

Effects of deposition parameters on microstructure and thermal conductivity of diamond films deposited by DC arc plasma jet chemical vapor deposition

QU Quan-yan(瞿全炎)^{1,2}, QIU Wan-qi(邱万奇)¹, ZENG De-chang(曾德长)¹,
LIU Zhong-wu(刘仲武)¹, DAI Ming-jiang(代明江)³, ZHOU Ke-song(周克崧)³

1. School of Materials Science and Engineering, South China University of Technology,
Guangzhou 510640, China;

2. Guangdong Institute of Special Equipments Inspection and Supervision, Guangzhou 510655, China;

3. Guangzhou Research Institute of Non-ferrous Metals, Guangzhou 510651, China

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Abstract: The uniform diamond films with 60 mm in diameter were deposited by improved DC arc plasma jet chemical vapor deposition technique. The structure of the film was characterized by scanning electronic microcopy(SEM) and laser Raman spectrometry. The thermal conductivity was measured by a photo thermal deflection technique. The effects of main deposition parameters on microstructure and thermal conductivity of the films were investigated. The results show that high thermal conductivity, 10.0 W/(K·cm), can be obtained at a CH₄ concentration of 1.5% (volume fraction) and the substrate temperatures of 880–920 °C due to the high density and high purity of the film. A low pressure difference between nozzle and vacuum chamber is also beneficial to the high thermal conductivity.

Key words: diamond film; microstructure; thermal conductivity; DC arc plasma jet CVD

1 Introduction

Due to the high thermal conductivity of the diamond, the diamond film fabricated by chemical vapor deposition(CVD) has been considered as an important material for the heat spreading applications[1]. Heat conduction in diamond film takes place primarily by phonon to phonon transfer and the thermal conductivity is affected severely by the phonon scattering caused by impurities, defects and boundaries[2–3], which depend on the deposition technique and the parameters of the technique[4]. The thermal properties of diamond films synthesized by microwave plasma CVD, combustion flame, r.f. plasma torch CVD and hot filament CVD have been studied[5–12]. GU et al[5] and BABA et al[6] investigated the effect of the CH₄ concentration on the thermal conductivity(σ) of diamond films produced by microwave chemical vapor deposition(MWCVD) and hot filament chemical vapor deposition (HFCVD), respectively. They found that as the CH₄ concentration

increased, σ decreased. They obtained a high σ value of 15.3 W/(K·cm) or 12.0 W/(K·cm) both at the CH₄ concentration of 1.0% (volume fraction, the same below if not mentioned). Unfortunately, these techniques cannot be extensively used for industrial production due to the low deposition rate. In contrast, the direct current arc plasma jet(DCAPJ) CVD technique is one of the most effective methods to fabricate the diamond film owing to the high deposition rate[13–15]. The quality of diamond films prepared by the DCAPJ CVD technique is determined by the main deposition parameters of CH₄ concentration, substrate temperature, pressure difference between nozzle and vacuum chamber. For the diamond deposited by DCAPJ CVD, GRAEBNER et al[16] studied the effects of the methane content on the thermal conductivity, and a high thermal conductivity of 9.5 W/(K·cm) was achieved at the lowest methane content of 2%. LEE et al[17] prepared crack-free freestanding diamond films by using step-down control of the substrate temperature and obtained a high thermal conductivity of 12–14 W/(K·cm). However, systematic

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Corresponding author: ZENG De-chang; Tel: +86-20-87111278; E-mail: medczeng@scut.edu.cn
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data of the effects of main deposition parameters on the microstructure and the thermal conduction are still inadequate.

In the present work, a series of diamond films were synthesized by DCAPJ CVD technique. During deposition, arc power and chamber pressure were fixed. The effects of other deposition parameters on σ were investigated to explore the optimized process for an improved thermal conduction and study how these parameters affect microstructure and thermal conductivity of the diamond films.

