



Chemical vapor deposited diamonds on Re substrate for the application of field emission

Xiaobin Wu^{a,b}, Zhiming Yu^{a,*}, Qjuping Wei^{a,b}, Jun Zhao^a, Lingcong Meng^a, Jian Wang^a

^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 1 November 2010

Accepted in revised form 14 September 2011

Available online 21 September 2011

Keywords:

Diamond film
Hot-filament CVD
Field emission
Rhenium

ABSTRACT

Boron-doped diamond (BDD) films were deposited on rhenium substrates using methane/hydrogen as reactant gases by hot filament chemical vapor deposition (HFCVD). The morphology, band structures and crystalline structure of the BDD films were characterized by the scanning electron microscope (SEM), Raman spectroscopy and X-ray diffractometer (XRD), respectively. The effects of the pre-treated on nucleation and quality of the diamond film were investigated. The mixture of sulfur acid and nitric acid enhanced diamond nucleation much more greatly than that of single acid. The highly boron-doped diamond films were deposited on rhenium substrate. The field emission characteristics of these films were analyzed. The minimum resistivity of doped diamond films reached $10^{-2} \Omega \text{ cm}$. Field emission studies revealed that the BDD film grown on rhenium substrate had the low threshold field ($3.3 \text{ v}/\mu\text{m}$).

© 2011 Published by Elsevier B.V.

1. Introduction

There has been a growing interest in the application of chemical vapor deposited (CVD) diamond films as field emitter materials owing to their unique electronic properties, chemical, and thermal stability [1–3]. It has been demonstrated that electron field emission from CVD diamond films occurs at very low turn-on fields. Many investigations have also been done on the origin of low field emission behavior from diamond crystal or CVD diamond films that are intentionally doped or not, but the electron field emission mechanism was not clearly understood [4–6]. The high melting point ($T = 3453 \text{ K}$) and good ductility make rhenium attractive as a high-temperature structural material. Compared with other refractory metals, Re has superior tensile strength, 1000–2500 MPa [7], and creep-rupture strength, 10 MPa for 100 h at 2200 °C [8], over a wide temperature range. The attribute ranges reflect different thermal conditions and suppliers of the commercially pure metal. At elevated temperatures, Re resists attack in hydrogen and inert atmospheres. Pure Re is vulnerable to oxidation in moist air above 600 °C, but it is also resistant to hydrochloric acid and seawater corrosion. Rhenium metal has attracted considerable interest for use as structural materials for applications in the aerospace fields due to their high temperature strength, high thermal conductivity and corrosion resistance and corrosion resistance [8].

HFCVD is the simplest low pressure CVD method and it gives reproducible results. Reaction conditions, such as gas composition,

substrate temperature, working pressure, and gas flow rate, have strong influences on diamond deposition, including the interface properties, morphology and quality of the diamond film.

In this paper, it is reported on that micro-crystalline diamond film deposited on rhenium substrate for cold field electron emission. We deposited highly boron-doped diamond films by hot filament chemical vapor deposition (HFCVD). The electron conduction in the diamond films is improved, and the electron emission is enhanced. Desirable crystal texture and low resistivity (at the level of $10^{-2} \Omega \text{ cm}$) can be simultaneously obtained by optimizing the $\text{B}_2\text{H}_6/\text{CH}_4$ ratios and temperature.

2. Experimental details

The deposition of diamond films was carried out in a hot filament CVD reactor. The hot filament CVD system consists of a steel chamber equipped with a tungsten filament which was employed for activation of gas-phase reactions; detail of this equipment was given in previous work [9]. The diamond film deposition was performed in super high vacuum chamber with a background pressure of less 10^{-5} Pa . The rhenium substrates of $10 \times 10 \times 0.5 \text{ mm}^3$ in size were first mechanically polished so as to get a mirror like smooth surface. In order to create suitable defects on the substrate surface, which favor the inhomogeneous nucleation of diamond from the gas phase, prior to diamond deposition, the substrates were put in a mixed solution (1 ml 96 wt.% $\text{H}_2\text{SO}_4 + 1 \text{ ml}$ 68 wt.% $\text{HNO}_3 + 50 \text{ ml}$ H_2O) for 30 min and then were abraded ultrasonically in a suspension of diamond powder (powder size $\sim 200\text{--}500 \text{ nm}$) in acetone for 30 min.

