Applied Surface Science 353 (2015) 548–552

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The effect of periodic magnetic field on the fabrication and field emission properties of nanocrystalline diamond films

Hangyu Long[a,b], Shasha Li[a], Hao Luo[a], Yijia Wang[a], Q.P. Wei[a,b,*], Z.M. Yu[a,b,*]

[a] School of Materials Science and Engineering, Central South University, Changsha 410083, PR China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China

ARTICLE INFO

Article history:
Received 8 March 2015
Received in revised form 12 June 2015
Accepted 24 June 2015
Available online 30 June 2015

Keywords:
Chemical vapor deposition
Periodic magnetic field
Nano-diamond film
Field emission

ABSTRACT

In this paper nanocrystalline diamond films have been deposited initially through a novel technique periodic magnetic field (PMF) (magnetic field $B = B_0 \sin \omega t$) assisted hot filament chemical vapor deposition. The effect of the increasing angular frequency (ω) on diamond film deposition was investigated. SEM and Raman spectroscopy were used to characterize film. It was found that higher ω was in favor of nano-diamond film growth. Field emission results show that the turn-on electric field of the nano-diamond film deposited at ω = 20,000 rpm was 2.9 V/μm, and its current density reached 32.7 μA/cm^2 measured at an applied field 6.5 V/μm.

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1. Introduction

Diamond possesses a negative electron affinity surface that, in principle, allows its surface to emit electrons under low electric fields [1,2]. Compared to the microcrystalline diamond thin film, nanocrystalline diamond (NCD) films with smaller grains attracts much interests as a promising cold cathode field emission material, due to its lower turn-on field, high current density, high power at high temperature and high stability and reliability on service [3]. This empowers NCD films appreciable application value in vacuum electronic devices like field emission displays and microwave amplifier.

Compared with other deposition techniques, the hot filament chemical vapor deposition (HFCVD) process is a potential alternative to grow nanocrystalline diamond films as it can be easier to scale up and far less expensive, however, its thermal-excited plasma density is insufficient and the nucleation rate is low. NCD films are usually grown in hydrogen-rich environment and require high nucleation density. Thus improving the nucleation density is a key factor in the preparation of NCD. There are two approaches to improve the nucleation. One is the pretreatment for substrate through a sputtered layer to improve the adsorption of nano-diamond particles [4]. While the multi-layer structure confronts complex technology and may bring binding ability degradation between layers. Another is exploiting assistant equipment to enhance the plasma density. A bias system assisted [5] and direct current plasma assistance chamber [6] have effectively improved the nucleation density and subsequent growth of diamond films. Little et al. [7] demonstrated a new technique for forming nano-diamond at atmospheric pressure by using strong static magnetic field and proved that magnetic field can promote the nucleation and growth of diamond, while the size of these particles is not uniform. To our knowledge, the application of PMF assisted HFCVD in nano-diamond film fabrication has not been reported. PMF would bring an electric field which changes periodically and these two are coupled easily. In the sputtering apparatus, the purpose of using a magnetic field is to make more efficient use of the electrons, and cause them to produce more ionization. For these reasons, we designed a PMF-HFCVD equipment to prepare nano-diamond film.

In the present work, we initially studied the influence of magnetic field on the nano-diamond growth. Continuous and dense nano-diamond films have been directly deposited on Mo–Re alloy substrates. Strong electron emission at low electric field was observed in nano-diamond film. The PMF are technologically useful because nano-diamond film can be easily and economically fabricated.

