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Enhanced electron field emission properties of diamond/microcrystalline graphite composite films synthesized by thermal catalytic etching

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ABSTRACT

Diamond/microcrystalline graphite composite films were synthesized by thermal catalytic etching method with nickel as the catalyst. The surface morphology and composition of the composite films were examined by scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD). The results show that the etching and graphitizing degree of diamond surface increased with the rising annealing temperature and the surface of as-grown diamonds were replaced by the tips of high aspect ratios and porous foam structure. The electron field emission (EFE) properties of composite films were improved compared to the as-grown diamond. The lowest turn-on field of 9.6 V/μm has been detected for the composite film annealed at 900 °C. The field emission current stability was influenced by graphite phase formed in the etching process. Gradual increase of emission currents along with time were observed for both samples annealed at 700 °C and 800 °C. However, there was a slightly decrease for the emission current of sample annealed at 900 °C.

1. Introduction

Field emission cathodes are promising new electron sources widely used in flat panel display [1], light sources [2], and X-ray tubes [3]. Most field emission cathodes are designed based on carbon materials. Carbon materials have various attractive features compared to other field emitter arrays composed of metal or semiconductor, such as easy preparation, non-pollution and higher operating pressure range (about 10^{-4} Pa) than metal microtips (usually 10^{-6} Pa) [4].

Diamond films have been extensively used as electron field emitters due to negative electron affinity, low effective work function, and excellent physical and chemical properties [5,6]. However, the emission current of diamond films is limited because of their insulating nature and smooth surface. Besides, the high preparation cost of diamond in micro-tips geometry makes it difficult to industrialize. Recently, carbon nanotubes have been developed as a promising candidate for field emitters owing to their high aspect ratios. However, carbon nanotubes often show unsatisfactory emission characteristics such as current degradation caused by structural deformation at the nano-tips, which is mainly attributed to Joule heating under excessively imposed emission current [7,8]. Graphite-like materials have appropriate properties such as strong interatomic interaction, high electrical conductivity and thermal stability, which are attractive for the field mission cathode application. However, the preparation of matrix cathode, including surface micromachining or chemical etching used to create an array of field emission sites, is also expensive.

In view of the various properties of different carbon materials, the combination of different carbon materials has recently been the focus of intensive study. Films prepared from combination of single-walled nanotubes (SWCNTs) and multiwalled nanotubes [9], SWCNTs and carbon fibers [10] have been demonstrated. In each case, these films have displayed attractive properties. Graphene-nanotube hybrids are formed and show stronger, stiffer and better conductive properties than films of either component alone [11]. The CNTs/diamond composite exhibits better intrinsic heat dissipation property and lower turn-on field during field emission [12,13].

The properties, such as structural stability and easy conversion, make diamond and graphite two of the most significant and functional forms of carbon, which are fully reliable materials for

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long-term application under high electric field. The diamond film is an excellent material for field emission device because of its negative electron affinity (NEA). However, its intrinsic insulating nature leads to the limit of electronic transmission, which is difficult to be improved effectively by doping or other methods. On the contrary, the conductivity of graphite is excellent but its work function is larger than that of diamond, meaning the electron emission from graphite surfaces is more difficult than that from diamond surfaces. In this paper, the diamond/microcrystalline graphite composite films are prepared by thermal catalytic etching with nickel as catalyst and their properties are studied. The composite films combine the advantages of diamond and graphite to improve the field mission properties by enabling electrons transport easily through the microcrystalline graphite phases to the emitting surface, then emit to vacuum without any difficulty as the diamond surfaces are NEA in nature. In addition, both the tips of high aspect ratios formed on the surface of composite films and the porous foam structure can help to improve the field enhancement factor, ensuring excellent electron field mission properties of the composite films.

2. Experimental

Single-crystal silicon (100) pieces with dimensions of 10 mm × 10 mm × 0.6 mm were used as substrate. Each sample was subjected to the following three treatment steps:

First, diamond films were grown on silicon substrate by hot filament chemical vapor deposition (HFCVD) method. The detail of this device was given in previous work [14]. Prior to deposition, the substrates were ultrasonically cleaned in acetone, ethanol and deionized water individually for 10 min, in the suspension of diamond nano-powder for 30 min to facilitate the nucleation of diamond.

Then, a 500 nm thick nickel films, composed of uniform nanoparticles (~50 nm), were deposited on the diamond films by DC magnetron sputtering in a high vacuum chamber with pressure $<10^{-3}$ Pa. Pure Nickel target (99.99 wt%) with diameter of 60 mm and argon gas (99.99 vol%) was used.

The following step is thermal catalytic etching of diamond films, which was carried out in a tube furnace for 2 h. After etching, samples were heated at 80 °C for 20 min in 3 mol/L HNO_3 water solution to remove the residual nickel. The detailed experimental parameters of each step are listed in Table 1.

