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Characterization of diamond films deposited on Re substrate by magnetic field-assisted hot filament chemical vapor deposition

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ABSTRACT

A periodically magnetic field (PMF) was used in a hot-filament chemical vapor deposited (HFCVD) for diamond growth on the rhenium substrate. The morphology, band structures and crystalline structure of the film were analyzed by the scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffractometer (XRD), respectively. The results show that the thickness of the diamond film is about 2900 nm by 4 h deposition with magnetic field-assisted. There is no interlayer between diamond film and the rhenium substrate. The result shows that the turn on voltage of the sample is enhanced from 3.3 to 2.6 V/μm with the PMF. Also the total emission current density at 6.2 V/μm increased from 6.3 to 21.5 μA/cm^2.

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 chemical vapor deposited (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 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. It is also resistant to hydrochloric acid and seawater corrosion. While pure Re is vulnerable to oxidation in moist air above 600 °C 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].

The hot-filament chemical vapor deposition is widely used in the deposited diamond films. One of its advantages is simple equipment and facilities of equipment upgrading, such as the applied dc bias voltage [9], the applied dc plasma assistance [10]. These methods have been proven that the nucleation of diamond films is greatly improved. 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 diamond film deposited on Re substrate for cold field electron emission. We deposited highly boron-doped diamond films by the external periodic magnetic field-assisted hot filament chemical vapor deposition (PMF-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} Ω cm) can be simultaneously obtained by optimizing the B_2H_6/CH_4 ratios and temperature.

2. Experimental details

Fig. 1 shows the schematic diagram of a PMF-HFCVD system used in this experiment. The applied PMF was generated by a stator winding of a three-phase electric motor with the changeable

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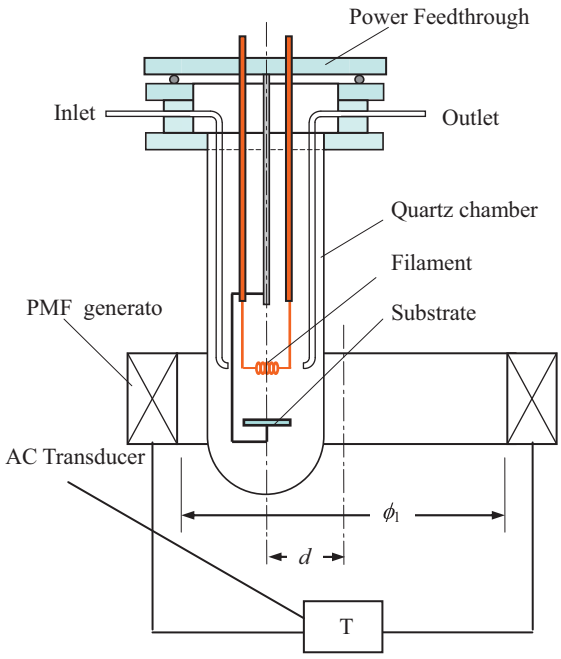

Fig. 1. Schematic diagram of the periodic magnetic field HFCVD system.

rotating rate (ω) from 3000 to 45000 rpm. The measured variation in magnetic field strength along the axial distance to the maximum length of the reactive area is less than 1%. The inner diameter of the pair coils is 210 mm. The vertical gradient of the pair magnet is 0.135 G/mm. So the periodic magnetic field in reactor area can be looked like a uniformed and even. Measured by the Gauss meter, with the increase of the ω (rpm), the magnetic field declined from 106 to 40 G. Despite this, its strength can play a significant role to plasma [11].

Prior to diamond deposition, the rhenium substrates were initially pretreated. All the rhenium substrates were first mechanically polished so as to get a mirror like smooth surface. Then the substrates were corroded in mixed acid for 30 min, the substrates were pre-treated for 30 min in an ultrasonic bath in the slurry of nano-diamond powder ($d < 500$ nm) in order to provide high diamond nucleation density. The gas mixture of methane and hydrogen was used as the gas reactant. The diamond film deposition was performed in super high steel vacuum chamber with a background pressure of less 10^{-5} Pa, detail of this equipment was given in previous work. Carburized tungsten wires were heated to 2100 °C to activate the reaction gas. The deposition conditions for the sample series investigated are summarized in Table 1.

The scanning electron microscopy (SEM) was carried out using FEI Sirion200 Field emission scanning electron microscoper, with 10 kV acceleration voltage. The XRD analysis was carried out by D/max2500 diffractometer, with a monochromatized Cu Kα 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. Laser power was set as 20 mW. *I*/*V* curve of field emission properties ware measured inside an ultrahigh vacuum chamber with a base pressure lower than 1×10^{-6} Pa using a turbo molecular pump and an ionic pump.