The methane and hydrogen were used as reactant, and the B_2H_6 as a dopant. Table 1 shows parameters which were typically maintained

* Corresponding author. Tel.: +86 731 8830335; fax: +86 731 8876692.

E-mail address: zhiming@csu.edu.cn (Z. Yu).

Table 1
Experimental parameters for diamond deposition.

Parameters	
Filament temperature (°C)	2100–2300
Substrate temperature (°C)	730 ± 30
Spacing between filament and substrate (mm)	8
The ratio of CH ₄ :H ₂	1:100
The concentrations of B ₂ H ₆ :CH ₄ (%)	0–3
Pressure (Torr)	30
Deposition time (min)	60,180,300
Total gas flow (cm ³ /min)	50–53

constant for each specimen and deposition. At least three specimens of each type were deposited under the same conditions. The results presented in this article are representative of those found for all specimens subjected to a given parameter set.

The scanning electron microscopy (SEM) was carried out using FEI Sirion200 Field emission scanning electron microscope, with 10 kV acceleration voltage. The XRD analysis was carried out by D/max2500 diffractometer, with a monochromatized Cu K α radiation of 10 kV and 20 mA. The Raman spectrum was measured using a LabRaman RH800 spectrometer with an argon laser source with a 488 nm wavelength; the laser power was set as 20 mw. The I–V curve of field emission properties was measured inside an ultrahigh vacuum chamber with a base pressure lower than 10^{−6} Pa using a turbo molecular pump and an ionic pump.

3. Results and discussion

Fig. 1 shows SEM photomicrographs of diamond grown on the surfaces after various pretreatment. A few small particles of diamond are formed on the rhenium substrate without pretreatment, as shown in Fig. 1(a). It reveals that the nucleation diamond is difficult on the rhenium surface. The pretreatment of the Re substrates is, therefore, indispensable for diamond growth. It is found that the as-deposited carbon film consists of high-density un-faceted small particles in Fig. 1(b,c). The morphology of fully micro-diamond covered rhenium surface was shown in Fig. 1(d). It takes 60 min to obtain a continuous micro-diamond film (Fig. 1(d)) whereas continuous micro-diamond film with a very few voids is obtained after 60 min deposition on sulfur or nitric acid pretreated substrate (Fig. 1(b,c)).