2 Experimental

The diamond films were synthesized by the improved DCAPJ CVD method[15,18]. The mixed source gases are composed of hydrogen(H_2) and methane(CH_4). The sintered Molybdenum block with a diameter of 60 mm was used as the substrate. The substrate was polished with abrasive paper and cleaned with acetone prior to deposition. Diamond films were peeled spontaneously from the substrate during cooling after deposition because of the difference between the thermal expansion coefficients of the film and the substrate. The uniform diamond films with 60 mm in diameter have been successfully obtained. The detailed deposition parameters are summarized as follows: CH_4 concentrations of 0.6%–3.0%, substrate temperature range of 750–950 °C, pressure difference between nozzle and vacuum chamber of 8.3–9.3 kPa, arc power of 17 kW and chamber pressure of 4.0 kPa.

The substrate temperature was measured by a SCIT-Infrared Thermometer. The morphologies of growth surface and cross section for films were observed by scanning electronic microscopy(SEM). The Raman spectra were used to characterize the purity of the diamond films. The in-plane thermal conductivity of the diamond film was determined by a photo thermal deflection(PTD) technique. Details of this method were described in Refs.[19–20].

3 Results

The surface morphologies of diamond films deposited at various CH_4 concentrations are shown in Fig.1. For 0.6% CH_4 , the grains are in facet shape (Fig.1(a)), while for 3.0% CH_4 (Fig.1(c)), the grains change to spherical shape. For these two cases interspaces between grains can be seen clearly which reduce the film density. The cracks in grains (Fig.1(a)) are also very clear, which may lead to phonon scattering. Fortunately, the CH_4 concentration of 1.5% is appropriate for forming grain structure with surface feature of facet shape and so-called second nuclei filled

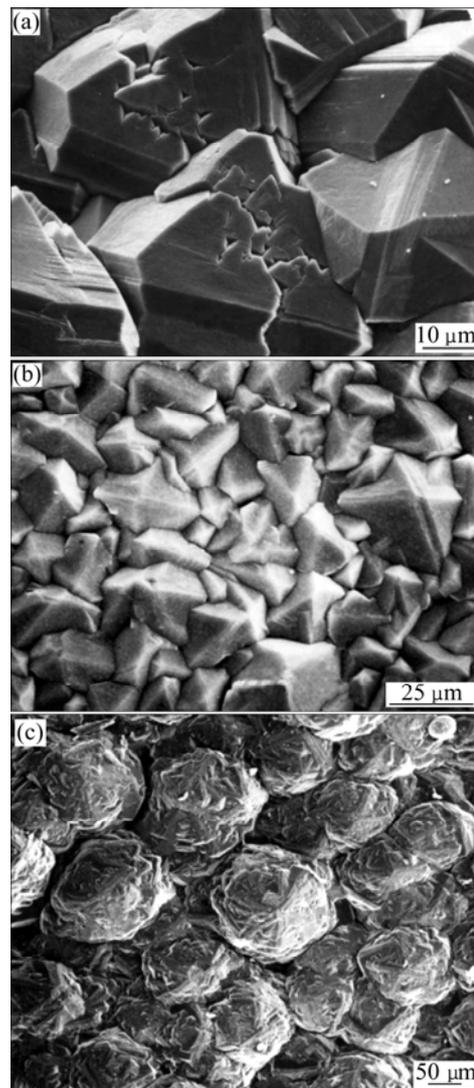


Fig.1 SEM micrographs of growing surfaces of diamond films deposited at CH_4 concentrations of 0.6% (a), 1.5% (b) and 3.0% (c)

in the interspaces.

Fig.2 shows the surface morphologies of diamond films fabricated at various temperatures. The different surface microstructures are also demonstrated. For each case, regular shape of surface grains implies the preferred crystalline plane and orientation. For the film synthesized at 770 °C, most exposed crystalline planes on surface are rectangular (Fig.2(a)), indicating exposed $\{220\}$ planes. At the temperature of 820 °C, the grains change into irregular shape (Fig.2(b)). This shape forms because the exposed planes are the mixture of $\{220\}$, $\{111\}$ and $\{100\}$ planes. When the diamond films were fabricated at higher temperatures of 870, 900 and 935 °C, most grains are almost in octahedron shape (Figs.2(c)–(e)), which indicates that the exposed crystalline planes are $\{111\}$ planes. Previous investigations reveal that the exposed crystalline planes of square $\{100\}$,