3. Results and discussion

Fig. 2 shows the cross-section SEM images of diamond films deposited for 4 h. It is clearly visible from Fig. 2 that there are only two layers in total, including the substrate, diamond thin film. So the rhenium substrate may be classified into non-carbon affinity materials. The thicknesses of the diamond film with and without the PMF are about 2900 nm and 1500 nm, respectively. Compared with the conventional HFCVD, the arithmetic mean thickness of diamond films under the applied PMF is prompted about one times. The combined effect both the magnetic field and thermal pyrolysis increase in the growth rate of diamond films [12].

X-ray diffraction patterns of diamond films deposited on the Re substrates are shown in Fig. 3. The diamond peak is weak, which indicates that the thickness of diamond films is thin. The XRD spectrum of diamond grown on rhenium substrate in Fig. 3 is dominated by Re features, but peaks at 2θ diffraction angels of 43.9°, 75.3°, 91.4° and 119.5° – corresponding to, respectively, the <1 1 1>, <2 2 0>, <3 1 1> and <4 0 0> reflections of the cubic diamond structure – are clearly identifiable. Note that the 2θ –75.3° peak matches closely with the diamond <2 0 0> peak at 75.302 and the Re <1 0 3> peak at 75.234; the observed feature is considered to be a blend of these two reflections. No obvious rhenium carbide phase can

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
The ratio of B_2H_6:CH_4 (%)	0–3
Pressure (Torr)	30
Deposition time(min)	60–300
Total gas flow (cm^3/min)	50

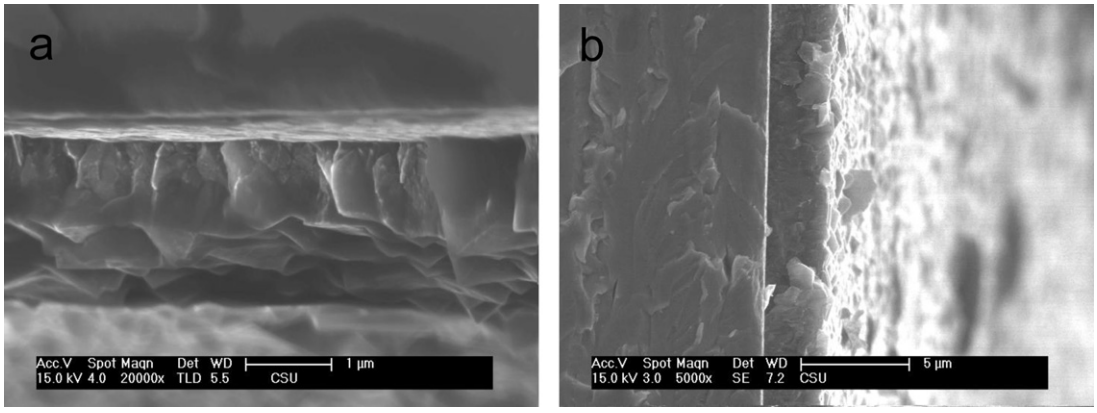

Fig. 2. The cross-section SEM image of diamond films grown at methane concentrations of 1%. (a) Without the PMF and (b) ω = 30,000 rpm under the PMF.

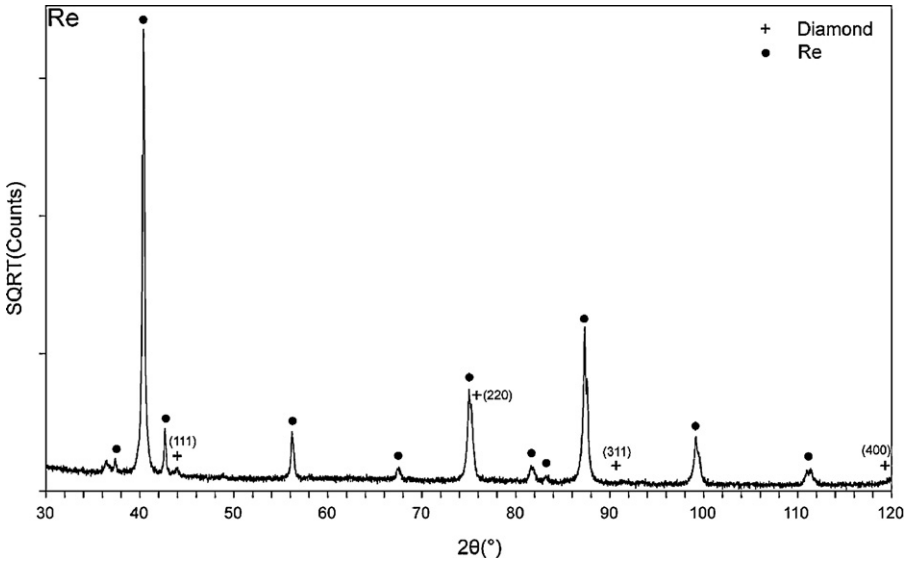

Fig. 3. X-ray diffraction patterns of diamond films deposited on Re substrate.

be observed after diamonds were deposited on the pure rhenium substrates for 3 h.