* Corresponding authors at: School of Materials Science and Engineering, Central South University, Changsha 410083, PR China.
E-mail addresses: qiupwei@csu.edu.cn (Q.P. Wei), zhiming@csu.edu.cn (Z.M. Yu).

http://dx.doi.org/10.1016/j.apsusc.2015.06.151
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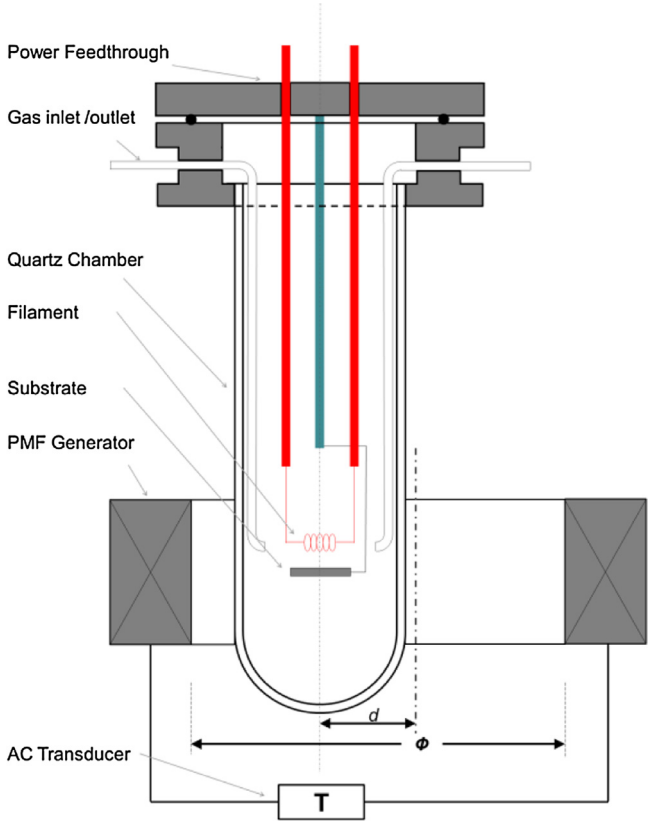

Fig. 1. Schematic diagram of the PMF–HFCVD system.

2. Experimental

Diamond film was deposited by the PMF–HFCVD system which was shown schematically in Fig. 1. The PMF–HFCVD system consists of a quartz chamber, a three-phase stator winding and an AC transducer. The PMF, with $B = B_0 \sin \omega t$, was generated by the stator winding of a three-phase electric motor, and its angular frequencies (ω) can be regulated from 3000 to 45,000 rpm. The magnetic field (B_0) declined from 106 to 32 Gauss with the increase of ω (rpm). Prior to diamond film deposition, the Mo–Re substrates ($10 \times 10\,mm^2$) were ultrasonic-cleaned in acetone and deionized water for 10 min consecutively. Then substrates were ultrasonically pretreated in nano-diamond colloid for 30 min and in ethanol for 2 min successively. Finally, Mo–Re substrates were mounted on the stainless steel stage in the chamber. The reaction parameters are presented in Table 1. The surface morphology of samples was analyzed by FEI Sirion200 field emission scanning electron microscopy. The diamond film quality was investigated by a micro-Raman spectrometer (Lab Raman HR800), at an excitation wavelength of 488 nm (argon ion laser) with a power of 20 mW. Briefly, current–voltage (I–V) curve of field emission properties measurement were performed at a high vacuum of 10^{-6} Pa, the anode–cathode separation was kept at 330 μm, and the anode area was 1 cm^2.

Table 1
The parameters of the diamond films deposition.

Parameters	Value
Frequency of the PMF/s^{-1}	0, 10,000, 20,000, 30,000
CH_4:H_2	1%
Total flow rate/sccm	20
Pressure/kPa	3
Substrate temperature/°C	650
Deposition time/min	20

3. Results and discussion

Fig. 2 gives the morphology of diamond films deposited under different angular frequencies of the PMF. The appearance of films varies with the introduction of PMF. With no PMF applied, the film is discontinuous and the diameter of well-faceted diamond grains is ~300 nm. The crystal size diminishes with the increase of ω. Grains of ~60 nm in size can be obtained under 10,000 rpm, while the film remains discontinuous. When the ω of 20,000 rpm is applied, dense and continuous film is obtained and the grain size becomes too small to be recognized. Moreover, structures resembling carbon nanotubes can be observed (represented by the red rows in Fig. 2(c)) [8], and the main result of increasing ω to 30,000 rpm is the growing number of such structures. Generally, methane concentrations for growth of nanotube need to be higher than for nanocrystalline diamond in the HFCVD. The appearance of this structure indicates that the concentration of active carbon particles probably increases along with ω. Based on the surface morphology analysis above, it can be seen that increasing nucleation density and diminishing crystal size can be reached by increasing ω of PMF.