The surface morphology of the composite films was investigated by field emission scanning electron microscopy (FEI, Nova NanoSEM 230). The structure and composition of the films were characterized by Raman spectroscopy (HORIBA, LabRAM HR800; λ = 488 nm, 10 mW) and X-ray diffraction (Rigaku, D/max-2500).

Field emission measurement of the composite films were carried out at room temperature in a high vacuum chamber of 10^{-5} Pa. A parallel plate diode structure was situated with an anode–cathode spacing of 200 μm and the effective area of metal anode was 19.63 mm^2. During measurements, a 10 kV DC power supply was applied to the anode–cathode electrodes.

Table 1
Experimental parameters for diamond deposition, sputtering and annealing.

Parameter	Description	Treatment process
Deposition temperature (°C)	700–730	HFCVD
Gas composition (CH_4:H_2:B_2H_6) (sccm)	3:97:0.3	
Deposition pressure (kPa)	3	
Deposition time (h)	4	
Sputtering current (mA)	400	PVD
Ar flow rate (sccm)	10	
Sputtering pressure (Pa)	0.4	
Sputtering time (min)	10	
Annealing temperature (°C)	700, 800, 900	Annealing
Annealing time (h)	2	
Heating rate (°C/min)	8	
Cooling rate	Furnace cooling (5–6 h)	

3. Results and discussion

Fig. 1 shows the morphological changes of samples annealed at different temperature before and after removing Ni layer. At annealing temperature of 700 °C, the Ni layer totally covered the diamond surface, in spite of slightly self-organized aggregation of Ni, as shown in Fig. 1(b). When annealing temperature ascends to 800 °C (Fig. 1(c)), due to further aggregation of Ni, a piece of Ni network formed and partially covered the diamond surface. When annealed at 900 °C (Fig. 1(d)), severe aggregation of Ni can be observed on the film surface. The SEM micrograph of samples after removing the Ni layer by HNO_3 is shown in Fig. 1(e–h). As the annealing temperature increased, the etching enhanced gradually. Diamond film annealed at 700 °C is etched partly that some regions are seriously corroded and many rugged ridges formed, while the rest still maintains the as-grown morphology (Fig. 1(e)). For film annealed at 800 °C, all the diamond grains are etched and replaced by many tips of high aspect ratios. Annealing at 900 °C and subsequent etching leads to the formation of porous foam structure in all areas of the diamond surface, rather than the tips produced in the lower temperature annealing.

The componential information from the thin films surface to the substrate at different depth can be accurately characterized by the Raman spectroscopy and X-ray diffraction. Fig. 2(a) and (b) depicts the Raman and XRD spectra of the samples after removing the Ni layer. For as-grown film, the Raman spectra shows four distinctive peaks at 500 cm^{-1}, 1200 cm^{-1}, 1332 cm^{-1} and 1580 cm^{-1}. The peaks at 500 cm^{-1} and 1200 cm^{-1} are related to the locally disordered structures induced by the heavily boron doping [15]. The sharp Raman resonance peak at 1332 cm^{-1} corresponds to the characteristic peak of diamond [16] and the broad peak at 1580 cm^{-1} (the so-called G bands) is the traditional evidence for the presence of sp^2 carbon [17], which can be associated with bond stretching of all pairs of sp^2 atoms in both rings and chains [18]. The only difference between sample annealed at 700 °C and as-grown diamond is the diamond peak intensity of former one is higher. While annealing at 800 °C leads to the appearance of sharp characteristic graphite peaks D at 1350 cm^{-1} and G at 1580 cm^{-1} and the sharpening of this two Raman peaks may indicate that the film is covered by microcrystalline graphite rather than the amorphous carbon [19]. Finally, after annealing at 900 °C, the distinctive peaks at 500 cm^{-1}, 1200 cm^{-1} and 1332 cm^{-1} are replaced by the sharp graphite D and G peaks with higher intensity than the peaks of 800 °C. Since the visible-Raman spectroscopy is more sensitive to sp^2-bonded carbon as compared to that of sp^3-bonded one [20], the coverage of microcrystalline graphite on the surface of sample annealed at 900 °C may weaken the penetration of Raman spectroscopy, therefore no diamond peak can be detected.

XRD pattern for different samples are shown in Fig. 2(b). For the as-grown film, only typical Bragg reflections of diamond peak at $2\theta = 43.8°$ and silicon peak at $2\theta = 38.2°$ can be observed. Annealing at 700 °C results in the appearance of peak corresponding to another silicon peak at $2\theta = 32.9°$, indicating that the film is etched slightly during the annealing process and thinner than as-grown films. Upon annealing at 800 °C, the silicon peak increases in intensity and sharpens while the diamond peak intensity decreases. However, no reflection associated with graphite phases can be distinguished, probably due to their lower intensity compared to the diamond and silicon. Finally, when annealing at 900 °C, more silicon signals are detected which located at $2\theta = 28.6°$ and 47.7°, indicating that the diamond film has been severely etched and become very thin. In addition, the appearance of the (002) reflection of