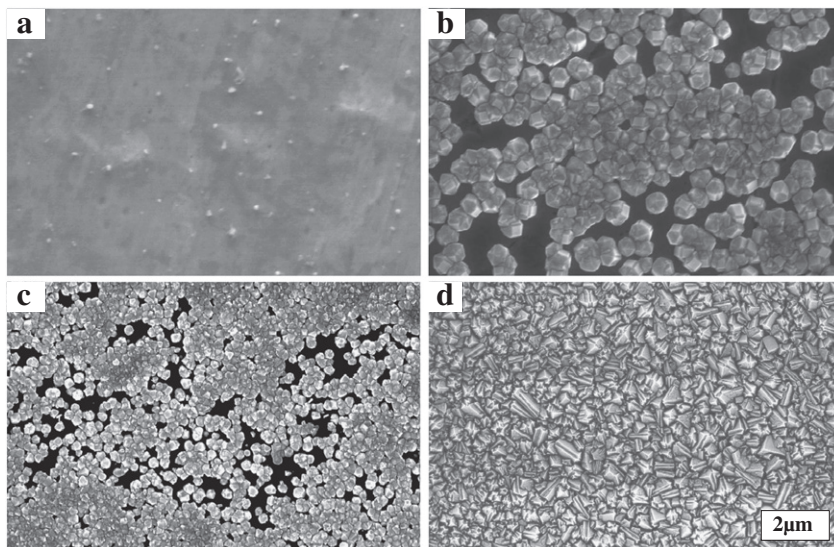


Fig. 1. SEM photomicrographs of diamond grown on the Re surfaces after various pretreatments: (a) without pretreatment; and the Re substrates were etched for 30 min by various acids: (b), (c) and (d); b: etching by sulfur acid (1 ml 96 wt.% H₂SO₄ + 50 ml H₂O) 1:50, c: etching by nitric acid (1 ml 68 wt.% HNO₃ + 50 ml H₂O), d: etching by mixed acid (1 ml 96 wt.% H₂SO₄ + 1 ml 68 wt.% HNO₃ + 50 ml H₂O). All samples were, then, abraded ultrasonically in a suspension of nano-diamond powder and acetone for 30 min.

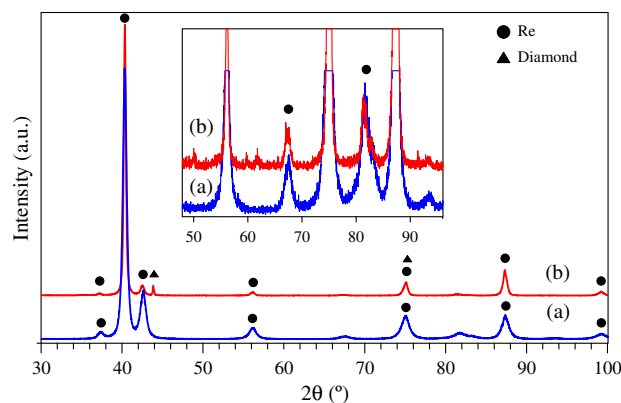


Fig. 2. X-ray diffraction patterns of the Re substrate and the diamond film on the Re with a pretreatment by etching in a mix-acid. (1 ml 96 wt.% H₂SO₄ + 1 ml 68 wt.% HNO₃ + 50 ml H₂O).

The results of X-ray diffraction of the pure rhenium and the diamond film deposited on the rhenium substrate are shown in Fig. 2, respectively. Comparing to Fig. 2(a), the spectrum of Fig. 2(b) is indexed to a mixture of cubic diamond phase and a hexagonal close packed phase of rhenium metal. Note that the peak in the range 2θ –75.4° matches closely with the diamond (220) peak at 75.302° and the Re (103) peak at 75.234°. We therefore assign this peak to overlapping diamond (220) and Re (103) peaks. No carbides can be found in Fig. 2(b). Furthermore, from the XRD date it is found that the lattice parameters of rhenium are $a = 0.2762$ nm and $c = 0.4457$ nm; a difference of the lattice parameter is within 0.5% comparing with the literature value [10]. The measured lattice parameter of the cubic diamond is 0.3569 nm; a deviation of the lattice parameter is within 0.1% comparing with the literature value.

Diamond films deposited for 3 h of growth and different B-doped concentrations are shown in Fig. 3: (a) 0%, (b) 0.75%, (c) 1.5% and (d) 3% B₂H₆ in CH₄. Fig. 3 shows a typical high-magnification SEM image in which diamond deposited on rhenium substrates can be seen in significant variations among different grains. The SEM images illustrate that the whole surface is covered by a continuous and dense diamond film. For all doping levels studied the films averaged grains of 1–3 μ m size, which is decreasing as the B-doping level increased. In the sample of high B-doped concentrations in Fig. 3(c,d), there are clusters of the micro-particles of diamond. It implies that the quality

