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Diamond-like carbon decoration enhances the field electron emission of silicon nanowires

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ABSTRACT

Diamond-like carbon decorated silicon nanowires (DLC-SiNWs) have been fabricated using magnetic filtered vacuum plasma deposition process at room temperature on SiNW array substrates. DLC-SiNWs are composed of uniformly distributed amorphous carbon and a few diamond nano-grains, in which there are more than 70% sp^3 bonds in the carbon film. The turn-on field (E_{on}) of DLC-SiNWs changes with the thickness increase of DLC layer. E_{on} of DLC-SiNWs with a thickness of 60 nm reaches at a lowest value, i.e. 4.36 V/μm, which is better than the original SiNWs. These indicate that the field emission (FE) property of SiNWs decorated with a suitable thickness DLC is enhanced due to the work function reducing of the tip of SiNWs, at which the amorphous carbon phase layer embedded with a few diamond nano-particles has been decorated.

1. Introduction

Dating from the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1], many researchers have paid their attention to the study of one-dimensional nanostructures due to their promising properties, especially the FE property applied to the flat-panel displays, such as carbon nanotubes and semiconductor nanowires [2]. With the development of micromachining and integration techniques, SiNWs, firstly fabricated in 1964 [3], exhibit good FE property through the effort made by the researchers. Huq et al. [4] and Zhao et al. [5] fabricated the ultra sharp silicon field emitters, which had relatively high and stable emission current. Zeng et al. [6] improved the field emission property of the SiNWs fabricated by CVD method by post-annealing the samples at a high temperature for 24 h. Many other means, such as doping [7], and catalyst etching [8], to improve the FE property of SiNWs have also been examined. On the other hand, modification with sputtering thin film is an efficient approach to the development of the FE of SiNWs [9], and DLC thin films with negative electron affinity present better FE property than that of a diamond film and silicon tips [10]. In this paper, the fabrication and FE characteristics of DLC-SiNWs have been investigated.

2. Experiment

A relatively simple chemical etching approach is utilized here to synthesize SiNWs [11,12]. N type (100) silicon wafer is used as the substrate and cut into regular shapes. After cleaning ultrasonically in turn in acetone and ethanol for 5 min to degrease, the silicon slices were transferred into 1% diluted HF solution to remove the oxide layer. Each procedure ended with rinsing the samples under flowing deionized water and drying naturally at room temperature. After cleaning, the silicon slices are put into the solution of $AgNO_3$/HF, whose concentrations are 0.01 mol/L and 8%, respectively, for 1 min to synthesize silver catalyst particles, and then would be quickly immersed into H_2O_2/HF solution to carry out the chemical etching process for 1 h when SiNWs are gradually fabricated. In order to decrease the influence of SiO_2 layer covered on SiNWs, the as-grown SiNWs samples are treated in HF aqueous solution to remove the SiO_2 layer existing on SiNWs before DLC film deposition. DLC layers are prepared on SiNWs substrates at room temperature by the magnetic filtered vacuum plasma deposition (MFVPD) process during which the carbon plasma is produced with high purity by an arc source with a filter. The operation current of the arc source is about 100 A and a bent magnetic filter duct is used to remove the unwanted large particles. The base pressure of the deposition chamber is maintained below 2×10^{-4} Pa. The thickness of DLC layers is selected from 10 to 100 nm.

Scanning electron microscope (SEM S-4800, Hitachi) and transmission electron microscope (FEI TECNAI F30, PHILIPS) were employed to characterize the morphology and structure of SiNWs. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to determine the chemical state of coating. Field electron emission measurement was carried out in a diode system whose base pressure was below 3×10^{-7} Pa. The distance between the anode (diameter of the polished anode plate is about 50 mm) and cathode (to be ground) was about 500 μm, and controlled by an electric manipulator which

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was a drive engine connected to a computer and could control the movement of the anode with the accuracy of 1 μm. During the measurement of the field emission, the working voltage varying from 0 to 10 kV was applied, and the sample size is about 3×3 mm^2. The measurement data were automatically recorded by a computer connected to the measurement system, and analyzed by the Fowler–Nordheim (F–N) equation.