Fig. 3 shows the Raman spectra of films deposited with and without PMF. Due to the characteristic peak broadening and overlapping, multi-Lorentzian fit has been used to determine the location and intensity of each peak. Each fitted spectrum consists of different parts representing different phases in the film. The characteristic peak of diamond appears as a single sharp line at 1332 cm^{-1} (denoted as Dia). The broad band at 1350 cm^{-1} and 1580 cm^{-1} are assigned to graphite phase (D band and G band, respectively). The G peak can be associated with bond stretching of all pairs of sp^2 atoms in both rings and chains, while the D peak can be viewed in terms of breathing modes of sp^2 atoms in rings [9,10]. The bands at 1150 cm^{-1} and 1480 cm^{-1} are attributed to the presence of transpolyacetylene at grain boundaries, and they are normally viewed as the evidence of the existence of nano-diamond [11]. The broad band at 1200–1250 cm^{-1} represents the existence of nano-diamond clusters or the VDOS of tetragonal amorphous carbon [12]. It can be found that the characteristic peak of diamond appears in all samples, and with the increasing of ω, both decreasing of intensity and broadening are observed. This indicates that the purity and quality of diamond degrade gradually. While, those peaks related to sp^2 phase increase in intensity. We know that the ratio of intensities of diamond peak and G band (I_{Dia}:I_G) could be used to assess the relative amount of sp^3 phase [13]. With the increase of ω, the ratio of I_{Dia}:I_G decreases from 5.9, 1.7, 0.88, to 0.83, corresponding to no PMF, 10,000 rpm, 20,000 rpm and 30,000 rpm respectively, indicating growing amount of sp^2 phase. Considering that the sensitivity of sp^2 is about 50 times stronger than that of sp^3 [14], and the existence of sharp peak at 1332 cm^{-1} under PMF, we conclude that there remains large amount of sp^3 phase in the films. The decrease of intensity ratio from 10,000 to 20,000 rpm is much larger than that from 20,000 to 30,000 rpm implies that increasing the ω does not necessarily increase the amount of sp^2 phase obviously. However, the appearance of 1150 cm^{-1} and 1480 cm^{-1} peak evidence that the fabricated films with PMF are composed of diamond grains of nanometric dimensions, which corresponds with SEM analysis. The above analysis reveals that increasing ω can effectively minimizing grain size and enhancing the amount of boundaries, but only in a certain range.

We performed the field emission test on different samples. Field emission current density–electric field (J–E) curves and Fowler–Nordheim (F–N) plots of diamond films at different angular frequency (ω) are shown in Fig. 4. The comparison among field emission characteristics of different samples has been carried out by defining a turn-on field corresponding to current density of 1 μA/cm^2. The emission current of the diamond film without applying PMF is almost undetectable with electric field lower than 6 V/m.

