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Electron field emission characteristics of nano-catkin carbon films deposited by electron cyclotron resonance microwave plasma chemical vapour deposition

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This paper reported that the nano-catkin carbon films were prepared on Si substrates by means of electron cyclotron resonance microwave plasma chemical vapour deposition in a hydrogen and methane mixture. The surface morphology and the structure of the fabricated films were characterized by using scanning electron microscopes and Raman spectroscopy, respectively. The stable field emission properties with a low threshold field of $5\text{V}/\mu\text{m}$ corresponding to a current density of about $1\mu\text{A/cm}^2$ and a current density of 3.2mA/cm^2 at an electric field of $10\text{V}/\mu\text{m}$ were obtained from the carbon film deposited at CH_4 concentration of 8%. The mechanism that the threshold field decreased with the increase of the CH_4 concentration and the high emission current appeared at the high CH_4 concentration was explained by using the Fowler–Nordheim theory.

Keywords: field emission, carbon films, nano-catkin, microwave plasma chemical vapour deposition
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1. Introduction

In recent years, great efforts have been devoted to the development of electron field emitters for the application of display products.[1,2] So much attentions have been paid to carbon-based emitters, such as diamond,[3] diamond-like carbon,[4] carbon nanotubes,[5] and amorphous carbon (a-C),[6] and so on, because these materials have good electron field emission properties with a low electric field[7] and high current density.[8] Recent reports indicated that a-C films were a promising field emitter due to its unique chemical, electrical, optical, and mechanical properties.[9] In particular, low electron affinity of amorphous carbon films was very favourable to enhancing field emission.[10] In order to obtain good field emission properties with low threshold voltage and high current density, it may be essential to fabricate nano-structured carbon films. Various nano-structured carbon films had recently been investigated. Zhang *et al* reported that the low threshold field of carbon nanotubes attributed to the random distribution which brought on the high geometric enhancement factor.[11] Wang and co-workers found that the good field emission properties of carbon nanosheets[12] and carbon nanoflakes[13] might be due to the high density of graphite edges with potential emission sites. Based on two-dimensional geometry, the sheet-like carbon nanostructure was expected to be a more robust edge emitter than carbon nanotubes.[12] The research results Theanemura *et al* indicated that the carbon nanocones with the great aspect ratio had higher emission current and lower threshold field.[14] The field emission properties of other nano-carbon films had been studied, too.[15]

Carbon films were often prepared by hot-filament chemical vapour deposition (HFCVD),[16] RF plasma enhanced CVD,[17] electrodeposition technique,[18] filtered cathodic vacuum arc technique,[19] magnetron sputtering method.[20] Electron cyclotron resonance (ECR) microwave plasma chemical vapour deposition (MPCVD) was used to uniformly nucleate diamond

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over a large area.[21] In comparison with other deposition methods, ECR is a rather new technology for steady-state growth of carbon films due to its high-density plasma production at low gas pressures and low-energy ion transportation.[22,23] Currently, a number of investigations on the carbon film deposition by ECR have been performed.[24−26]

In this study, nano-catkin carbon films were prepared by ECR MPCVD and their field emission characteristics were studied.

2. Experimental

Carbon films were deposited on p-type (100) Si substrates by using an ECR MPCVD process with a high-power of 5kW, where a hydrogen–methane mixture was activated. ECR MPCVD system was located at a magnetic field strength of 0.0875T in deposition in order to satisfy the ECR condition. Si substrates were socked by 25% HF acid for 10min in order to remove the oxidized layer and rinsed by deionized water, and then ultrasonically scratched with diamond powder prior to the deposition process. A pretreatment was carried out in H_2 plasma for 10min before deposition. The experiment parameters employed are shown in detail in Table 1.

Surface morphologies of the carbon films were observed by a scanning electron microscope (SEM). The structure of the carbon films was characterized by Raman spectroscopy. The field emission testing was performed in high vacuum ($< 6.7\times10^{-4}$Pa) system at room temperature. A film sample (2mm×5mm) acted as the cathode and an aluminium plate was utilized as the anode. The anode was set to be 100μm away from the sample surface by using two 50-μm-thick Teflon sheets as a spacer. Macroscopic electric fields ranging from 0 to 10V/μm were applied between anode and cathode.

Table 1. Deposition parameters of carbon films deposited by ECR MPCVD.