3. Results and discussion

Fig. 1(c) shows that well aligned SiNWs about 10 μm in length are uniformly formed on the Si substrates by the chemical etching process. Fig. 1(a) and (b) reveals that the SiNWs are about 100 nm in diameter and are [100] oriented. DLC layers with different thicknesses are deposited using MFVPD process on SiNW substrate. Morphology of DLC-SiNWs could change with thickness of the layer, as shown in Fig. 2. Non-uniform structures are formed on the DLC layer with a lower thickness, and only discrete and sparse carbon particles are observed. The uniformity of DLC-SiNWs gradually increases with the thickness of layer. Thus continuous layer can be formed when the thickness of the DLC layer is larger than 20 nm. Fig. 3 shows the morphology of the DLC layer with the thickness of 60 nm decorated on the surface of SiNWs, where Fig. 3(a), (b) and (c) are HRTEM and SEM images of DLC-SiNWs, respectively. The continuous DLC layer decorated on the top surface of SiNWs has been observed. For the DLC layer fabricated using MFVPD process at room temperature, most of the phases are amorphous carbon, and only a few diamond particles dispersive embed in the DLC layer. The particle size is about several nanometers.

For DLC layer, content of sp^3 bond is an important parameter and can be determined using Raman spectrum and XPS. The Raman spectrum of DLC-SiNWs with an excitation wavelength of 532 nm is illustrated in Fig. 4(a). A broader band can be observed in the range from 1000 to 1800 cm^{-1}. This confirms that the deposited layer is mainly composed of amorphous carbon. To analyze the spectrum in detail, the spectrum can be decomposed into a high-frequency component (G band) at 1540 cm^{-1} and a low-frequency one (D band) at 1360 cm^{-1}. Both D and G bands are typical features of highly disordered graphite-like structures [13].

Raman's spectrum is unreliable in quantitative analysis of DLC. To get quantitative results of DLC layer composition (sp^2:sp^3), XPS analysis is employed. Fig. 4(b) indicates C1s peak and the XPS spectrum of the DLC layer. The C1s peak is fitted by a Gaussian function with two components centered at 284.4 and 285.12 eV, respectively. The C1s peak for graphite is at 284.0–284.5 eV, for diamond at 285.0–285.2 eV [14–16]. These components are correspondent to sp^2 bonded carbon and sp^3 bonded carbon, respectively. Since the area of each peak is directly related to the concentration of the corresponding phase, the sp^3 content is estimated by taking the ratio of the sp^3 peak area over the sum of sp^3 and sp^2 peak areas [10]. As a result, it is found that the fraction of sp^3 bonded carbon atoms [sp3/(sp3 + sp2)] is about 70.37% for the DLC layer.

The curves of field emission current density (J) versus electric field (E) and the corresponding Fowler–Nordheim (F–N) plots of the SiNWs and DLC-SiNWs for different thicknesses are shown in Fig. 5. The main parameters of field electron emission calculated from the J–E curves and F–N plots are listed in Table 1. From Fig. 5(a), it can been seen that the field electron emission of original SiNWs can be turned on at 5.01 V/μm, at which the emission current density is 10 μA/cm^2, and the emission current density can reach 101 μA/cm^2 at the applied field of 5.94 V/μm. It indicates that the turn-on field (E_{on}) of SiNWs fabricated by the chemical etching process is about 5.01 V/μm. Comparing with the reports in which the E_{on} of SiNWs was usually in the range from 8.6 to 15 V/μm [17], the E_{on} of SiNWs fabricated by the chemical etching process is lower. DLC is a negative affinity material with high FE property. The application of DLC layer can improve the FE of emitters. Due to DLC layer deposition on the top surface of SiNWs, the J–E curves of SiNWs gradually move to a low field, and the J of SiNWs increases to 294 μA/cm^2 at the applied field of 5.94 V/μm for 60 nm DLC layer, which is two times higher than that of the original SiNWs. At the same time, the minimum E_{on}, 4.36 V/μm, can be obtained after the DLC layer was deposited on the top surface of SiNWs. Compared with original SiNWs, the E_{on} of DLC-SiNWs is reduced by 13%. It is indicated that the DLC layer deposition has enhanced the FE of SiNWs.