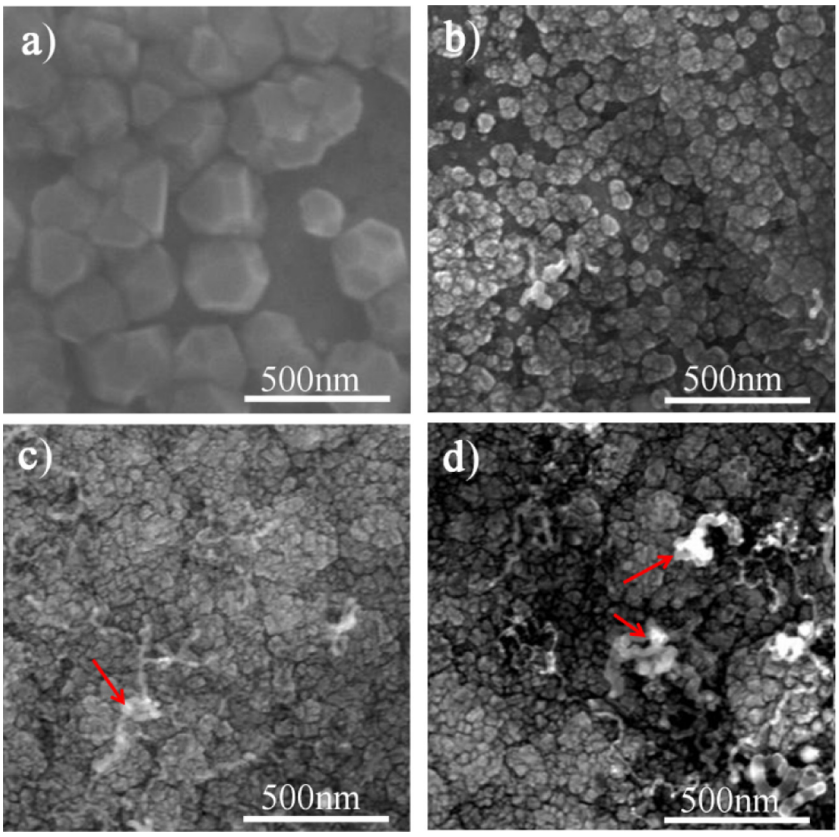

Fig. 2. SEM images of diamond films deposited with different angular frequencies, (a) no PMF, (b) **ω** = 10,000 rpm, (c) **ω** = 20,000 rpm, (d) **ω** = 30,000 rpm. (For interpretation of reference to color in this figure, the reader is referred to the web version of this article.)

With the increase in **ω**, the turn-on field decreases from 4.2 V/μm at 10,000 rpm with a discontinuous diamond film to 2.9 V/μm at 20,000 rpm with a continuous and dense diamond film. Interestingly, as the **ω** increased to 30,000 rpm, the *J*–*E* plot of diamond film is similar to that with 20,000 rpm. The turn-on field for film with 30,000 rpm is 3 V/μm, slightly higher than that with 20,000 rpm. At the same electric field in the whole range, the current emission density at 10,000 rpm is much less than at 30,000 rpm and 20,000 rpm.

