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Electron field emission properties on UNCD coated Si-nanowires

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Abstract

The electron field emission (EFE) properties of Si-nanowires (SiNW) were improved by coating a UNCD films on the SiNWs. The SiNWs were synthesized by an electroless metal deposition (EMD) process, whereas the UNCD films were deposited directly on bare SiNW templates using Ar-plasma based microwave plasma enhanced chemical vapor deposition (MPE–CVD) process. The electron field emission properties of thus made nano-emitters increase with MPE–CVD time interval for coating the UNCD films, attaining small turn-on field (E_0=6.4 V/μm) and large emission current density (J_e=6.0 mA/cm^2 at 12.6 V/μm). This is presumably owing to the higher UNCD granulation density and better UNCD-to-Si electrical contact on SiNWs. The electron field emission behavior of these UNCD nanowires emitters is significantly better than the bare SiNW ((E_0)$_{SiNWs}$=8.6 V/μm and (J_e)$_{SiNWs}$<0.01 mA/cm^2 at the same applied field) and is comparable to those for carbon nanotubes.

Keywords: Ultra-nano-crystalline diamond (UNCD); Silicon nanowires (SiNWs); Electron-field-emission (EFE)

1. Introduction

Diamond films have been extensively investigated for the applications as electrion field emitter in the vacuum microelectronics devices owing to the negative electron affinity with low effective work functions [1], However, the electron field emission properties of these materials are inferior to those of carbon nanotubes (CNTs) due to large electric field required for turning on the electron field emission phenomenon [2]. How to reduce the turn-on field for diamond films is thus urgently required. There are several methods been proposed to enhance the electron field emission properties of the diamond films, which include reducing the grains size for diamonds [3], doping semiconduting species for increasing conductivity of the diamond [4], and using high aspect ratio tips as template for fabricating the diamond tips [5].

Over the past years, many researchers have reported successful fabrication of diamond tip using aligned silicon tip arrays as templates, which were prepared by using the conventional chemical vapor deposition, laser ablation, thermal evaporation/ decomposition techniques, in conjunction with the microelectronic processes, resulting in good electron field emitters [6–8]. However, most of these methods require sophisticated apparatus and complicated processing steps, which are time consuming and expansive. Recently, we have developed a self-aligned process, which is simple and can fabricate aligned silicon nano-wires (SiNWs) in large area on a single-crystal wafer based on a micro-electrochemical redox reaction process [9,10].

In this article, we used the SiNWs as template to grow ultra-nanocrystalline diamond (UNCD) films for synthesizing the UNCD nano-emitters. The electron emission properties of thus obtained UNCD nano-emitters are observed to be pronouncedly superior to those of the bare SiNWs.

2. Experimental

The silicon nanowires (SiNWs) were fabricated by an electroless metal deposition (EMD) process, in which (i) the (100) silicon wafer (1×1 cm^2) were sputter-coated with a thin gold film (~10 nm), followed by post-annealing in argon

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atmosphere at 1073 K for two hours to form small gold nanoparticles (~15 nm) on the Si-substrate; (ii) the Si wafer containing Au nanoparticles on the surface was then immersed into a HF-based aqueous solution (12 ml of 48% HF and 0.103 M of $AgNO_3$) for 30 min, followed by cleaning with nitric acid as well as deionised water, and then dried. SiNWs about 35 nm in diameter were thus formed on Si-substrate via such a self-aligned Galvanic anisotropic etching process. UNCD films was deposited on the SiNW-templates by a MPECVD process for 2 h (IPLAS, cyrannus), with the total pressure of 100 Torr and the gas flow of 1 and 99 sccm for methane and argon, respectively. The microwave power was 600 W (2.45 GHz) and the reaction temperature was about 673 K.

The morphologies of the SiNWs and UNCD nanowires were examined using SEM (Jeol JSM-6500F), whereas the crystal structure of these nanowires was investigated by a high-resolution transmission electron microscopy (HRTEM, Jeol JEM-4000EX). The structure of the diamond nanowires was examined by Raman spectroscopy (Renishaw, 632.8 nm) and NEXAFS in Sychrotron radiation. The electron field emission properties of the UNCD nanowires were measured with a parallel plate set-up, in which the sample-to-anode distance was tunable. The current–voltage (I–V) characteristics were measured by an electrometer (Keithley 237) under pressure of below than 10^{-6} mTorr. The electron field emission parameters were extracted from thus obtained I–V curves by using Fowler–Nordheim model [11,12].

3. Results and discussion

Fig. 1(a) and (b) shows cross-sectional and plan-viewed micrographs of the Si-nanowires (SiNWs), respectively, indicating that SiNWs are about 35 nm in size. The inset in Fig. 1(a) shows the SEM micrograph of the gold nano-particles (~20–30 nm) used for synthesizing SiNWs. The SiNWs are well aligned and are uniformly distributed on the Si-substrates. The untra-nanocrystalline diamond (UNCD) films can be deposited directly on these SiNW-templates without the necessity of pre-treatment process. This is contrary to the behavior commonly observed for nucleation of UNCD films on Si-substrates, in which, the UNCD can hardly form on a bare Si-substrates and require a special pre-treatment process for forming densely populated diamond nuclei prior to the growth of UNCD films. The phenomenon that UNCD films can be deposited directly on these SiNWs indicated that the as etched SiNWs surface contains abundant active sites which readily react with carbon species in the plasma, forming diamond nuclei.