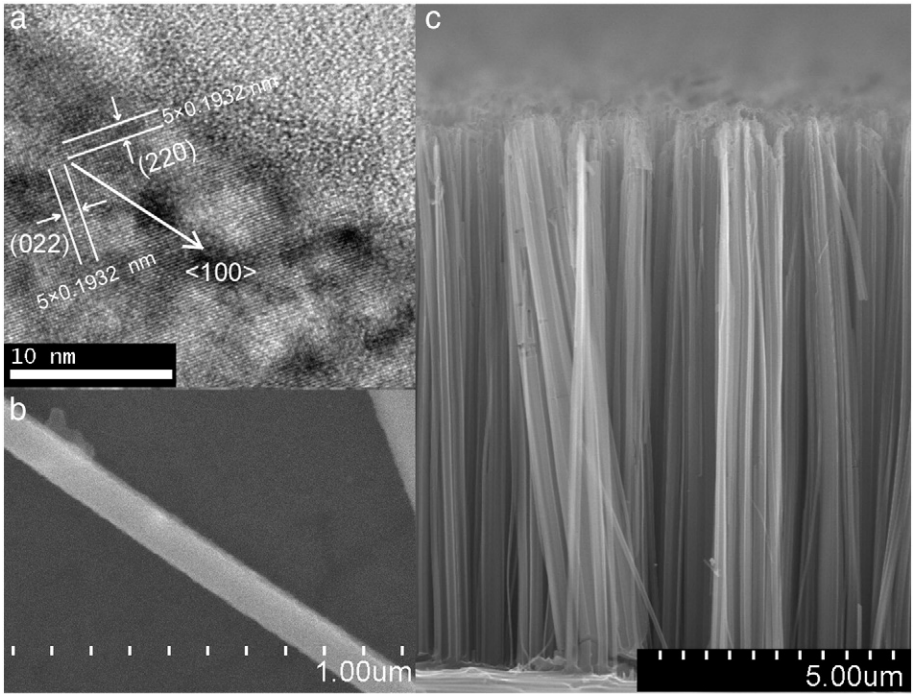

Fig. 1. HRTEM (a), TEM (b) and SEM (c) images of the SiNWs fabricated by using chemical etching at room temperature.

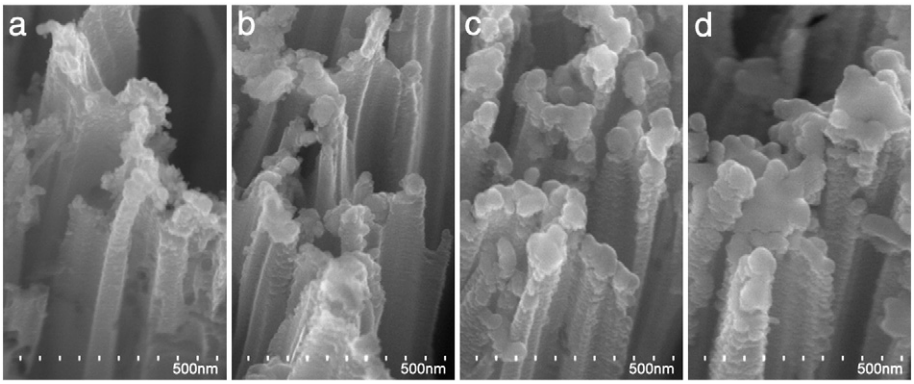

Fig. 2. Cross sectional SEM images of the SiNWs decorated with DLC film at different thicknesses. a) Original; b) 20 nm; c) 60 nm; d) 100 nm.