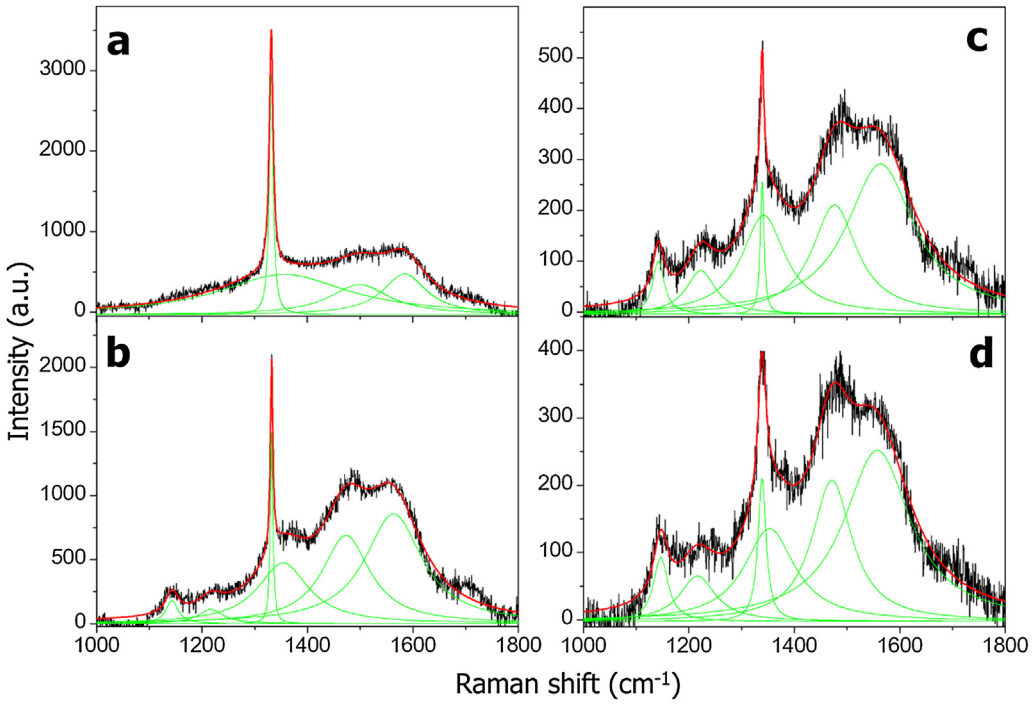

Fig. 3. Raman spectra of diamond films deposited with (a) no PMF, (b) **ω** = 10,000 rpm, (c) **ω** = 20,000 rpm, (d) **ω** = 30,000 rpm.

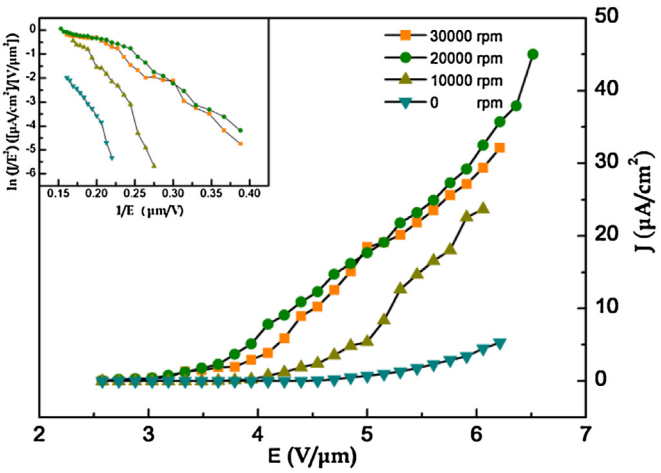

Fig. 4. *J–E* plots from samples deposited with different angular frequencies **ω**. The insets are the corresponding F–N plots.

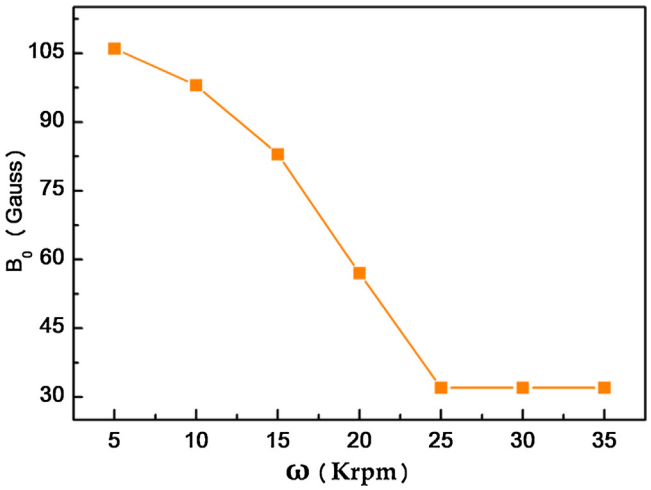

Fig. 5. Measured relationship between max magnetic field (B_0) and angular frequency (**ω**).

A current emission density of 32.7 μA/cm^2 for film at 20,000 rpm is achieved at 6.5 V/μm, which is the highest current emission density among these samples. The similar result between films with 20,000 rpm and 30,000 rpm is ascribed to the similar structure and quality of these two films, which also has been verified by SEM and Raman above. From the F–N curve of the samples, the negative slope indicates that the electron emission of our samples follows the F–N model. Obviously, the diamond film with 20,000 rpm possesses the outstanding performance among these samples. The comparison of these samples indicates that the field emission properties of diamond film deposited without or with low **ω** magnetic field are inferior, since the nucleation density is quite low and the film is discontinuous, while for dense and continuous films grown under high **ω** magnetic field, the increasing sp^2 phase at grain boundaries and carbon nanotube like phase probably result in better field emission [15,16].

