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Carbon nanofibres from diamond film using Ar-ion bombardment and their field emission property

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Abstract: Carbon nanofibres (CNFs) have been fabricated by oblique ion sputtering diamond films at room temperature. Scanning electron microscopy shows that the ordered carbon protrusions with a size of $\sim$1 μm are formed after 1 h ion irradiation and CNFs on the protrusions with a density of $1 - 2 \times 10^8/\text{cm}^2$, diameter of $\sim$40 nm and length of 1 − 4 μm are achieved after 2 h ion sputtering. Raman spectra indicates that the amorphous or defect content increases with the duration of irradiation. The investigation of field emission shows that the turn-on field is 1.8 V/μm and the threshold field is 4.6 V/μm.

1 Introduction

Carbon nanofibres (CNFs) have attracted much attention owing to their unique physical properties that are suitable for a wide range of potential applications such as field emitters, micro-electric devices and scanning probe tips of atomic force microscopy and scanning tunnelling microscopy [1]. Up to now, there have been two means to achieve CNFs. One is the high temperature method, such as chemical vapour deposition and thermal dissolving graphite and so on [2–5]. The other is ion sputtering carbon materials at room temperature [6–12]. Compared with the high temperature method, the ion sputtering method is very simple with low costs and achievable CNFs of controlled morphology. Carbon materials such as graphite, glass carbon and diamond-like carbon have been investigated in the ion sputtering method. It is believed that diamond also could be used to fabricate CNFs by the ion sputtering method.

Owing to the unique mechanical and electrochemical properties, high hardness, exceptional chemical inertness, biocompatibility and negative electron affinity, diamond has been considered to be one of the most promising candidates for the application of protective coating tools, a hermetic and corrosion-resistant coating for biodevices and structural material in micromechanical systems [13]. Therefore it is speculated that the combination of diamond and CNFs could give rise to materials with novel properties that could be used advantageously in applications such as electronic devices or micromechanical systems. In this Letter, the CNFs on diamond films have been achieved by oblique ion sputtering at room temperature and the field emission property of CNFs on diamond films have been investigated.

2 Experimental section

At first, the diamond films were deposited in a typical hot-filament chemical vapour deposition apparatus. N-type (1 1 1)-oriented mirror polished silicon wafers were used as substrates. The background pressure was 1×10^{-5} Torr. The mixture of gas containing methane and hydrogen with the flow ratio of 1/40 sccm (CH_4/H_2) was introduced into the chamber at the working pressure of 20 Pa. The substrate temperature was stabilised at 700°C and the deposition time was 6 h.

Then, the diamond films were placed into the chamber of the Kaufman ion source. An Ar^+ beam with energy of 1200 eV, current density of 0.5 mA/cm^2 and incident

angle with respect to the substrate surface normal of 60° was used to sputter the samples at room temperature. The sputtering time was 1 and 2 h.

The morphology evolution of samples before and after the ion sputtering was observed through SEM (LEO, 1530VP). The characteristic of the structural changing of the diamond film was investigated by micro-Raman spectroscopy (Dilor LabRam-1B) at room temperature.

Field emission measurement was carried out under a high vacuum of 2×10^{-5} Pa at room temperature. The cathode-to-anode electrode spacing was maintained at a constant value of 400 μm. Current–voltage (I–V) characteristic curves were obtained by adjusting the voltage from 100 to 3000 V.

3 Results and discussion

Fig. 1 shows the SEM images of as-grown diamond films and the samples by ion sputtering with 1 and 2 h; the inset is the corresponding cross-section image. The as-grown diamond film was a continuous film with a thickness of 5–6 μm, the size of the diamond particles were 50–200 nm. After 1 h ion irradiation, the ordered surface protrusion structures with a size of ~1 μm were achieved. After 2 h ion sputtering, nanofibres with a diameter of ~40 nm, length of 1–4 μm and density of ~$1–2 \times 10^8/cm^2$ were formed on the surface of samples.

Typical micro-Raman spectra of the as-grown diamond film and diamond films by Ar-ion irradiation with 1 and 2 h at room temperature are shown in Fig. 2. There are three bands between 1000 and 2000 cm^{-1} corresponding to the typical Raman peaks of carbon materials. The sharp peak at 1332 cm^{-1} is the characteristic peak of diamond, the peak at 1546 cm^{-1} (G band) corresponds to an E_{2g} mode of graphite and the peak at 1358 cm^{-1} (D band) is associated with the vibration of carbon atoms with turbostratic carbon. The Raman spectrum is considered to depend on the clustering of the sp^2 phase, bond disorder, presence of sp^2 rings or chains and the sp^2/sp^3 ratio. The intensity ratio of the D to G-band models (I_D/I_G) represents the amorphous phase content or the degree of crystallinity of the carbonaceous materials [14, 15]. The area integrated intensity ratio I_D/I_G from Gaussian function fitted Raman spectra increases from 0.85 of as-grown diamond to 1.17 of diamond film sputtered for 2 h. This implies the increased degree of disorder and defect concentration induced by the ion irradiation.