	Pretreatment	Deposition
Pressure/Pa	10	10
Temperature /°C	600	600
MW power/kW	3	5
Bias voltage/V	–30	–50
Time/min	10	10
Gas/100sccm	H_2	CH_4/H_2=2/98–8/92

3. Results and discussion

The SEM images of carbon films deposited at the CH_4 concentration range from 2% to 8% are shown in Fig.1. Figs.1(a), 1(b), 1(c) and 1(d) correspond to the CH_4 concentration of 2%, 4%, 6% and 8%, respectively. The film deposited at the CH_4 concentration of 2% and 4% was composed mainly of carbon cluster without and with few nano-threads, respectively. The films deposited at the CH_4 concentration of 6% and 8% were composed of a lot of nano-catkins. This kind of structure, at first glance, is similar to nano-sheets, so large numbers of potential field emission sites were expected to be formed on the carbon nano-films.[12] The Raman spectra of the carbon film prepared at the CH_4 concentration of 8% are showed in Fig.2. Two Raman peaks at about 1340cm^{-1} and 1582cm^{-1} are found, this fact indicates that standard features are observed for carbon films.

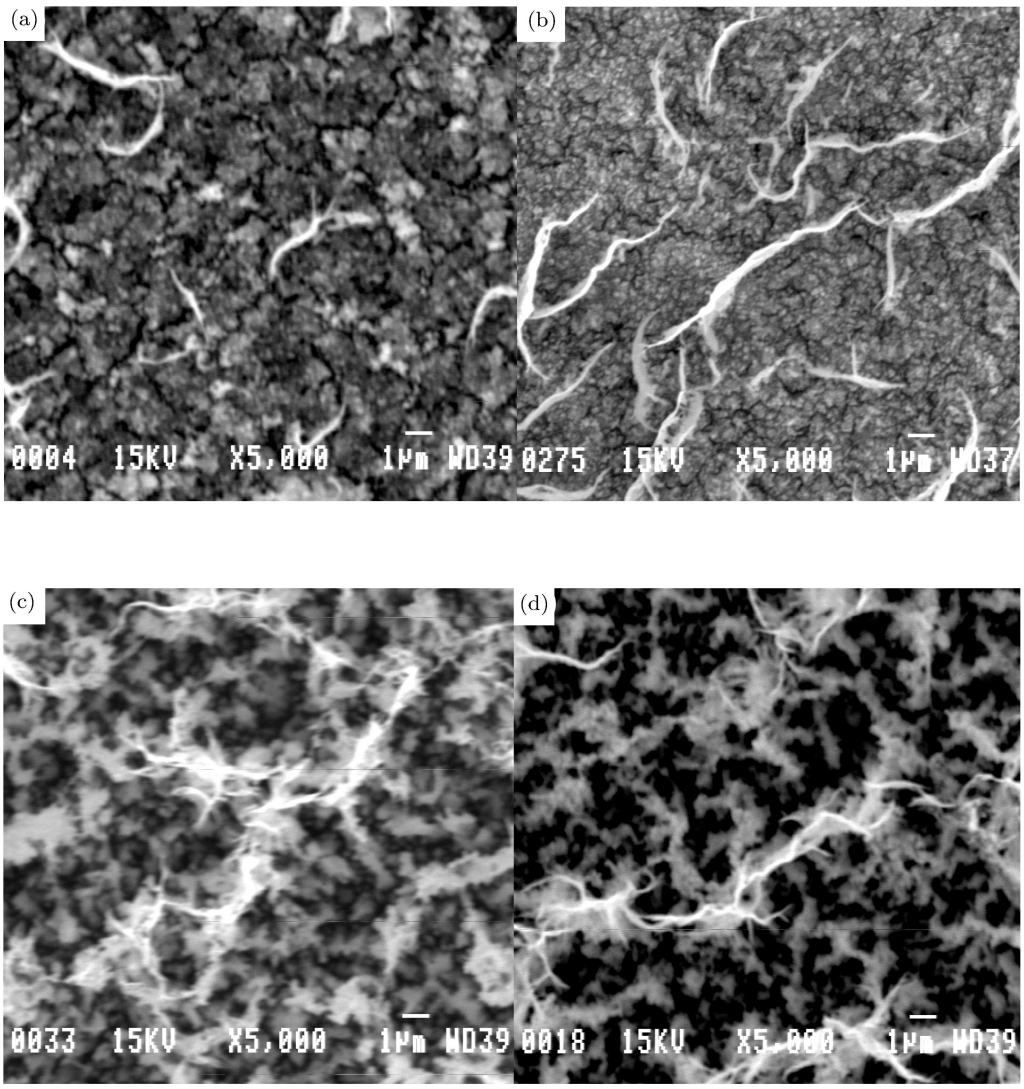


Fig.1. SEM images of carbon films deposited at the CH_4 concentration of (a) 2%, (b) 4%, (c) 6% and (d) 8%.