Fig. 1(c) indicates that UNCD films can be grown on SiNW-templates by MPECVD process, forming nano-emitters. The UNCD grains are scarcely distributed on SiNWs when deposited for only 1.0 h (Fig. 1(c)). The number density of UNCD grains coated on SiNWs increases with deposition time interval and fully covering the SiNWs finally when deposited for longer than 2.0 h (Fig. 1(d)). Typical Raman spectrum of thus obtained UNCD coatings acquired using 623 nm laser is shown in Fig. 2,

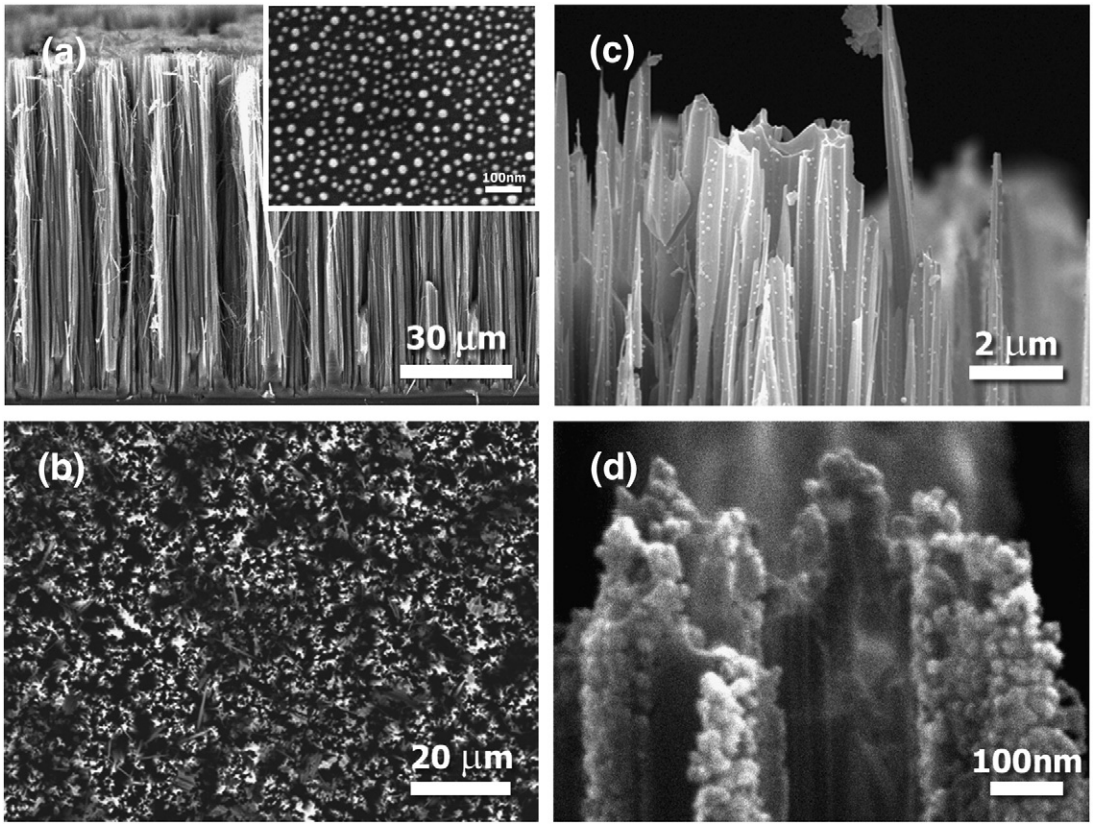

Fig. 1. (a) Cross-sectional and (b) plan-viewed SEM micrographs for Si-nanowires (SiNWs) fabricated by electroless metal deposition (EMD) process using [100] Si substrates. The inset in (a) shows the gold nanoparticles coated on [100] Si substrates used for fabricating the SiNWs. SEM micrographs of UNCD nanowires fabricated using SiNWs template by MPECVD process for (c) 1 h and (d) 3 h.