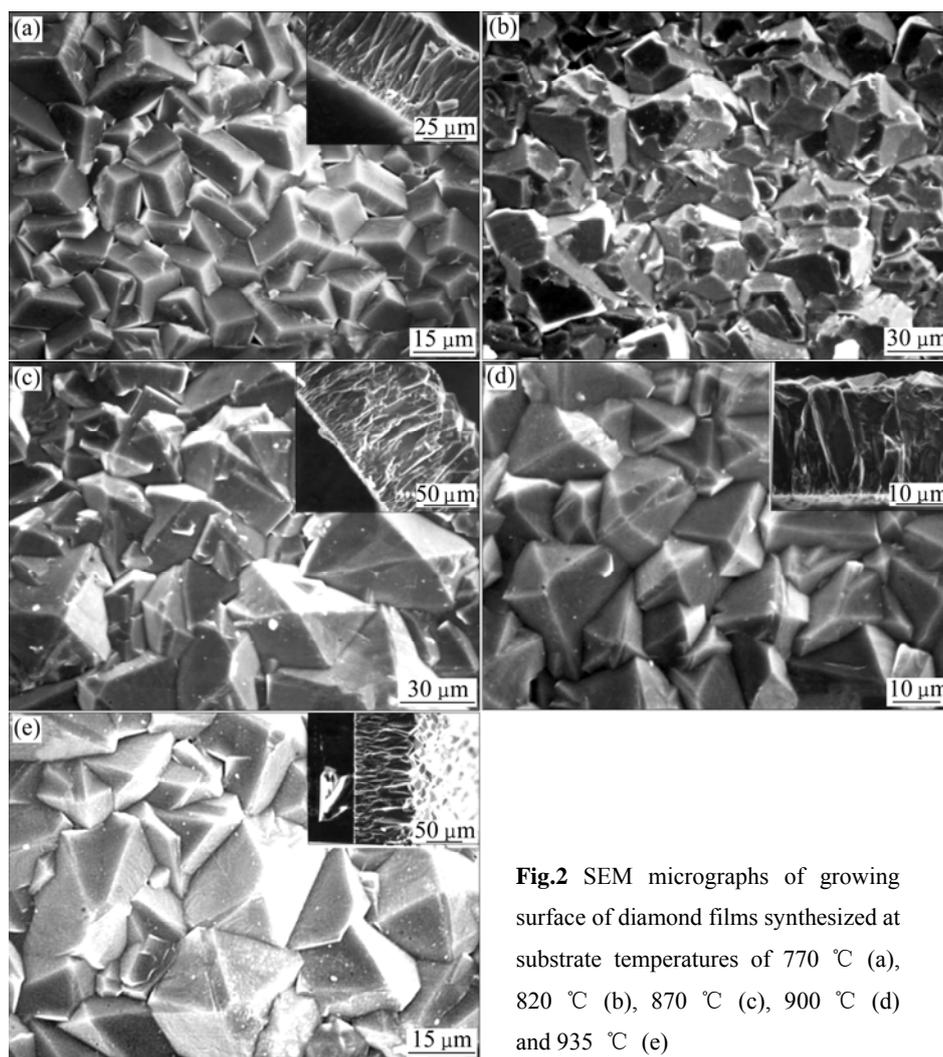


Fig.2 SEM micrographs of growing surface of diamond films synthesized at substrate temperatures of 770 °C (a), 820 °C (b), 870 °C (c), 900 °C (d) and 935 °C (e)

rectangle {220}, and triangle {111} correspond to the preferred orientations of [100], [220] and [111], respectively[21–22]. Therefore, the results indicate that as the temperature increases from 750 to 935 °C, the exposed crystalline planes on film surfaces change from {220} to {111} planes and the preferred orientations change from [220] to [111].