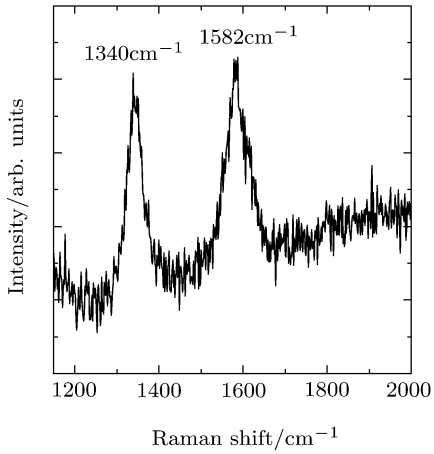


Fig.2. Raman spectrum taken from the carbon film fabricated at the CH_4 concentration of 8%.

The field emission characteristics were analysed by using the current density versus electric field ($J-E$) curves and Fowler–Nordheim (F-N) curves. The threshold electric field was defined as the electric field under which a $1\mu A/cm^2$ current density appeared.[7] $J-E$ plots and F-N plots are shown in Figs.3(a) and 3(b), respectively. The threshold electric field of $5.0V/\mu m$, approaching the value observed from carbon nano-sheets,[12] and the emission current density of about $3.2mA/cm^2$ at an electric field of $10V/\mu m$ were obtained for the carbon film deposited at the CH_4 concentration of 8%. The threshold electric field of 5.5, 6.4 and $6.9V/\mu m$ and the emission current density of about 3.4, 0.4, and $0.2mA/cm^2$ at an electric field of $10V/\mu m$ were attained for carbon films deposited at the CH_4 concentration of 6, 4 and 2%, respectively.

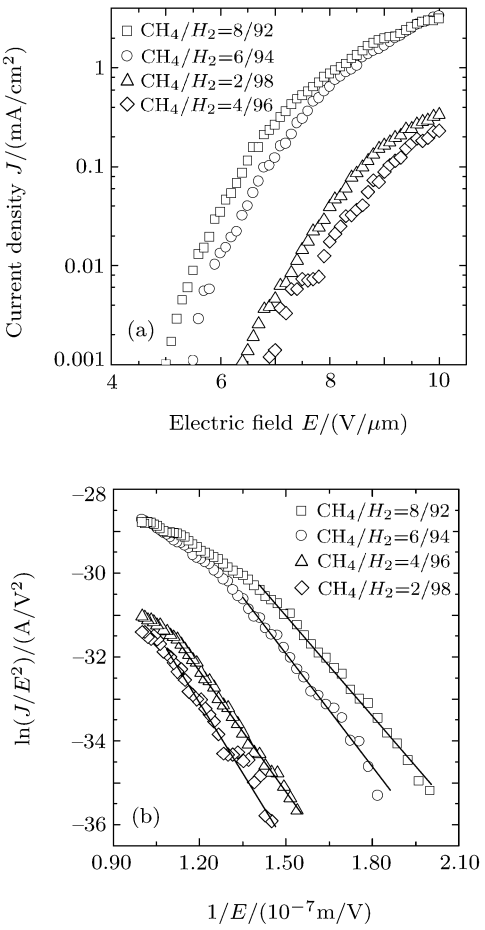


Fig.3. Field emission characteristics of carbon films deposited at various CH_4 concentration: (a) $J-E$ plots with (b) corresponding F-N plots.

As shown in Fig.3(a), it was shown that the threshold electric field evidently decreased with the increasing CH_4 concentration in the range from 2% to 8%. However, the emission current density at 10V/μm evidently increased in the CH_4 concentration range from 2% to 6%, then slightly decreased in the CH_4 concentration range from 6% to 8%.