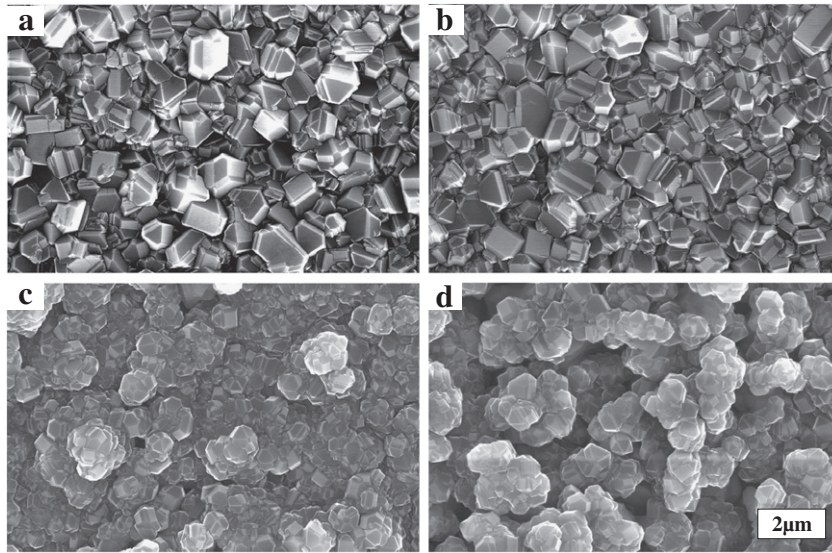


Fig. 3. The SEM images of diamond films in different boron-doped levels: (a) 0%, (b) 0.75%, (c) 1.5%, (d) 3%.

of diamond downgrades in the case of too high B_2H_6/CH_4 ratio. This result demonstrates that appropriate amounts of boron doping concentration are crucial for keeping the structural properties of diamond films. The observed grain refining under highly boron doping conditions can be explained by the increase of diamond nucleation density due to boron element added in vapor phase [11].

Fig. 4 shows a drastic change of diamond films Raman spectra with the boron doping levels. The characteristic peak for diamond at 1338 cm^{-1} appears for un-doping. The diamond characteristic peaks shift to 1332 cm^{-1} and 1328 cm^{-1} when B concentrations are 0.75% and 1.5%, respectively. Finally, it shifts to 1320 cm^{-1} when B concentrations are 3%. There could be a “red shift” of the characteristic peak as B-doping level increases. At the same time, two broad Raman peaks at around 500 cm^{-1} and 1230 cm^{-1} appear noticeably when the B doped and become stronger as B increases. It is the same with other works [12–14]. The peaks relate to the locally disordered structures induced by the heavily boron doping [15,16]. In Fig. 4 a downward shift of the peak at 500 cm^{-1} is found, while the position of the peak at 1230 cm^{-1} has not changed obviously.

Fig. 5 shows field-emission properties from the I/V curves of the three different diamond films, which are in the different B doping levels: (a) 0%, (b) 0.75%, (d) 3% B_2H_6/CH_4 . The three kinds of diamond films present the rather different field emission features. The field emission efficiency of the boron-doped diamond film is much better

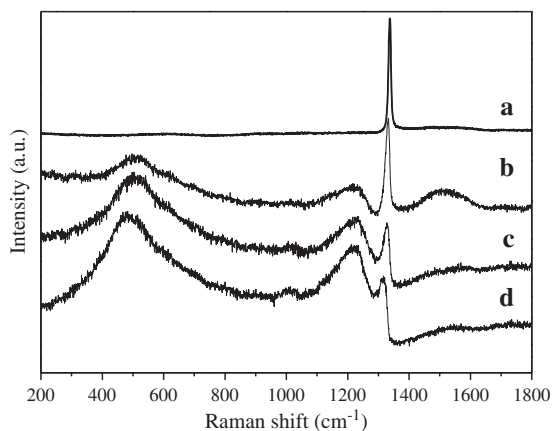


Fig. 4. Raman spectra for the boron-doped diamond films in different boron-doped levels: (a) 0%, (b) 0.75%, (c) 1.5%, (d) 3%.

