Vacuum 86 (2011) 356–360

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Synthesis and improved electron field emission characteristics of Au-coated nano-carbon needle films

Jing Wang [a], Ying-Ai Li [b], Guang-Rui Gu [a,*], Toshimichi Ito [c]

[a] Department of Physics, College of Science, Yanbian University, Yanji 133002, China
[b] National Laboratory of Superhard Materials, Jilin University, Changchun, Jilin 130012, China
[c] Division of Electrical, Electronic and Information Engineering, Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan

ARTICLE INFO

Article history:
Received 18 April 2011
Received in revised form
16 July 2011
Accepted 16 July 2011

Keywords:
Nano-carbon needle films
Au layer
Microwave plasma chemical vapor deposition
Field emission

ABSTRACT

Nano-carbon needle films (NCNFs) coated with a 5-nm Au layer were prepared on p-type Si (100) substrates by means of quartz-tube type microwave plasma chemical vapor deposition (MWPCVD) at different total gas pressures and an electron beam (EB) method. The NCNF deposited at the total gas pressure of 60 Torr had better field emission (FE) characteristics due to the dense structure of carbon sheets, good direction and high density of carbon needles. The FE properties were obviously improved due to depositing Au thin layer on NCNFs. The FE current density at a macroscopic electric field, *E*, of 10 V/μm was increased from 68.2 mA/cm^2 to 154.6 mA/cm^2 and the threshold field was decreased from 2.4 V/μm to 2.1 V/μm for the Au-coated NCNF deposited at the total gas pressure of 60 Torr. The three-region *E* model was employed to reasonably explain the FE data.

1. Introduction

Since carbon nano-tubes (CNTs) were discovered by Iijima in Japan in 1991 [1], the investigation on CNTs has become a hot topic in the world due to their unique one-dimensional tubular structure and subtle physical and chemical properties. In recent years, many novel types of nano-structured carbon films have been investigated, such as nano-sheets [2] and nano-cones [3]. Such materials will be widely used in chemistry, chemical engineering, materials science, biology, medical science and other fields because of their excellent properties. In particular, good electron field emission (FE) characteristics with low threshold electron fields [4] and high FE current densities [5] have been obtained from the nano-structured carbon films. So nano-structured carbon films have become promising cold cathode materials of display products. Moreover, it was reported that sulfur and nitrogen doping could improve the FE characteristics of carbon films [6]. Besides, Wang et al. reported that good FE characteristics of nano-sheet carbon films were attained due to the vertically standing nano-carbon flat sheets which had larger field enhancement factors and FE areas [7].

Many recent studies indicate that Fowler–Nordheim (F–N) curves of the nano-carbon films often have features which cannot be reasonably explained in terms of the standard F–N theory [4,8,9]. Therefore, it may be necessary to modify the F–N theory for explaining the above problem. In order to enhance the FE characteristics of nano-structured carbon films, surface modification to nano-structured carbon films may be necessary. We had researched the influence of metal surface modification on the FE characteristics of nano-sheet carbon films [10–12], and the enhanced field emission characteristics of thin-Au-coated nano-sheet carbon films had been obtained [12]. In order to further verify the enhanced FE effectiveness of the surface modification of Au layer to other nano-structured carbon films, the as-deposited NCNF and Au-coated NCNF were prepared and their FE characteristics were studied in this paper.

2. Experimental

For maintaining stabile low input power microwave plasma, typical quartz-tube MWPCVD apparatus was used in this work. Prior to carbon film depositions, a 10-min pretreatment with H_2 plasma irradiation was carried out for the scratched Si surfaces in a quartz-tube MWPCVD apparatus at 30 Torr. Then, NCNFs were deposited on p-type Si (100) substrates with a gas mixture of hydrogen and methane by using the same apparatus. Finally, an Au layer of about 5-nm thickness was deposited on NCNFs by EB evaporation. The synthesis conditions of NCNFs are shown in detail in Table 1.

* Corresponding author. Tel.: +86 0433 2733769; fax: +86 0433 2732596.
E-mail address: grgu@ybu.edu.cn (G.-R. Gu).

0042-207X/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2011.07.057

Table 1
The growth conditions of nano-carbon needle films deposited by MWPCVD.

Experimental parameter	CH_4/H_2 gas flows (sccm)	Substrate temperature (°C)	Total gas pressure (Torr)	Microwave power (W)	Deposition time (h)
Sample a	5/15	900 ± 10	40	450	2
Sample b	5/15	1050 ± 10	60	450	2

The surface morphologies of NCNFs thus deposited were observed with an FE scanning electron microscope (FESEM). Furthermore, the FE characteristics were measured at room temperature (RT) in a stainless-steel vacuum chamber with working pressures below 5.0×10^{-6} Torr. A film sample acted as a cathode while an aluminum plate was utilized as its counter anode. The distance between the cathode and anode was set to be about 100 μm, which was the thickness of an insulating spacer made of two sheets of 50-μm-thick teflon films. The typical FE area of these samples was about 10 mm^2. Macroscopic electric fields ranging from 0 V/μm to 10 V/μm were applied between the anode and cathode.