As we know, the interspaces are closely related to the exposed crystalline planes and the preferred orientation of the film. For the diamond film with exposed crystalline planes of {220}, the interspaces are easy to be formed between the rectangular solid grains. But the films with exposed crystalline planes of {111} have fewer interspaces due to the octahedron shape of the grains. In the case of the mixed exposed planes, the content of interspaces falls between the two cases above. The above analysis can be verified by SEM micrographs of the cross sections of the films. In the inset of Fig.2(a), the interspaces among the columnar grains can be clearly seen. For the diamond film fabricated at 870 °C, there is still a few interspaces (the inset in Fig.2(c)), but for the

films deposited at 900 °C and 935 °C, the films are similarly very dense (the insets in Fig.2(d) and Fig.2(e)). Above results indicate that the temperature has an important effect on the film density.

Laser Raman spectrometry can be employed to evaluate the film quality. For diamond films, the broad scattering peak around 1 556 cm^{-1} on the laser Raman spectrum is caused by amorphous carbons, the sharp scattering peak around 1 332 cm^{-1} is caused by diamond carbons, and the background intensity is determined by a small number of amorphous carbons, cavities, defects, etc[22]. Generally, for high quality of diamond film, the Raman spectrum shows a sharp scattering peak, low background intensity, and no broad scattering peak. Fig.3 shows the Raman spectra of three diamond films synthesized at 870, 900 and 935 °C. All three spectra have a sharp peak at 1 332 cm^{-1} . For the film deposited at 870 °C, the broad scattering peak around 1 556 cm^{-1} can be distinguished, and the background intensity is higher than the other two cases. The result indicates that this film has relatively more interspaces and low purity.

For the diamond film fabricated at 900 °C, the background intensity is extremely low, and no broad scattering peak can be seen clearly, which refers to a very high purity. By comparing spectrum III with spectrum II, there are no broad scattering peaks on both spectra, but the background intensity of spectrum III is higher than that of spectrum II. Although the background intensity can be caused by both the interspaces or defects and the amorphous carbons in the materials, the background intensity of spectrum III is only caused by the amorphous carbons, since from the SEM images (the insets in Fig.2(d) and Fig.2(e)), almost no interspaces or defects can be observed on the cross sections of the films corresponding to these two spectra. Thus, the purity of the diamond film prepared at 935 °C is lower than that prepared at 900 °C. Based on the above results, the purity of the film increases with the increasing temperature in the range of 750–900 °C, and when the temperature exceeds 900 °C, the purity decreases.

Fig.4 shows the variation of the thermal conductivity (σ) for the diamond film with respect to the

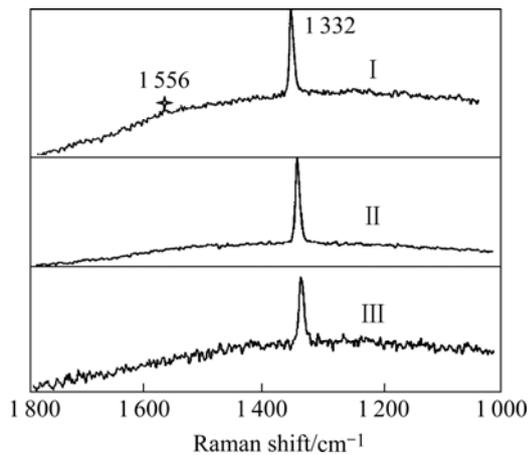


Fig.3 Raman spectra of diamond films synthesized at 870 °C (spectrum I), 900 °C (spectrum II) and 935 °C (spectrum III)

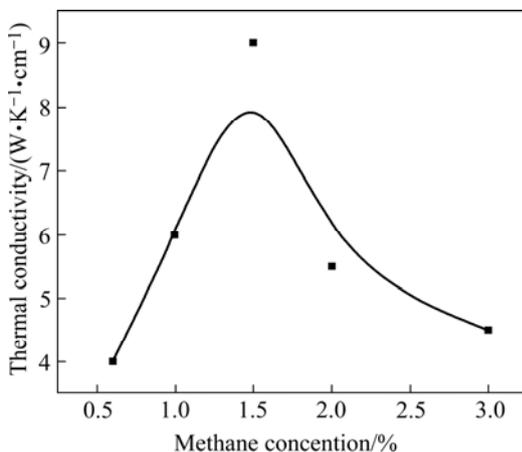


Fig.4 Thermal conductivity as function of CH₄ content for diamond films deposited at 900 °C

CH₄ content in the mixed gas. As we can see, σ increases with increasing CH₄ content from 0.5% to 1.5%. For a CH₄ content of 1.5%, σ reaches the maximum value of 9.0 W/(K·cm).