The formation of carbon cones or carbon nanofibre-tipped-cones induced by oblique Ar^+-ion bombardment on various carbon surfaces such as graphite [16], glassy carbon and silicon coated by carbon [6, 10], and carbon paste [9], has been demonstrated by some groups. In our previous work [11, 12, 17], carbon cones and carbon nanofibre-tipped-cones with controlled apex angles have been fabricated by sputtering diamond like carbon and graphite, respectively. The investigation of cone formation on graphite by Floro *et al.* [16] shows that there are two different processes contributing to carbon cone formation. The first process is a rapid growth process in which cones grew to some critical length and radius. After the initial growth process, the rates of lengthening and thickness appear to be constant and the carbon cones were formed. The experimental result of fabricating carbon nanofibre-tipped-cones by Tanemura *et al.* [6, 10] and our previous work [11, 12, 17] demonstrate that the cone formation is a prerequisite for carbon nanofibre growth and the redeposited massive C atoms would diffuse towards the cone tips, resulting in carbon nanofibre formation. In this work, the protrusions were formed in the first process by sputtering diamond films and then the carbon nanofibres were achieved on the tip of protrusions, which accorded with the results of our previous work.

In general, the ripple-like or ordered structure [18, 19] is formed on solid surfaces by the off-normal ion beam irradiation. The ion-induced surface morphology is accounted for by two competitive effects, the roughening process and the smoothing process. The roughening

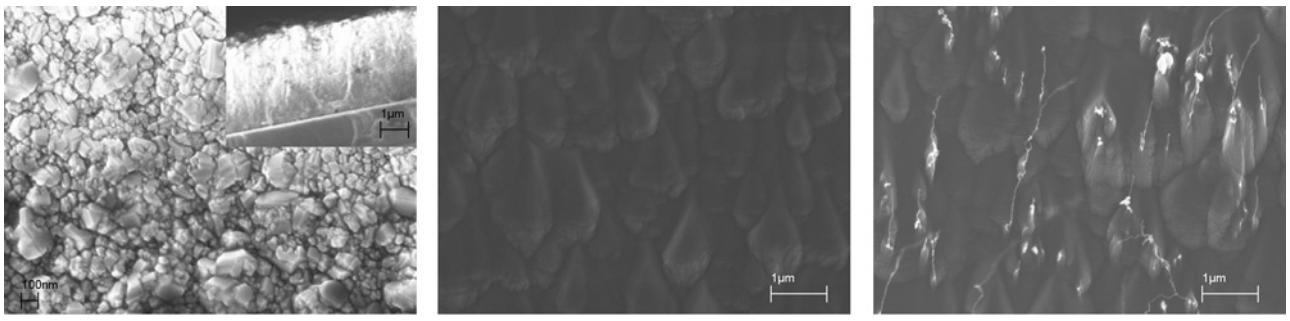

Figure 1 *SEM images of as-grown diamond films and the samples by ion sputtering with 1 and 2 h*

a SEM images of as-grown diamond film
b Diamond films by ion sputtering with 1 h
c Diamond films by ion sputtering with 2 h
Inset is the corresponding cross-section image

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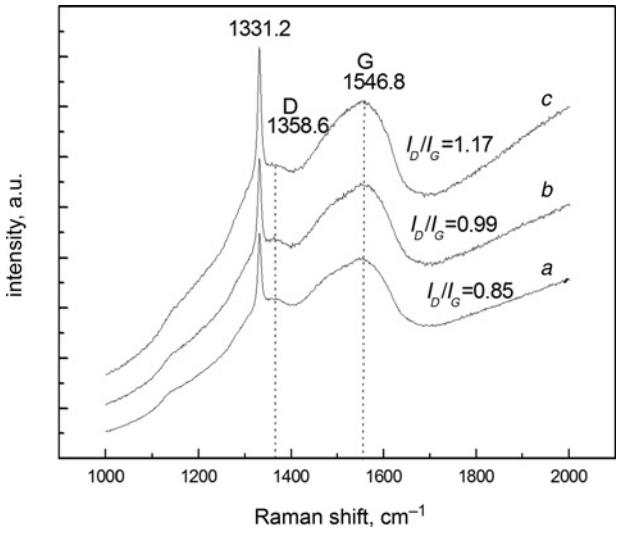