Diamond films in Fig. 4 were deposited by maintaining the substrate temperature at 730 °C in different doped concentrations: (a) 0.5%, (b) 0.5%, (c) 2% and (d) 2% B_2H_6 in CH_4.

Fig. 4 shows a typical low-magnification SEM image in which diamond deposited on polycrystalline rhenium substrates can be seen in significant variations among different grains. The SEM images illustrate that after 10 min of nucleation and 2 h of growth, the whole surface is covered by a continuous and dense diamond film, the film morphology is comparable for the whole range of nucleation. It is obvious that the average B-doped diamond grain sizes are reduced; also the average diamond grain sizes of film deposited with the periodically magnetic field are reduced.

Fig. 5 displays the Raman spectra of the diamond films with different boron contents. The classical 1332 cm^{-1} diamond peak still appears [13]. Compared to the sample without boron-doped diamond film, the intensity of characteristic peak for diamond film

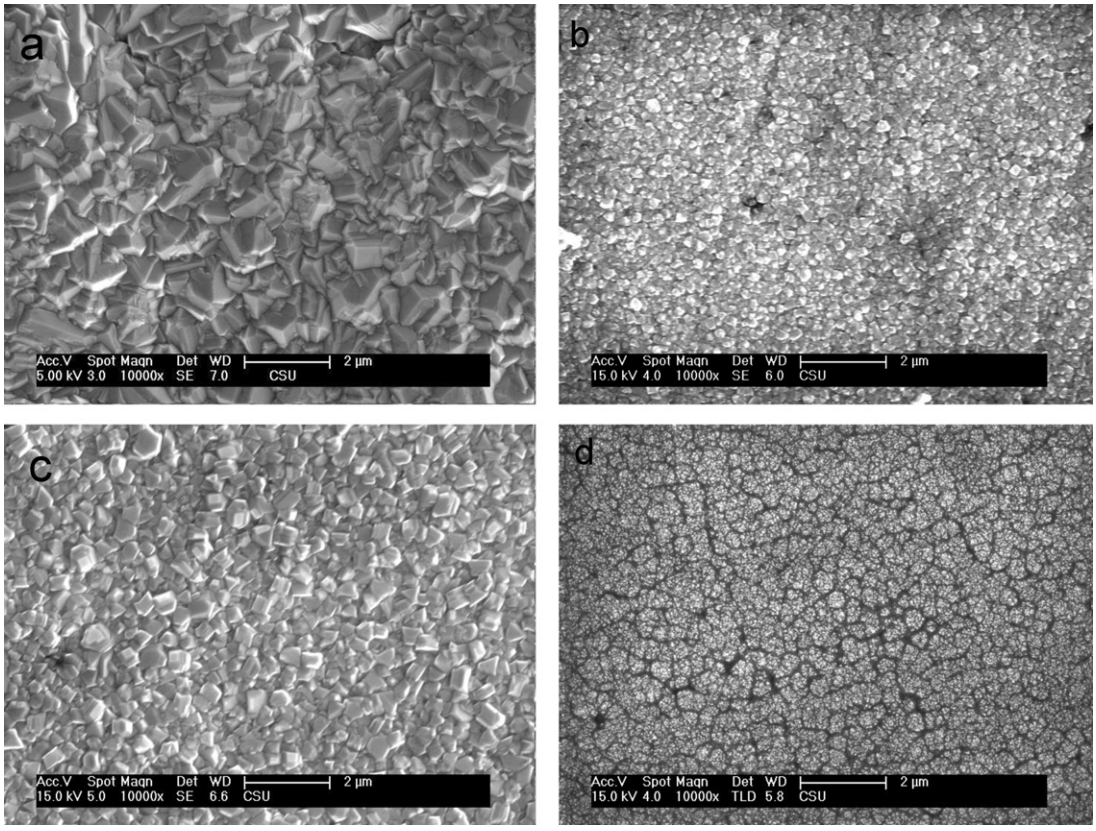

Fig. 4. The SEM images of diamond films in different doped concentrations: (a) 0.5% (without the PMF), (b) 0.5% (ω = 30,000 rpm under the PMF), (c) 2% (without the PMF) and (d) 2% (ω = 30,000 rpm under the PMF).