Field emission characteristics of DLC-SiNWs are analyzed by using the Fowler–Nordheim (F–N) equation given below [18]

$$\ln\left(\frac{J}{E^2}\right) = \ln\left(ra\varphi^{-1}\beta^2\right) - \frac{sb\varphi^{\frac{3}{2}}\beta^{-1}}{E} \quad (1)$$

where Φ is the work function, β is the field enhancement factor, a and b are the F–N constants, r and s are appropriate values of the intercept and slope correction factors, respectively. F–N plot is expected to be a good straight line because of small variation of r and s with 1/E. Further to simplify the equation above, r multiplied by a equals a constant 1.54×10^{-6} A (eV) V^{-2} and s multiplied by b equals a constant 6.83×10^{3} $(eV)^{-3/2}$ V $(\mu m)^{-1}$. According to the Fowler–Nordheim (F–N) equation, we define a parameter K, which associates with the structures (composition, tip sharpness, aspect ratio, etc.) and electrical parameters (conductivity, work function, etc.) of emitters and indicates an ability of field electron emission from materials, and is given as:

$$K = \frac{\beta}{\varphi^{\frac{3}{2}}} = -\frac{sb}{S} \quad (2)$$

where, S is a slope of Fowler–Nordheim plots. From Eq. (2), it can be seen that large β and low Φ in the emitter make the parameter K increase, and show the high ability of field electron emission for the emitter. As shown in Fig. 5(b), it has been observed that all the F–N plots are approximate lines in the high-current density areas and fitted with the F–N equation, which suggests that the electrons are emitted by the cold FE process. The K of DLC-SiNWs can be calculated by the F–N plots and Eq. (2), and listed in Table 1. Obvious increase of the K for DLC-SiNWs has been observed due to the DLC deposition, and the K reaches at a maximum value, i.e. 148.98, when 60 nm DLC layer are deposited on SiNWs. This indicates that a suitable deposition

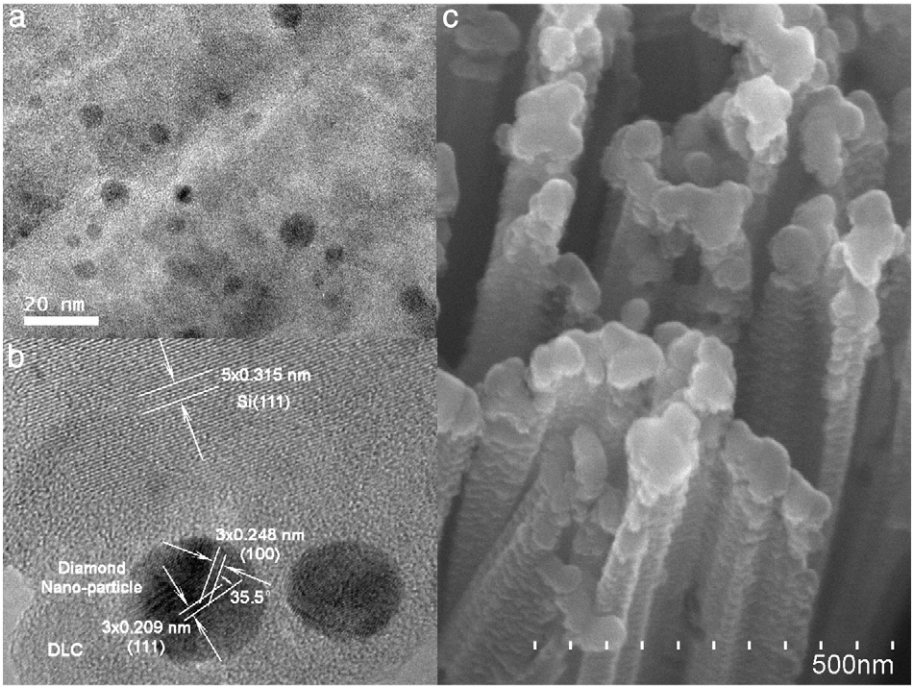

Fig. 3. TEM image (a), HRTEM image (b) and SEM (c) image of the SiNWs decorated with DLC film at thickness of 60 nm.

thickness of DLC layer could enhance the field emission properties of SiNWs.