The results show that the parameter of CH_4 concentration apparently influences the field emission characteristics of carbon films. The threshold electric field of carbon films was reduced with increasing the CH_4 concentration. This can be attributed to the field enhancement factor's increase due to the surface morphology's change from cluster carbon to nano-catkin carbon with increasing the CH_4 concentration. In addition, the H-terminated surface can be another reason. The increase of CH_4 concentration corresponds to the reduction of H_2 concentration, so H-terminated surface weakened with the increasing CH_4 concentration. The field emission was restrained by H-terminated surface.[27] The high CH_4 concentration corresponding to the low H_2 concentration induced the increase of sp2 carbon clusters. These rich sp2 carbon clusters with good connectivity in the films acted as conduction part of the amorphous network, which leaded to degrading the electron emission barriers and raising Fermi level to enhance electron emission.[28]

As shown in Fig.3(b), it is known that the field emission data do not follow the original F-N theory. F-N plots accorded with classic F-N behaviour at low electric field, but the absolute value of the slope of F-N plots decreased at high electric field. This was possibly attributed to the change of the field emission sites[7] or the effect of space-charge-limited current at high electric field.[29] This awaits further investigation.

The F-N equation is given approximately as follows:[7]

$$\ln\frac{J}{E^2} = \ln\left(\frac{A\beta^2}{\varphi}\right) - \frac{B\varphi^{3/2}}{\beta}\left(\frac{1}{E}\right), \qquad (1)$$

where $A = 1.54\times10^{-10}$J (AV^{-2}eV), B=6.83×10^9 (Vm^{-1}eV$^{-3/2}$), J is the emission current density, E is the applied electric field, φ is the work function, and β is the field enhancement factor. Here $\varphi_e = \varphi/\beta^{2/3}$, φ_e is the effective work function which can be used to characterize the field emission properties of emitters. Hence, φ_e were estimated by using Eq.(1) and the F-N data in the low electric field region.

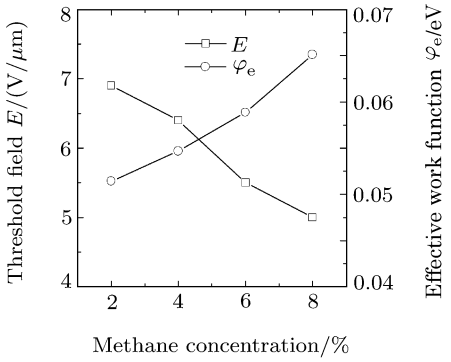


Fig.4. Threshold field E and effective work function φ_e as a function of the CH_4 concentration.

The threshold field E and the effective work function φ_e as a function of the methane concentration are shown in Fig.4. The effective work function increased and the threshold field decreased with increasing CH_4 concentration as shown in Fig.4. This suggested that when a low electric field was applied to different samples, the sample with low φ_e was emitted easily. This meant that the effective potential barrier height of F-N

tunnelling was reduced due to the enhancement of surface roughness and the increase of sp2 carbon clusters for carbon films with increasing CH_4 concentration. In addition, the higher current density was obtained for the carbon films deposited at the CH_4 concentration of 6% and 8%, this could attributed to the increasing effective emission area due to possessing sheet-like surface on which large numbers of potential field emission sites might be formed.[12]

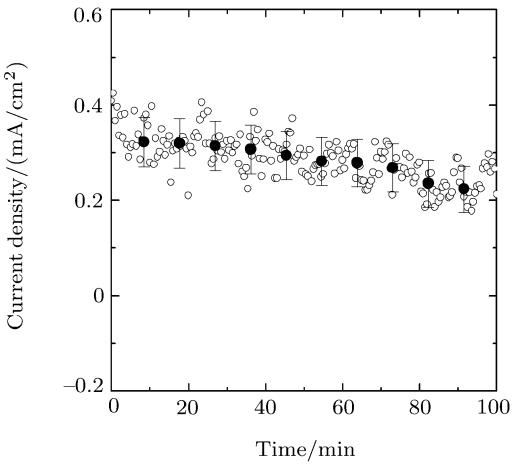


Fig.5. Field emission current density as a function of time at an electric field of 7V/μm for the carbon film deposited at the CH_4 concentration of 6%.

Besides, the emission stability of the sample deposited at the CH_4 concentration of 6% was measured at a constant applied electric field of 7V/μm. As shown in Fig.5, the average current density of 0.6mA/cm^2 was determined with a small deviation of 3%. No slight degradation in the current density was observed over approximately 100min.

4. Conclusion

In summary, nano-catkin carbon films were prepared by ECR MPCVD. The field emission characteristics of carbon films were tested in a high vacuum system. A stable field emission with a low threshold field of 5V/μm and a current density of 3.2mA/cm^2 at a electric field of 10V/μm were obtained for the carbon film deposited at CH_4 concentration of 8%. The field emission data at the low electric field was explained by F-N theory. The threshold field decreased with increasing the CH_4 concentration due to the increase of effective work function.

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