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Plasma-enhanced synthesis of carbon nanocone arrays by magnetic and electric fields coupling HFCVD

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ABSTRACT

In this paper, magnetic and electric fields coupling hot filament chemical vapor deposition (HFCVD) was used to fabricate a series of carbon films varying from nanocrystalline diamonds (NCD) to carbon nanocone arrays. The surface morphology and composition of the film were examined by scanning electron microscopy and Raman spectroscopy. After adding magnetic field, the morphology of the as-grown NCD film was a serried form instead of a rugged topography obtained under the absence of magnetic field. As electric field intensity increased, the etching degree of NCD films enhanced and the structural transformation of NCD to microcrystalline graphite occurred. We proposed that magnetic and electric fields can effectively introduce plasma into HFCVD system to optimize the film deposition process and studied the impact of magnetic and electric fields. The presence of electric field promoted ionization of reactive gas, and magnetic field made these ionic gases bound to a certain area around the sample, increasing the regional density of plasma. Specially, unique carbon nanocone arrays were obtained by synergistic effect of magnetic and electric fields, which exhibited optimal electron field emission properties, showing the lowest turn-on field of 5.65 V/μm.

1. Introduction

Electron field emission (EFE) has gradually replaced the traditional hot electron emission source in preparation of miniaturized electron source because of its low energy consumption, long lifespan and short response time. Since it effectively reduces the preparation cost and effective size, EFE is widely used in many fields such as X-ray source [1,2], flat panel display [3], communication equipment [4], electron microscope and vacuum microelectronic devices [5]. In recent years, much attention has been paid to the EFE properties of the diamond films. It has been reported that the nanocrystalline diamond (NCD) films exhibited a lower turn-on field than that of diamond. A series of studies has shown that there are three main factors affecting the EFE properties of NCD films: (1) the emission site of electron is directly related to the grain size of the film, and generally the smaller the grain size is, and the higher the density of grain boundary is obtained; (2) the second is the content of graphite phase that can easily act as a channel for electron transport compared with sp^3 phase [6]; (3) the last one is the field enhancement factor β corresponding with the geometrical morphology of emission tip [7].

Several methods have been investigated to enhance the EFE properties of NCD films. For example, NCD films synthesized by microwave plasma-assisted chemical vapor deposition (MPCVD) could reduce the grain size and increase density of sp^2 phase at grain boundaries [8] but the corresponding cost was too high. Reactive ion etching (RIE) method was used to obtain the conical arrays on the as-prepared NCD film surface in order to increase its field enhancement factor [9]. However, the preparation methods were too complex that the structuring processes were based on several fundamental steps. The common purpose of the above methods was to introduce plasma during the preparation process and fabricate the films with better EFE properties. To produce much region-controlled plasma during CVD, one coupled method of magnetic and electric fields were utilized, like electron cyclotron resonance-microwave plasma chemical vapor deposition (ECR-MPCVD) [10–12]. However, the plasma discharge produced by ECR-MPCVD was relatively instable. Thus, this paper advocates the use of magnetic and electric fields coupling HFCVD (MEFC-HFCVD) to synthesize carbon material.

Hot filament chemical vapor deposition (HFCVD) is generally considered as a simple and low-cost experiment method to fabricate emitters, but it is not a plasma enhanced CVD process, which limits its relevant application. Many previous attempts have demonstrated that

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the introduction of electric field [13–15] could significantly increase the content of plasma in the CVD chamber owing to collision-induced gas ionization. Many carbon nanocomposites such as carbon nanocones, carbon nanofibers and carbon nanotubes were synthesized by applying the electric field and they showed better EFE properties than that fabricated by conventional CVD [16]. Our previous works have reported that magnetic field played an important role in improving the EFE property of diamond and the introduction of magnetic field [17–20] could increase the collision probability of gas molecules. Therefore, we propose to introduce both of electric field and magnetic field into the HFCVD system to control the plasma separately. Under the applied electric field, additional energy could be generated to produce a large amount of plasma. Moreover, the presence of magnetic field could bound the movement of ionic species, resulting in increasing the regional density of plasma.

In this work, a new and low-cost method, MEFC-HFCVD, was developed to control the plasma by altering the electric field intensity with the presence or absence of magnetic field. A series of carbon film varying from NCD to carbon nanocone arrays was obtained and the corresponding EFE properties were also investigated. The results demonstrated that the EFE properties of the film were significantly enhanced by applying magnetic and electric fields (MEFs) as the external field of HFCVD.

2. Experimental section

2.1. Experimental device

The schematic diagram of MEFC-HFCVD system is shown in Fig. 1. In this work, the Nd-Fe-B permanent magnet with a size of 50 mm × 100 mm × 10 mm is placed outside the HFCVD chamber. The magnetic field strength beside the substrate is around 8 mT. The electric field is generated between two steel grids by using an applied negative bias current to the substrate. Direct-current (DC) biasing in a constant current mode is applied to achieve high negative biasing voltage. The bias current variables are set as 0, 20 mA and 40 mA, respectively. When an applied negative bias current of 20 mA or 40 mA is forced to flow between two counter electrodes through the plasma, a corresponding approximate biasing voltage of 200 V or 320 V is applied.