Based on above analysis, we see that by coupling PMF in HFCVD, nano-diamond films with good field emission property could be obtained without using Ar gas. Generally, electrons are emitted from heated filament in HFCVD, counteracting with reaction gases in an elastic or inelastic manner. In this way, gases like CH_4 and H_2 decompose into methyl groups and hydrogen atoms, which serve as the precursors forming the films [17]. While some of the emitted groups would collide with the chamber, causing a loss about 5% [18]. Once away from the center of filament, the activated particles would be regrouped together. In our experiment, the Lorentz force is introduced by using PMF. It can change the moving path of electrons and prolong their life in the depositing process. The constriction of the magnetic field is to prevent the electron from the wall and reduce recombination losses. The applied PMF follows the law: $B = B_0 \sin \boldsymbol{\omega} t$. Fig. 5 gives the relationship between max magnetic field B_0 and angular frequency **ω**. It is observed that B_0 decreases with the increase of **ω**, however, B_0 stays constant when ω is over 25,000 rpm. Due to the Lorentz force, the charged particles (include electrons) will do spiral movement in magnetic field and are constrained in the helical region. The moving radius $\boldsymbol{r}$ is inversely proportional to magnetic field B. B_0 decreases from 98 G to 57 G, 32 G when **ω** increases from 10,000 rpm to 20,000 rpm, 30,000 rpm, respectively. Therefore, the max moving radius $\boldsymbol{r_0}$ increase with the increase of **ω**. That means more reaction gas molecular collides with charged particles when the moving radius $\boldsymbol{r}$ enlarges. Increasing collision probability results in more carbon precursor. This leads to the decrease of grain size of the film, the increase of grain boundary and sp^2 phase. From 20,000 rpm up to 30,000 rpm, the grain size of the films does not significantly decrease and the content of sp^2 phase content does not significantly increase. One reason is that the magnetic field possesses a minimum at 25,000 rpm. In addition, according to charged cluster model (CCM) [19,20], the majority of carbon groups were negatively charged in HFCVD and higher carbon concentration facilitated the formation of larger charged clusters which contain hundreds to thousands of atoms. Combined with above analysis on the increasing collisions between charged particles and gas molecules, the resulting higher carbon concentration and larger charged clusters should be the direct influencing factor. This may results in decreasing $\boldsymbol{r}$ since it is inversely proportional to electric quantity **q**. That reduces the collision probability as well. The decreasing of grain size would be inhibited by above side effects when **ω** increases to a certain extent. Moreover, the dangling bonds on the surface of diamond films make the carbon more sp^3 hybrid in magnetic field, thus stabilizing the methyl group in gas and promote the growth of diamond phase [18]. It makes it easier for diamond to nucleate and grow in HFCVD. However, further research is needed to validate this conclusion.

4. Conclusion

Dense and continuous nano-diamond films have been deposited on Mo–Re alloy by utilizing PMF–HFCVD in this paper. The new technique effectively improves the shortcoming of insufficient nucleation rates in traditional HFCVD and provides a simple and efficient method for the preparation of nano-diamond. From our results, the high angular frequency PMF is advantageous to obtain fine grains and continuous nano-diamond films. The field emission efficiency of nanocrystalline diamond film deposited with a high angular frequency PMF is better than that without PMF. The diamond film deposited under 20,000 rpm show an outstanding field emission performance. Its turn-on field reaches 2.9 V/μm, and a current emission density of 32.7 μA/cm^2 is achieved at 6.5 V/μm.

Acknowledgements

The authors are grateful to the Natural Science Foundation of China (Nos. 21271188 & 51301211), the China Postdoctoral Science Foundation (No. 2012M521541), and the State Key Laboratory of Powder Metallurgy (No. 20110933K) for financial support.