The current results are different from those for the diamond films fabricated by hot filament chemical vapor deposition (HFCVD) and direct current discharge system obtained by GU et al[5] and GRAEBNER et al[16] respectively. Their results indicate that the thermal conductivity decreases with the CH₄ content in the range of 1%–5% or 2%–10%.

Fig.5 shows the thermal conductivity of the diamond films as a function of substrate temperature. When the temperature is 770 °C, σ is only 2.6 W/(K·cm). In the temperature range of 750–900 °C, σ increases with increasing the temperature. A large value of around 10.0 W/(K·cm) is obtained at 880–900 °C. When the temperature exceeds 900 °C, the thermal conductivity decreases.

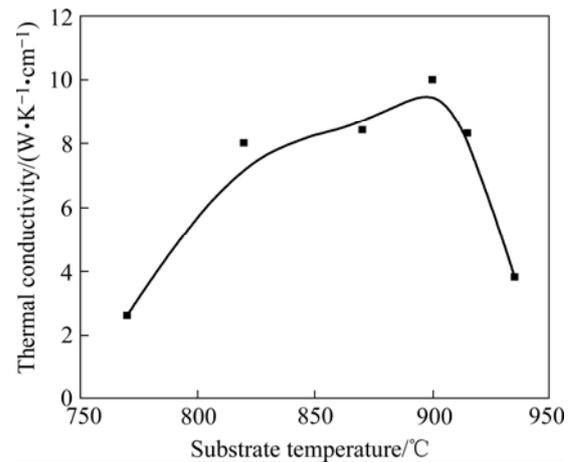


Fig.5 Thermal conductivity as function of substrate temperature for diamond films deposited at 1.5% CH₄

Fig.6 shows the dependence of thermal conductivity on the pressure difference between nozzle and chamber. As the pressure difference decreases in the range of 9.3–8.3 kPa, the thermal conductivity increases. Therefore, the high thermal conductivities are obtained at relatively low pressure difference.

4 Discussion

4.1 Effects of deposition parameters on microstructure

During deposition of the film, nucleation and growth of diamond is a kind of non-equilibrium thermal dynamic process. The gas phase species of CH, CH₂, CH₃ and H rest on nuclei or on the substrate and then transfer to a favorable position to nucleate or grow. The diamond carbon phase and non-diamond carbon phase are formed simultaneously. Non-diamond carbons can be

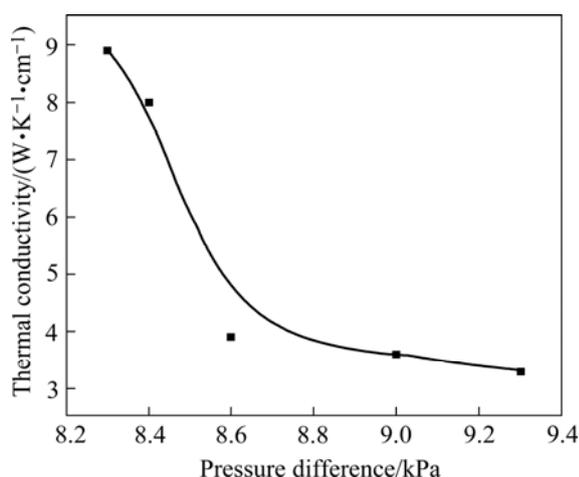


Fig.6 Thermal conductivity as function of pressure difference between nozzle and chamber for diamond films deposited under atmosphere with 1.5% CH₄ at 900 °C

etched by H atoms.