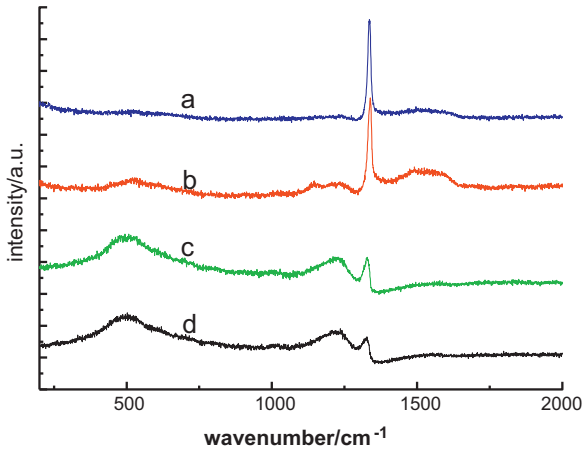

Fig. 5. Raman spectrum for the diamond films in different doped concentrations: (a) 0.5% (without the PMF), (b) 0.5% (ω = 30,000 rpm under the PMF), (c) 2% (without the PMF) and (d) 2% (ω = 30,000 rpm under the PMF).

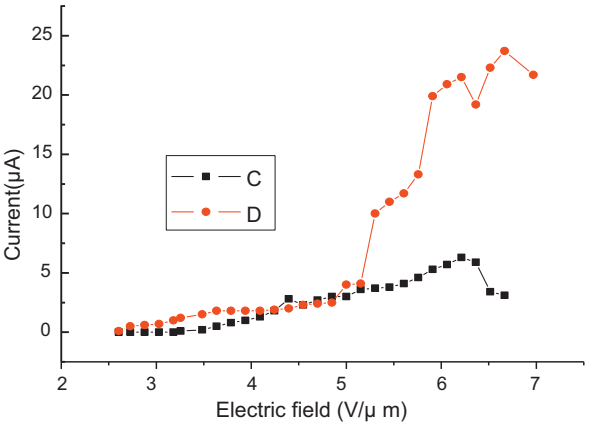

Fig. 6. Characteristics of field emission of the diamond film.

at 1332 cm^{-1} reduces remarkably. At the same time, New broad Raman peaks around 500 cm^{-1} and 1220 cm^{-1} becomes noticeable, which can be related to the locally disordered structures induced by the heavily boron doping [14]. Fig. 5 indicated a downward shift of the 500 cm^{-1} and 1332 cm^{-1} peaks while the frequency of the 1220 cm^{-1} peak remained constant. Finally, compared with the intensity of the structure around 1220 cm^{-1} and 500 cm^{-1} signals respectively increased when the boron contents was increased [15,16].

Fig. 6 is a comparison of the *I–V* characteristic for samples with and without the periodically magnetic field. Both samples were deposited under identical conditions. The field emission characteristics were measured at room temperature as a function of electric field between the sample and the anode under a vacuum of 10^{-6} Pa.

Threshold field (here, we name the electric field required for the emission current of 0.1 μA as the threshold field) was 2.6 and 3.3 V/μm for the samples with, without the PMF, respectively. Minimum values for emission currents and emission site densities were obtained with PMF, and maximum values without PMF. Maximum emission current, 23.7 μA at 6.7 V/μm, obtained for the sample with the PMF. Emission current increased with increasing applied voltage. However, over 6.7 V/μm, electric discharge and emission degradation occurred, and the emission property did not recover the initial condition. Recent research has indicated that the electron field emission originates from the sp^2 regions and is facilitated by the large field enhancement from a more conductive sp^2 cluster in an insulating sp^3 matrix. The field emission depends on the connectivity between sp^2 clusters. The number and size greatly affect the emission characteristics [17,18]. The modification on the field emission characteristics of the diamond films can be attributed to the change in the grain size and the effects due to the boron-doped.

4. Conclusion

We have synthesized boron doped diamond films on rhenium substrate by hot-filament vapor chemical deposition (HFCVD). The result shows that the Threshold field of the sample is enhanced from 3.3 to 2.6 V/μm with PMF. Also the total emission current density at 6.2 V/μm increases from 6.3 to 21.5 μA/cm^2. The results infer that the electron conduction in the boron doped diamond films is improved and the electron emission is enhanced. The thickness of the diamond film with the period magnetic field-assisted is about 2900 nm after 4 hour deposition. From the observed results, it is clear that the diamond films deposited with the period magnetic field-assisted leads to improvement of its field emission characteristics.

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