During the DLC layer deposition, the SiNW diameter increases with the ever-increasing DLC thickness. β is a parameter describing the aspect ratio of SiNWs, and it decreases with the increase of SiNW diameter, which deteriorates the field emission of the DLC-SiNW hybrids. However, DLC is a negative electron affinity material, which can greatly facilitate electrons tunneling barriers. Additionally, DLC is full of defects, especially vacancy-related defects, which are supposed to increase the field electron transmission traces, i.e., increase the number of effective emission sites during field electron emission and therefore improve the field emission of DLC-SiNW hybrids [19]. That's to say, both the SiNW diameter and the number of emission sites influence the β, but in the defect-rich DLC decorated SiNWs, the later is dominative. Furthermore, the increased state density of defects ascends the Fermi Lever, and thus decreases the work function of the DLC-SiNW hybrids [20]. In a word, the concurrent effect of emission site increase induced promotion of β and the decrease of work function improve the field emission of DLC-SiNW hybrids within a certain DLC thickness, which is ~60 nm in our study. However, with further increase of the DLC thickness, the SiNW diameter induced β decrease is dominative, and therefore deteriorates the field emission of DLC-SiNW hybrids.

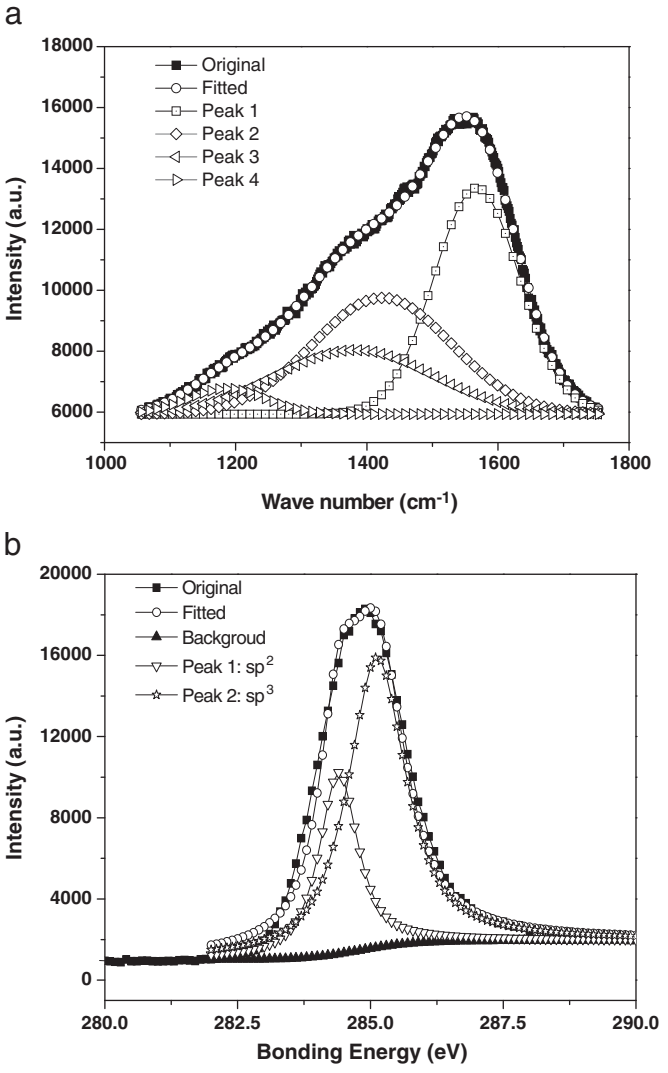

Fig. 4. Raman spectrum (a) and XPS analysis (b) of the SiNWs decorated with DLC film at thickness of 60 nm.