At a low CH₄ concentration, the high H etching rate leads to a high purity and also the nucleation rate is reduced. As the CH₄ concentration increases, a high active gas phase species is achieved, which leads to a high nucleation rate and also a high growth rate of the diamond. Under this condition, the H etching rate increases slowly or even remains unchanged, but the growth rate of non-diamond phases increases rapidly. At a very high CH₄ concentration, the active species cannot move along the diamond nucleus in time and the diamond nucleates or grows locally, which makes spherical pseudo-grains form with many micro-crystalline grains [23], as shown in Fig.1(c). Also, at a very high CH₄ concentration, since the H etching rate is lower than the formation rate of non-diamond carbon phase, a low purity is obtained in the film. The above analysis explains the effects of the CH₄ content on microstructure of diamond films, as shown in Fig.1.

The substrate temperature has important effects on the structure and purity of the diamond films. During diamond growth, the different exposed grain planes and preferred orientations are determined by the dynamic growth rate of crystalline plane and the plane with the smallest growth rate will be exposed[24]. It is accepted that the growth rate of {220} planes is higher than that of {100} or {111} planes, and the ratio of growth rate of {100} to {111} planes depends on the deposition atmosphere, which is determined by the activating energy and the source gas content[25]. The activating energy is related to the depositing temperature and the atmosphere is not changed by the CH₄ concentration in current case. In the deposition atmosphere, gas phase species of CH, CH₂, CH₃ and H co-exist. The CH₂

content determines the growth rate of the {100} planes while the CH content determines the growth rate of {111} planes[25]. CH formation from CH₄ needs more activating energy than CH₂ formation when the temperature increases, as discussed in Ref.[25]. The CH content increases and the CH₂ content decreases due to increasing activating energy. At 820 °C, the CH and CH₂ contents are not high enough to make any {220}, {100} or {111} planes grow faster than others, thus the growing surface is irregular and the orientation is the mixture of [220], [100] and [111] (Fig.2(b)). In the temperature range of 870–935 °C, the CH content is higher than that of CH₂, which makes {100} planes grow faster than {111} planes and causes the exposure of {111} planes (Figs.2(c), (d) and (e)). The results in the temperature range of 870–935 °C are in good agreement with those of some previous researches[21, 24–25]. Despite many experimental data about exposed {100} and {111} planes, no exposed {220} planes were observed before. In the present work, we found that {220} planes were exposed at 770 °C. The reason for this should be further studied in details.

The effect of the temperature on film purity can be explained as follows. In the range of 750–900 °C, when the temperature increases, the gas phase species moves more quickly along the surface of diamond nuclei and the conversion rate of sp² C to sp³ C increases, therefore, more diamond phases are formed and the film purity and quality are improved. However, when the temperature exceeds 900 °C, H atoms bonded to the surface of diamond nucleus will be excited and have enough energy to run away, thus the sp³ C will become unstable and be possible to change back to sp² C.

4.2 Effects of deposition parameters on thermal conductivity

Heat conduction in diamond film can be severely reduced by the phonon scattering caused by impurities, defects and boundaries. Impurities are mainly non-diamond carbon phases, compounds, etc. Non-diamond carbon phase will cause isotope-phonon scattering. Compounds are formed by the reaction of carbon and elements from substrate and locate in the superficial zone of the bottom surface. These compounds will not affect the value of σ because σ is measured along the film surface in the present work. Boundaries and defects, such as dislocations, cracks in the grains, and cavities between grains, also lead to phonon scattering and reduce thermal conduction. These impurities, defects and grain boundaries are mainly determined by the growing conditions of the film, such as gas content, temperature and chamber pressure. It is

accepted that high density and high purity are beneficial to the high thermal conductivity of diamond films.

The analysis of the influence on the microstructure for CH₄ concentration indicates that as the methane concentration increases, the density increases first and then decreases, and the purity decreases. At a CH₄ content lower than around 1.5%, the density is low and the purity is very high, while at a CH₄ content higher than around 1.5%, the density and the purity are both low, which indicate that the thermal conductivity is low. However, at the CH₄ content of 1.5%, the high density and medium purity are obtained, which implies the highest thermal conductivity. The above analysis explains the function of the CH₄ content on the thermal conductivity, as shown in Fig.4.