3. Results and discussion

The surface morphology of NCNFs was investigated by using FESEM, typical FESEM images are shown in Fig. 1 for sample a and sample b. These pictures indicate that the film surfaces are composed mainly of carbon nano-sheets twisted against each other and there are different densities of nano-carbon needles embedded in the carbon nano-sheets. The direction of nano-carbon needles is straight, and only a small quantity of nano-carbon needles are disorderly. It is found that the structure of carbon nano-sheets of sample b is more compact than sample a. Fig. 1(a2) and (b2) shows that the quantity of nano-carbon needles increases with increasing total gas pressure. Moreover, the approximate number of nano-carbon needles deposited at the total gas pressure of 60 Torr is estimated to be $2 \times 10^5/mm^2$, and the length of nano-carbon needles is about 1–4 μm. In addition, upon increasing total gas pressure, the direction of nano-carbon needles has the preferential orientation along the perpendicular direction to the surface of NCNFs. To sum up the above arguments, the higher the total gas pressure is, the better the growth is.

The difference in surface morphology of the samples deposited at different reaction pressures may be due to differences in etching rate by H radicals in the growth processes. This means that total gas pressure strongly influences deposition temperature, and the deposition temperature which is a key factor to influence the structure of nano-carbon needle films increases with increasing total gas pressure. The higher the growth temperature is, the more quickly the etching occurs. Such carbon needles having no sheet edges in the structure might more probably be left especially at the relatively higher temperatures during the deposition process since the carbon needles should be more chemically stable than the carbon sheet edges due to relatively less numbers of the C–C bonds to be broken. It is probably similar to carbon nano-tubes which grow at high temperature by CVD, because high temperature was more favorable to form carbon nano-tubes which have small diameters [13–15].

The FESEM image taken from sample c coated with a 5-nm Au layer and its corresponding magnification are shown in Fig. 1(c1) and (c2), respectively. These images show that large numbers of about 10-nm particles are formed on the Au-coated carbon film. The formation of nano-sized Au particles may be attributed to a self-assembly process due to little reactivity between the Au atoms and the carbon atoms.

Typical Raman spectrum of NCNFs fabricated in the present work is shown in Fig. 2. Two Raman peaks at about 1354 cm^{-1} and 1587 cm^{-1} are found, suggesting that standard features are observed for carbon films [16].

The research method of the current density versus electric field (J–E) curves is a good way to analyze field emission characteristics of NCNFs. The emission areas of the samples were about 10 mm^2. The FE current density, J is a function of the macroscopic electric field, E. J–E plots are shown in Fig. 3. In this study, the threshold E was defined as E at which $J = 1$ μA/cm^2 appeared [4]. Fig. 3 indicates that the NCNFs have good FE properties. The threshold E is estimated to be 3.1 V/μm and 2.4 V/μm for sample a and sample b, respectively. Meanwhile the maximum J value was as large as 61.5 mA/cm^2 and 68.2 mA/cm^2 at $E = 10$ V/μm. The threshold E is estimated to be 2.1 V/μm and the maximum J value is as large as 154.6 mA/cm^2 at $E = 10$ V/μm for sample b coated with a 5-nm Au layer.

From what has been discussed above, it is easy to find that the FE characteristics of the NCNF deposited at the total gas pressure of 60 Torr become better than the NCNF deposited at the total gas pressure of 40 Torr on this account. This is attributed to the dense structure of carbon sheets and good direction and high density of carbon needles for the NCNF deposited at the total gas pressure of 60 Torr. The dense structure of carbon nano-sheets can induce a large number of potential field emission sites [17] which make a greater contribution to FE current density of NCNFs in the high E region, and good direction and high density of nano-carbon needles can make the effective field enhancement factor increased. The nano-Au particles may have an enhanced effect on the number of potential field emission sites and the effective field enhancement factor. As a result, the Au-deposited NCNF has the highest FE current density and the lowest threshold E. To sum up the above arguments, the field emission characteristics of the as-deposited NCNF become better upon increasing the total gas pressure. Furthermore, the field emission characteristics of the NCNF coated with a 5-nm Au layer markedly improve.

In order to analyze the FE mechanism of NCNFs, as an example, the discussion taken from the as-deposited NCNF and the Au-deposited NCNF will be done. A three-region E model is used to discuss in the low, middle and high E regions separately in terms of our previous method [10]. In the low E region, a modified F–N model considering the statistical distribution in the structure of FE tips and E-dependent parameters gives the following formula of J in mA/cm^2 and E in V/μm [18]:

$$\ln \frac{J}{E^2} \approx \ln\left(\frac{1.54 \times 10^{-6} S_r \beta^2}{\varphi}\right) - \frac{6.83 \times 10^9 \varphi^{3/2}}{\beta}\left(\frac{1}{E}\right) \tag{1}$$

where S_r is an effective relative emission area, β is an effective field enhancement factor, and φ is the work function in eV.

Then, the work function φ is assumed to have a constant value of 4.5 eV [19] and 5.1 eV for the as-deposited NCNF and the Au-deposited NCNF, respectively. S_r and β are assumed to change with E while they are regarded as constant values in each E sector of about 0.2 V/μm. Fig. 4 shows the observed J–E data for the as-deposited NCNF and the Au-deposited NCNF in the low J region and those fitted in every sequential 0.2-V/μm E region by using a local fitting method [10,11], indicating that the modified F–N model can reasonably reproduce the experimental data.