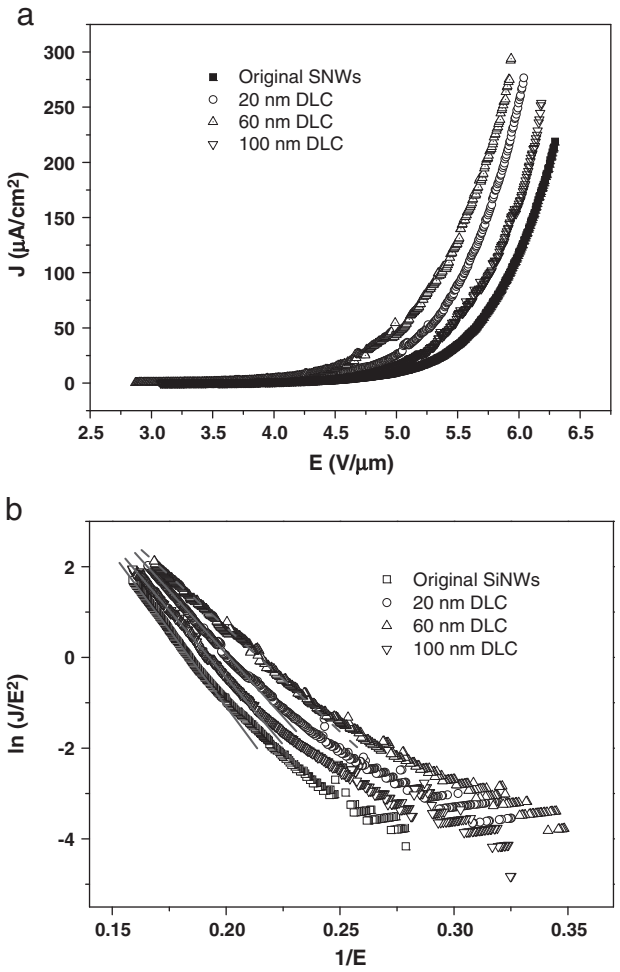

Fig. 5. Field emission from the SiNWs decorated with DLC film at different thicknesses. a) J–E curves; b) F–N plots.

4. Conclusions

In summary, DLC-SiNWs with uniform distribution have been fabricated using MFCPD process at room temperature on a well aligned SiNW array substrate. Raman spectra and XPS analysis prove that there are more than 70% sp^3 bond existing in the DLC layer. Due to the coupling interaction between DLC nanolayer and SiNWs making the electrons much easier to emit from the tip of the emitter under the applied field, and reducing the Φ of the emitter materials, the decoration of DLC layer with an appropriate thickness at the tip of SiNWs can induce the K of the emitter increasing from 99.38 to 148.98, and enhance the FE property of SiNWs. The lowest E_{on} of the DLC layer decorated is about 4.36 V/μm and the J can reach 294 μA/cm^2 at the applied field of 5.94 V/μm. The FE property of DLC-SiNWs is better than that of SiNWs.

Table 1
Field electron emission results of the DLC-SiNWs with different DLC thicknesses.

	SiNWs	20 nm decorated	60 nm decorated	100 nm decorated
J (μA/cm^2)[a]	101	223	294	149
E_{on} (V/μm)[b]	5.01	4.59	4.36	4.82
$K=(\beta/\Phi^{3/2})$[c]	99.38	126.54	148.98	117.82

[a] J is the field emission current density at applied field of 5.94 V/μm.
[b] E_{on} is the turn-on field obtained from J–E curves.
[c] K is calculated by using the F–N plots and Eq. (2).

Acknowledgments

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