Fig.2 demonstrates that the film density increases when the temperature increases from 770 °C to 870 °C. High density was obtained at temperature of 870 °C or higher. As discussed earlier, the purity of the diamond film also increases with temperature increasing in the range of 750–900 °C and decreases when the temperature exceeds 900 °C. Since improved density and purity will enhance the thermal conduction that is improved with temperature increasing in the range of 750–900 °C and drops when the temperature exceeds 900 °C, as shown in Fig.5. At 880–900 °C, a large value of around 10.0 W/(K·cm) is achieved naturally due to the high purity and high density.

The velocity of plasma jet is determined by the pressure difference between nozzle and vacuum chamber. Basically, a larger pressure difference will cause a higher velocity, thus a lower density and a worse quality of the film, which will reduce the thermal conductivity, as shown in Fig.6. Generally, for a lower pressure difference, more active species CH, CH₂, CH₃ and H form in the high density plasma. The high collision rate and low energy of these species are beneficial to the nucleation and growth. As we know, for a low velocity, the species of diamond growing gas phase from arc plasma has enough time to diffuse to a favorable position on the diamond surface for epitaxial growth, by which the free energy of the system can be reduced. Therefore, the defects and impurities will be diminished, thus, the high thermal conductivity can be obtained. On the other hand, for a high velocity of plasma jet, more gas phase species can contribute carbon to the mass diamond growth. Since there are a lot of species, one species can only diffuse a short distance before meeting another (or more) and form a second nucleus of diamond. This increases the grain boundaries of the diamond film, which will enhance the phonon scattering and then reduce the thermal conductivity.

5 Conclusions

1) The uniform diamond films with a large thermal conduction of 10.0 W/(K·cm) is obtained, which is comparable to that of II b type natural diamond, deposited by improved DCAPJ CVD technique.

2) The effects of main deposition parameters on microstructure and thermal conductivity of the films were studied. It is found that the high thermal conductivity can be obtained in the film produced under the argon atmosphere with 1.5% CH₄ and at the substrate temperatures of 880–920 °C. Decreasing the pressure difference between nozzle and vacuum chamber is beneficial to the high thermal conductivity. High density and high purity which are functions of deposition parameters make large contributions to the high thermal conductivity.

References

- [1] BUSCH J V, DIMUKES J P. Trends and market perspectives for CVD diamond [J]. *Diamond and Related Materials*, 1994, 3: 295–302.
- [2] SLACK G A. Nonmetallic crystals with high thermal-conductivity [J]. *Journal of Physics and Chemistry of Solids*, 1973, 34(2): 321–335.
- [3] GRAEBNER J E, MUCHA J A, BAIOCCHI F A. Sources of thermal resistance in chemically vapor deposited diamond [J]. *Diamond and Related Materials*, 1996, 5: 682–687.
- [4] GRAEBNER J. E. Thermal conductivity of CVD diamond: Techniques and results [J]. *Diamond Films Technology*, 1993, 3: 77–130.
- [5] GU Chang-zhi, JIN Zeng-sun, LU Xian-yi, ZOU Guang-tian, ZHANG Ji-fa, FANG Rong-chuan. The deposition of diamond film with high thermal conductivity [J]. *Thin Solid Films*, 1997, 311: 124–127.
- [6] BABA K, AIKAWA Y, SHOHATA N. Thermal conductivity of diamond films [J]. *Journal of Applied Physics*, 1991, 69: 7313–7315.
- [7] BACHMANN P K, HAGEMANN H J, LADE H, LEER D, WIECHERT D U, FOURIER H, PLAMANN K. Thermal-properties of C/H-grown, C/H/O-grown, C/H/N-grown and C/H/X-grown polycrystalline CVD diamond [J]. *Diamond and Related Materials*, 1995, 4: 820–826.
- [8] ONO A, BABA T, FUNAMOTO H, NISHIKAWA A. Thermal conductivity of diamond films synthesized by microwaves plasma CVD [J]. *Japanese Journal of Applied Physics*, 1986, 25(10): 808–809.
- [9] MA Ying, WANG Lin-jun, LIU Jian-min, SU Qing-feng, XU Run, PENG Hong-yan, SHI Wei-min, XIA Yi-ben. Characterization of (100)-orientated diamond film grown by HFCVD method with a positive DC bias voltage [J]. *Trans Nonferrous Met Soc China*, 2006, 16(s): 313–316.
- [10] YI Jian-hong. Synthesis of high grade octahedron diamond through epitaxial growth [J]. *Trans Nonferrous Met Soc China*. 1999, 9(3): 477–480.
- [11] YANG Kan-cheng, XIA Yi-ben, WANG Lin-jun, LIU Jian-min, SU Qing-feng, XU Run, PENG Hong-yan, SHI Wei-min. Influence of intermittently etching on quality of CVD diamond thin films [J].