than that of the without boron-doped diamond grown on rhenium substrate. In Fig. 5, it is found that lightly doped sample b can be turned-on at relatively low field ($E=3.3\text{ V}/\mu\text{m}$; here, we name the electric field required for the emission current of $0.1\text{ }\mu\text{A}$ as the threshold field) and the emission current density attains $J=6.3\text{ }\mu\text{A}/\text{cm}^2$, at $3.3\text{ V}/\mu\text{m}$ applied field. By contrast, the heavily doped samples need larger turn-on field ($E=5.0\text{ V}/\mu\text{m}$) and show relatively small electron emission capacity ($J=4.0\text{ }\mu\text{A}/\text{cm}^2$) shown as solid diamond. It is well known that the field emission properties depend on the film topography and the film component. Hideo Kiyota et al. [17] indicate that the small grain films or the films containing much non-diamond carbon have shown more promise, due to the presence of abundant grain boundaries and higher level of non-diamond carbon which could increase the material's conductivity. Recent studies [17,18] showed that the grain boundary or non-diamond carbon might lead to formation of the extra states within bulk diamond band gap, and the emission should be enhanced by directly emitting the electrons from these states into vacuum.

Fig. 6 shows the corresponding $\ln(J/E^2)$ vs. $1/E$ plots of samples (a, b, d) according to the Fowler–Nordheim (F–N) equation [19]. It can be seen that there is a significant variation in the emission characteristics for the boron-doped diamond films compared with that of un-doped one. In fact, the decrease of threshold electric field

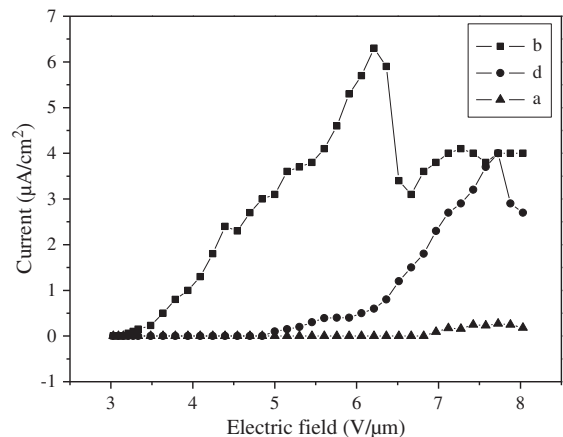


Fig. 5. Characteristics of field emission of the boron-doped diamond films in different boron-doped levels: (a) 0%, (b) 0.75%, (d) 3%.

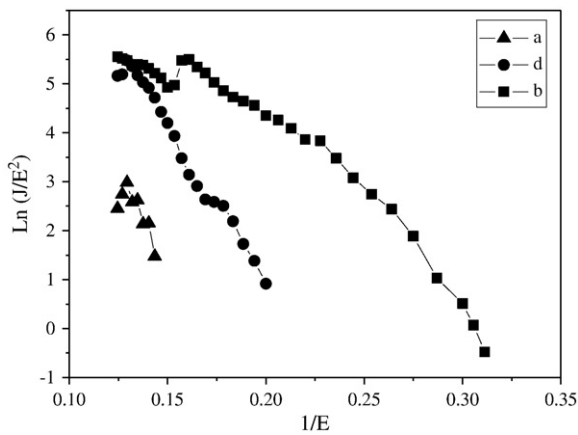


Fig. 6. Fowler–Nordheim (F–N) plots for diamond films deposited in various boron levels.

originates from the reduction of the work function of the films. The effective work function of the films is determined using FN plots shown in Fig. 6. The linear F–N characteristics indicate that the field emission is responsible for the acquired current, which is consistent with the conventional F–N equation [20]:

$$J = A\beta^2 E^2 \div \phi^* \exp(-B\phi^{3/2}\beta E)$$

where ϕ is the work function, E is the applied field, β is the dimensionless field enhancement factor, A and B are constants. The boron doped samples possess markedly larger effective work function than the un-doped one, viz. $\phi(a) = 0.012$ eV, $\phi(b) = 0.051$ eV and $\phi(d) = 0.108$ eV [21]. These results infer that only when proper amount of p-type dopants are incorporated, the electron conduction in diamond crystals is improved and the emission of electrons is enhanced.