References

[1] W. Zhu, G. Kochanski, S. Jin, Low-field electron emission from undoped nanostructured diamond, Science 282 (1998) 1471–1473.
[2] J. Van der Weide, R. Nemanich, Argon and hydrogen plasma interactions on diamond (1 1 1) surfaces: electronic states and structure, Appl. Phys. Lett. 62 (1993) 1878–1880.
[3] D. Pradhan, I.N. Lin, Grain-size-dependent diamond-nondiamond composite films: characterization and field-emission properties, ACS Appl. Mater. Int. 1 (2009) 1444–1450.
[4] N.N. Naguib, J.W. Elam, J. Birrell, J. Wang, D.S. Grierson, B. Kabius, et al., Enhanced nucleation, smoothness and conformality of ultrananocrystalline diamond (UNCD) ultrathin films via tungsten interlayers, Chem. Phys. Lett. 430 (2006) 345–350.
[5] T.D. Makris, R. Giorgi, N. Lisi, L. Pilloni, E. Salernitano, Bias enhanced nucleation of diamond on Si(1 0 0) in a vertical straight hot filament CVD, Diam. Relat. Mater. 14 (2005) 318–322.
[6] C.S. Cojocaru, M. Larijani, D. Misra, M.K. Singh, P. Veis, F. Le Normand, A new polarised hot filament chemical vapor deposition process for homogeneous diamond nucleation on Si(1 0 0), Diam. Relat. Mater. 13 (2004) 270–276.
[7] R.B. Little, X. Wang, R. Goddard, Nano-diamond synthesis in strong magnetic field, J. Clust. Sci. 16 (2005) 53–63.
[8] Y. Shirazi, M.A. Tofighy, T. Mohammadi, A. Pak, Effects of different carbon precursors on synthesis of multiwall carbon nanotubes: purification and functionalization, Appl. Surf. Sci. 257 (2011) 7359–7367.
[9] N. Woehrl, V. Buck, Spectroscopic characterization of nanocrystalline diamond, J. Optoelectron. Adv. Mater. 10 (2008) 2819–2826.
[10] A. Ferrari, J. Robertson, Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon, Phys. Rev. B 64 (2001) 075414.
[11] A. Ferrari, J. Robertson, Origin of the 1150 cm^{-1} Raman mode in nanocrystalline diamond, Phys. Rev. B 63 (2001) 121405.
[12] S. Prawer, K. Nugent, D. Jamieson, J. Orwa, L.A. Bursill, J. Peng, The Raman spectrum of nanocrystalline diamond, Chem. Phys. Lett. 332 (2000) 93–97.
[13] S.J. Harris, A.M. Weiner, S. Prawer, K. Nugent, Diamond film quality: effects of gas phase concentrations on the Raman spectra, J. Appl. Phys. 80 (1996) 2187–2194.
[14] B. Sun, X. Zhang, Z. Lin, Growth mechanism and the order of appearance of diamond (1 1 1) and (100) facets, Phys. Rev. B 47 (1993) 9816.
[15] S. Wang, Q. Zhang, S. Yoon, J. Ahn, D. Yang, Q. Wang, et al., Electron field emission from carbon nanotubes and undoped nano-diamond, Diam. Relat. Mater. 12 (2003) 8–14.
[16] O. Ternyak, R. Akhvlediani, A. Hoffman, W.K. Wong, S.T. Lee, Y. Lifshitz, et al., Field electron emission from undoped, continuous, submicron-thick diamond films, J. Appl. Phys. 98 (2005) 123522–123527.
[17] K. Byrappa, T. Ohachi, Crystal Growth Technology, Elsevier, 2003.
[18] Y.A. Mankelevich, M.N. Ashfold, J. Ma, Plasma-chemical processes in microwave plasma-enhanced chemical vapor deposition reactors operating with C/H/Ar gas mixtures, J. Appl. Phys. 104 (2008) 113304.
[19] M.H. Nong, J.H. Hahn, D.Y. Yoon, Charged cluster model in the low pressure synthesis of diamond, J. Cryst. Growth 162 (1996) 55–68.
[20] I.D. Jeon, J.P. Chang, D.Y. Kim, M.H. Nong, Effect of methane concentration on size of charged clusters in the hot filament diamond CVD process, J. Cryst. Growth 223 (2001) 6–14.