Trans Nonferrous Met Soc China, 2006, 16(s): 321–323.

- [12] WORT C J H, SWEENEY C G, COOPER M A, SCARSBROOK G A, SUSSMANN R S. Thermal properties of bulk polycrystalline CVD diamond [J]. *Diamond and Related Materials*, 1994, 3: 1158–1167.
- [13] KURIHARA K, SASAKI K, KAWARADA M, KOSHINO N. High rate synthesis diamond by plasma jet chemical vapor deposition [J]. *Applied Physics Letters*, 1988, 52(6): 437–438.
- [14] SUZUKI K, SAWABE A, YASUDA H, INUZUKA T. Growth diamond thin films by dc plasma chemical vapor deposition [J]. *Applied Physics Letters*, 1987, 50(12): 728–729.
- [15] BOHM V, BUCK V, LIESENFELD M, NAUBERT T, ZENG J. Influence of plasma parameters on the properties of diamond films deposited the arc technique [J]. *Diamond and Related Materials*, 1994(4): 33–42.
- [16] GRAEBNER J E, RALCHENKO V G, SMOLIN A A, OBRAZTSOVA E D, KOROTUSHENKO K G. Thermal conductivity of thin diamond films grown from d.c. discharge [J]. *Diamond and Related Materials*, 1996, 5: 693–698.
- [17] LEE J K, EUN K Y, CHAE H B, BAIK Y J. Free-standing diamond wafers deposited by multi-cathode, direct-current, plasma-assisted chemical vapor deposition [J]. *Diamond and Related Materials*, 2000, 9: 364–367.
- [18] QU Q Y. Study on affecting elements of quality for thick diamond films synthesized by CVD [D]. Guangzhou: South China University of Technology, 2000.
- [19] ZHANG Ji-fa, WANG Guan-zhong, CUI Jing-biao, FANG Rong-chuan. Photothermal deflection thin films and its applications [J]. *China High Technology Letters*. 1995, 21: 31–34.
- [20] JACKSON W B, AMER N M, BOCCARO A C, FOURNIER D. Photothermal deflection spectroscopy and deflection [J]. *Applied Optics*, 1981, 20: 1333–1344.
- [21] GU Chang-zhi, JIANG X, JIN Zeng-sun. The preparation of high quality oriented diamond thin films via low temperature and hydrogen ion etched nucleation [J]. *Diamond and Related Materials*, 1999, 8: 262–266.
- [22] LI Duo-sheng, ZUO Dun-wen, CHEN Rong-fa, XIANG Bing-kun, ZHAO Li-gang, WANG Min. Microstructure and growth mechanism of diamond film prepared by DC-plasma CVD [J]. *Rare Metals Materials Science and Engineering*, 2007, 36(4): 648–651.
- [23] QIU Wan-qi, LIU Zheng-yi, CHEN Jian-hui. Formation mechanism of ball-like diamond [J]. *The Chinese Journal of Nonferrous Metals*, 2002, 12(3): 566–569. (in Chinese)
- [24] BREZA J, KADLECIOVA M, VOJS M, MICHALKA M., VESELY M, DANIS T. Diamond icosahedron on a TiN-coated steel substrate [J]. *Microelectronics Journal*, 2004, 35: 709–712.
- [25] SUN Bi-wu, ZHANG Xiao-pin, LIN Zhang-da. Growth mechanism and the order of appearance of diamond (111) and (100) facets [J]. *Physical Review B*, 1993, 47(15): 9816–9824.

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