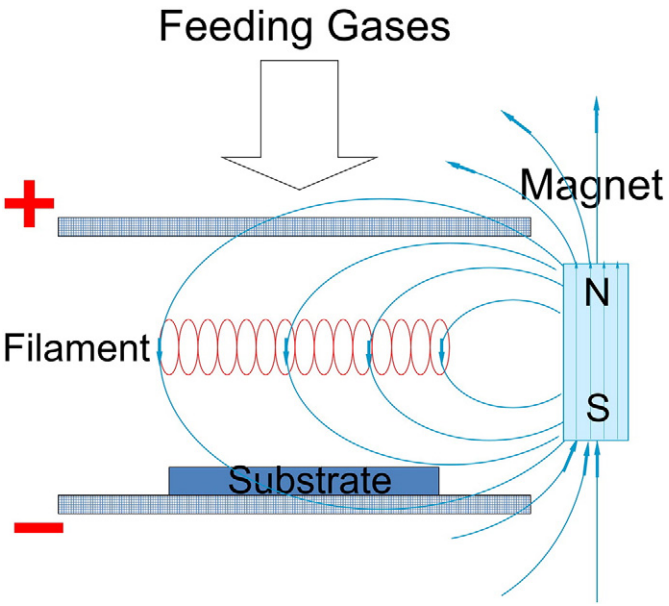

Fig. 1. Schematic diagram of MEFC-HFCVD system.

2.2. Experimental parameters and pretreatment

Monocrystalline silicon wafer with a size of 10 mm × 10 mm was used as the substrate. Prior to deposition, the substrate was in sequence pretreated ultrasonically in acetone, nano-diamond suspension and anhydrous ethanol for 20 min, 20 min and 5 min, respectively, and finally rinsed by distilled water and dried. During the deposition process, the pressure was kept at 2 kPa and the substrate temperature was remained at 973.15 K. During the first 0.5 h, the flow rate ratio of methane and hydrogen was 0.3:30, while the flow rate ratio was altered to 1.5:30 in the subsequent 1.5 h. The parameters of external fields of each sample are shown in Table 1. The notations 'E' stands for the sample fabricated by coupling HFCVD with electric field and the notations 'ME' with MEFs. The subscript numbers are the corresponding applied negative bias current.

2.3. Characterization

The surface morphology of the films was characterized by field emission scanning electron microscopy (FEI, Nova NanoSEM 230, Netherlands). The composition of the film was analyzed by Raman spectroscopy (HORIBA, LabRAM HR800) at excitation wavelength of 488 nm. The EFE test was performed at a high vacuum of 10^{-5} Pa under room temperature. The distance of the parallel diodes between the anode and the cathode was set as 200 μm, and the effective electron receiving area of the planar anode was 19.63 mm^2. During measurement, the emission voltage was provided by a DC power supply (Bohr, Model 71010PA, England) and the emission current of the film was measured by a picoammeter (Keithley, Model6485, US).

3. Results and discussion

3.1. Morphologies of samples under different external field

Fig. 2(a) shows morphologies of samples fabricated by coupling HFCVD with different external fields, from which one can see that in the absence of the electric field, both E_0 and ME_0 possess nano-grain structures. The micron clusters of E_0 with size of 500–1000 nm are composed of 30–50 nm nanocrystals. After adding the magnetic field, the clusters of ME_0 possess the smaller size (100–200 nm) compared to E_0 and show a more compact morphology. Under the applied negative bias current of 20 mA, no significant cluster is observed on E_{20} and ME_{20}, but E_{20} has a relatively denser nanocrystal surface compared to ME_{20}. When the applied negative bias current increases to 40 mA, the surface of E_{40} is seriously etched and the pits form on the surface. In contrast, when coupling with magnetic field, the surface of ME_{40} presents orientated cone-like morphologies, where diameters of small and lager cones are 50–100 and 500 nm, respectively.

Fig. 2(b) presents the corresponding slant map of samples in Fig. 2(a) at an angle of around 7°. It is observed that the grain clusters of E_0 are relatively coarse, with some pits on its surface, which is consistent with the gaps in E_0 as shown in Fig. 2(a). After adding magnetic field, the grain clusters of ME_0 become compact and its surface is smooth. E_{20} and ME_{20} are both etched to form the rough surface at applied negative bias current of 20 mA. In addition, nano-hills with 500–600 nm in heights appear in E_{40}, while the nanocones with 400–600 nm in height and 30–60 nm in width present in ME_{40}. These nanocrystals grow substantially perpendicular to their surfaces.

Table 1
Parameters of different samples.

Samples	E_0	ME_0	E_{20}	ME_{20}	E_{40}	ME_{40}
Negative bias current (mA)	–	–	20	20	40	40
Magnetic field (mT)	–	8	–	8	–	8