4. Conclusion

Boron doped diamond (BDD) films were deposited on rhenium substrate by hot-filament vapor chemical deposition (HFCVD). The effects of pretreatments and the B doping level on diamond growth were studied. A mixture acid, 1 ml 96 wt.% H_2SO_4 + 1 ml 68 wt.%

HNO_3 + 50 ml H_2O , plays an important role to enhance diamond nucleation and growth on the Re. The levels of boron doping show remarkable influence on the surface morphologies and the qualities of the diamond films. Field emission studies revealed that the boron doped diamond films (1.5% B_2H_6/CH_4) grown on rhenium substrate had the low threshold field (3.3V/ μm).

Acknowledgments

We acknowledge the State Key Laboratory of Powder Metallurgy and the Open Fund for Valuable Instruments of Central South University for financial support, and the authors are also very grateful to Dr. Hu Chaoquan (State Key Laboratory of Superhard Materials; State Key Laboratory on Integrated Optoelectronics; and College of Electronic Science and Engineering, Jilin University) for field emission tests.

References

- [1] John C. Angus, Cliff C. Hayman, *Science* 241 (4868) (Aug. 19 1988) 913.
- [2] Shim Jae Yeob, Chi Eung Joon, Baik Hong Koo, Song Kie Moon, *Thin Solid Films* (1999) 355 (223–228).
- [3] F.J. Himpsel, J.A. Knapp, J.A. VanVechten, D.E. Eastman, *Phys. Rev. B* 20 (1979) 624.
- [4] W. Zhu, G.P. Kochanski, S. Jin, L. Seibles, *Jpn. J. Appl. Phys.* 78 (1995) 2707.
- [5] J. Robertson, M.J. Rutter, *Diamond Relat. Mater.* 7 (1998) 620.
- [6] X. Lu, Q. Yang, C. Xiao, A. Hirose, *Thin Solid Films* 516 (2008) 4217.
- [7] 10th ed, *ASM Handbook*, vol. 2, ASM International, Ohio, 1990, p. 1150.
- [8] A. Naora, N. Eliaz, E. Gileadi, *Electrochim. Acta* 54 (2009) 6028.
- [9] Z. YU, U. Karlsson, A. Flodström, *Thin Solid Films* 342 (1999) 74.
- [10] T. Bauer, M. Schreck, S. Gsell, et al., *Status Solidi a-Appl. Res.* 199/1 (2003) 19.
- [11] A.F. Azevedo, R.C. Mendes de Barros, H.P. Serrano, *Surf. Coat. Technol.* 200 (2006) 5973.
- [12] F. Pruvost, E. Bustarret, A. Deneuve, *Diamond Relat. Mater.* 9 (2000) 295.
- [13] P.C. Ricci, A. Anedda, C.M. Carbonaro, *Thin Solid Films* 482 (2005) 311.
- [14] H. Windischmann, K.J. Gruy, *Diamond Relat. Mater.* 4 (1995) 837.
- [15] A. Llie, A.C. Ferrari, T. Yagi, J. Robertson, *Appl. Phys. Lett.* 76 (2000) 2627.
- [16] J.D. Carey, R.D. Forrest, R.U. Khan, S.R.P. Silva, *Appl. Phys. Lett.* 77 (2000) 2006.
- [17] Hideo Kiyota, Eiichi Matsushima, Keisuke Sato, Hideyo Okushi, Toshihiro Ando, Junzo Tanaka, Mutsukazu Kamo, Yoichiro Sato, *Diamond Relat. Mater.* 6 (1997) 1783.
- [18] M. Roos, V. Baranauskas, M. Fontana, H.J. Ceragioli, A.C. Peterlevitz, K. Mallik, F.T. Degasperi, *Appl. Surf. Sci.* 253 (2007) 7381.
- [19] Pankaj M. Koinkar, Sandip S. Patil, Tae-Gyu Kim, Daisuke Yonekura, Mahendra A. More, Dilip S. Joag, Ri-ichi Murakami, *Appl. Surf. Sci.* 257 (2011) 1854.
- [20] R.H. Fowler, L. Nordheim, *R. Soc. London, Ser. A* 119 (1928) 173.
- [21] Yung-Hsin Chen, Chen-Ti Hu, I-Nan Lin, *Appl. Surf. Sci.* 142 (1999) 516–520.