D. Zuo, W. Lu, R. Chen, B. Xiang, M. Wang, Effects of methane concentration on diamond spherical shell films prepared by DC-plasma jet CVD. Solid State Ionics, 179 (2008) 1263-1267.
[2] D.M. Trucchi, C. Scilletta, E. Cappelli, P.G. Merli, S. Zoffoli, G. Mattei, P. Asearelli, Optimization of the performance of CVD diamond electron multipliers. Diam Relat Mat, 15 (2006) 827-832.
[3] N. Jiang, S. Kujime, I. Ota, T. Inaoka, Y. Shintani, H. Makita, A. Hatta, A. Hiraki, Growth and structural analysis of nano-diamond films deposited on Si substrates pretreated by various methods. J Cryst Growth, 218 (2000) 265-271.
[4] D. Takeuchi, C.E. Nebel, S. Yamasaki, Surface defect states analysis on diamond by photoelectron emission yield experiments. Diam Relat Mat, 16 (2007) 823-825.
[5] R. Ikeda, M. Hayashi, A. Yonezu, T. Ogawa, M. Takemoto, Fracture observation of polycrystalline diamond film under indentation test. Diam Relat Mat, 13 (2004) 2024-2030.
[6] A.I. Shames, A.M. Panich, S. Porro, M. Rovere, S. Musso, A. Tagliaferro, M.V. Baidakova, V.Yu. Osipov, A.Ya. Vul', T. Enoki, M. Takahashi, E. Osawa, O.A. Williams, P. Bruno, D.M. Gruen, Defects localization and nature in bulk and thin film utrananocrystalline diamond. Diam Relat Mat, 16 (2007) 1806-1812.
[7] J. Stiegler, A. Bergmaier, J. Michler, Y. von Kaenel, G. Dollinger, E. Blank, Impurity and defect incorporation in diamond films deposited at low substrate temperatures. Diam Relat Mat, 7 (1998) 193-199.
[8] J.H. Jeong, S.Y. Lee, W.S. Lee, Y.J. Baik, D. Kwon, Mechanical analysis for crack-free release of chemical-vapor-deposited diamond wafers. Diam Relat Mat, 11 (2002) 1597-1605.
[9] Y.L. Kang, Z.F. Zhang, H.W. Wang, Q.H. Qin, Experimental investigations of the effect of thickness on fracture toughness of metallic foils. Mat Sci Eng A-Struct 394 (2005) 312-

319.
[10] H.W. Wang, Y.L. Kang, Z.F. Zhang, Q.H. Qin, Size effect on fracture toughness of metallic foil, Int J Fracture, 123 (2003) 177-185.
[11] C.S.J Pickles, The fracture stress of chemical vapour deposited diamond. Diamond and Related Materials, 11 (2002) 1913-1922.
[12] D. Zuo, D. Li, W. Lu, R. Chen, Y. Sun, Methods and devices of uniform substrate temperature in preparing spherical diamond film. Chinese Patent No. 200810024384.5, 2010.
[13] D. Li, D. Zuo, R. Chen, B. Xiang, W. Lu, M. Wang, Growth of high quality spherical diamond film by DC plasma jet CVD. Synthesis and Reactivity in Inorganic Metal-Organic and Nano-Metal Chemistry 38 (2008) 325-328.
[14] O. Durand, R. Bisaro, C.J. Brierley, P. Galtier, G..R. Kennedy, J.K. Krüger, J. Olivier, Residual stresses in chemical vapor deposition free-standing diamond films by X-ray diffraction analyses. Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 288 (2000) 217-222.
[15] C. Li, H. Li, D. Niu, F. Lu, W. Tang, G. Chen, H.Zhou, F. Chen, 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. Surface & Coatings Technology, 201 (2007) 6553-6556.
[16] D. Dai, K. Zhou, Diamond film deposition preparation process and application, Beijing, Metallurgical Industry Press, 2001.