Figure 2 *Raman spectra of as-grown diamond film (a) and samples by ion irradiation for 1 h (b) and 2 h (c)*
Excitation wavelength was 632.8 nm

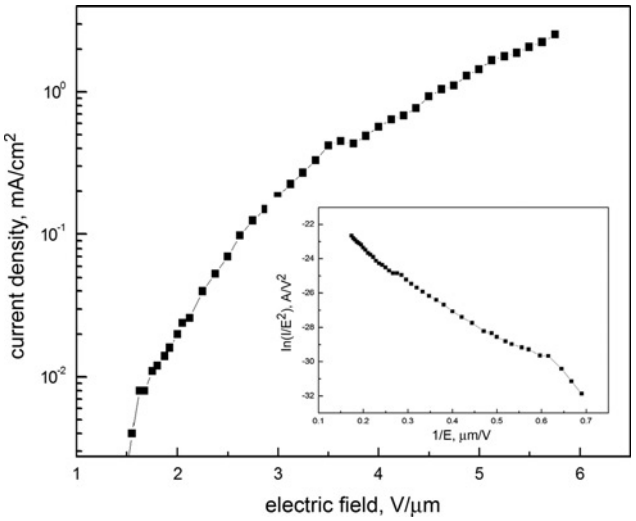

Figure 3 *Typical emission current density-electric field (J–E) curve of the carbon nanofibres on the diamond film by ion sputtering method*
Inset is the corresponding Fowler–Nordheim (*F–N*) plot

process is caused by the different sputtering yield depending on the curvature of the surface. The smoothing process is caused by the thermal or ion-induced diffusion driven by surface energy minimisation. For a ripple-like or cone structure, the sputtering yield at the trough is higher than that on the crest [19], which should enlarge the amplitude rapidly and the thermal or ion-induced diffusion would decrease the amplitude at the same time. When the sputtering process and diffusion process reach a balance, the steady amplitude is formed. Hence, the different sputtering yield, depending on the curvature results in the rapid growth process and the steady amplitude process, is induced by the balance of the sputtering process and diffusion process. It is believed that the formation of ordered protrusions on the diamond film in the initial process in our experiment is accounted for by the balance of the sputtering process and diffusion process. Compared with graphite and amorphous carbon, the sputtering yield of diamond is lower because of the network structure of sp^3 carbon atoms. Therefore the surface amplitude of the diamond sample is smaller than that of the graphite and amorphous carbon material during the rapid growth process of amplitude and the aspect ratio of the ordered protrusions on the surface of the diamond sample is smaller. This is the reason that the ordered protrusions with small amplitude are formed on the diamond surface, but the cones with high aspect ratio are formed on the graphite or amorphous carbon material surface under the same experimental conditions. Redeposited massive C atoms would then diffuse towards the protrusion tips, resulting in carbon nanofibre formation. The sparely formed CNFs on the tip of the protrusions may be attributed to the lower deposition velocity of the redeposited massive C atoms compared with the other carbon materials because of the lower sputtering yield of diamond.

A typical emission current density–electric field (*J–E*) curve of the CNFs on the diamond film is shown in Fig. 3. The corresponding Fowler–Nordheim (*F–N*) plot is also shown in the inset. From Fig. 3, the turn-on field (electric field for emission current density of 10 μA/cm^2) was estimated to be 1.8 V/μm and threshold fields (electric field for emission current density of 1 mA/cm^2) were estimated to be 4.6 V/μm. The field enhancement factor (β) calculated from the *F–N* plot was about 3810, assuming a work function of 4.6 eV. This emission characteristic was comparable to those reported for carbon nanotubes [20] and was better than those obtained for diamond films and nanodiamond films [21]. The field enhancement factor was comparable to those reported for CNFs from the graphite and flexible substrate with ion sputtering at room temperature by Tanemura *et al.* [6, 8]; it was ascribed to be the surface morphology of the CNFs-tipped-sharp protrusions. The investigation of emission property indicates that the combination of CNFs and diamond film is a very good field emission material.

4 Conclusions

A method to fabricate CNFs by oblique ion sputtering diamond films has been demonstrated. SEM shows that the ordered carbon protrusions were formed after 1 h ion irradiation and CNFs on the protrusion tips with a diameter of 40 nm, length of 1–4 μm and density of $1-2\times10^8$/cm^2 were achieved after 2 h ion sputtering. Raman spectra indicate that with the duration of irradiation, the amorphous or defect content increases. A typical emission current density–electric field curve shows that the turn-on field is 1.8 V/μm and the threshold field is 4.6 V/μm. It is believed that this method is very simple

and is suitable for the application in field emission devices of the combination of diamond and carbon nanofibres.

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