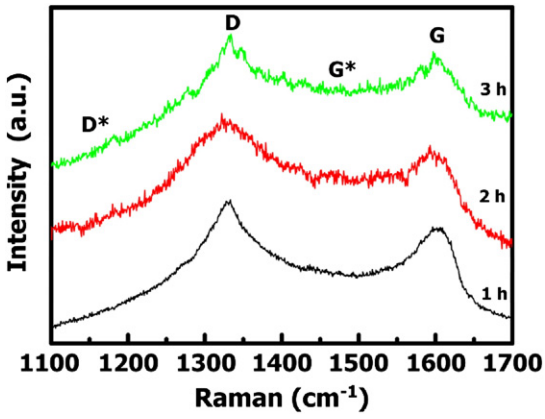

Fig. 2. Typical Raman spectra of UNCD nanowires, which are MPECVD for 1–3 h.

indicating there presence D-band resonance peak near 1330 cm^{-1} and G-band resonance peak near 1600 cm^{-1}. The Raman resonance peaks are very broaden, a characteristic of diamond films with nanocrystalline grains [13]. It should be noted that the Raman scattering is much more sensitive to sp^2-bonds than to sp^3-bonds, with the sensitivity ration about 50–230 times [14]. The smallness in the size of the diamond grains in UNCD probably induces the presence of transpoly-acetelene layer on their surfaces [15–17], which further broaden the Raman resonance peaks. Both phenomena render the unambiguous identification of UNCD nanowires using Raman spectroscopy extremely difficult. To unambiguously identify the UNCD materials, we examined these nano-wires by using transmission electron microscopy (TEM). Fig. 3(a) and (b) shows the TEM micrographs of UNCD films grown on SiNWs, revealing that they contain very small grains of diamond. Selected area electron diffraction (SAED) patterns shown as inset in Fig. 3(a) and the enlarged micrographs shown in Fig. 3(c) and (d) indicate that these grains, about 5 nm in size, are diamonds.

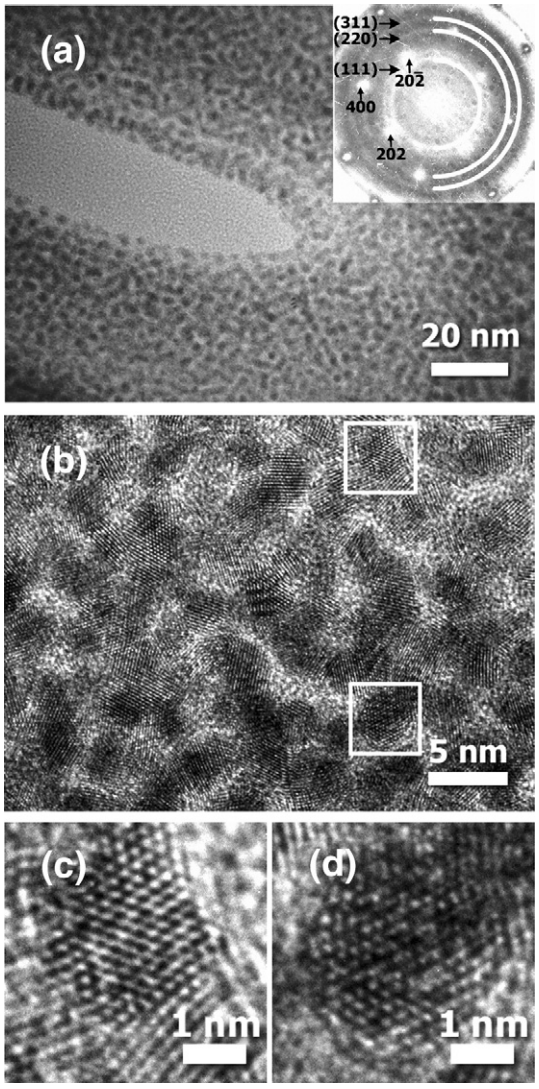

Fig. 3. (a), (b) TEM micrograph of UNCD nanowires MPECVD for 3 h (the inset in (a) shows the SAED pattern), and (c), (d) enlarged TEM micrograph of the area circled in (b).

The electron field emission (EFE) properties of these UNCD-coated SiNWs, which are designated as UNCD nano-emitters, are illustrated in Fig. 4. Although the SiNWs are of nano-sized dimension, possessing large field enhanced factor (β), they still need very large turn-on field, $(E_0)_{SiNW}$=8.6 V/μm, to induce electron field emission and can attain only $(J_e)_{SiNW}$=4.0 mA/cm^2 electron field emission current density at applied field of $(E_a)_{SiNW}$=22.0 V/μm (open squares, Fig. 4), It should be noted that the turn-on field was estimated from the Fowler–Nordhein plot of the current density-field (J–E) curve as the intersection of two straight lines extrapolated from the low-field and high-field segments of the F–N plot (shown as inset in Fig. 4). Assuming that the work function of SiNWs is the same as bulk silicon materials, i.e., ϕ_{Si}=4.1 eV, the β-factor of the SiNWs can be estimated from the slope of the Fowler–Nordein plot, as slope=$(\phi_{Si})^{3/2}/\beta$. The field enhancement factor of the SiNWs is thus calculated as β_{Si}=367, which is markedly lower than the β-value expected for such high aspect ratio geometry. The probable cause is the electrical screening due to too densely populated nanowires.

The UNCD film coated on SiNWs, the UNCD–NWn (n is the number of hours of deposition period), possess markedly superior electron field emission properties to the bare SiNWs.

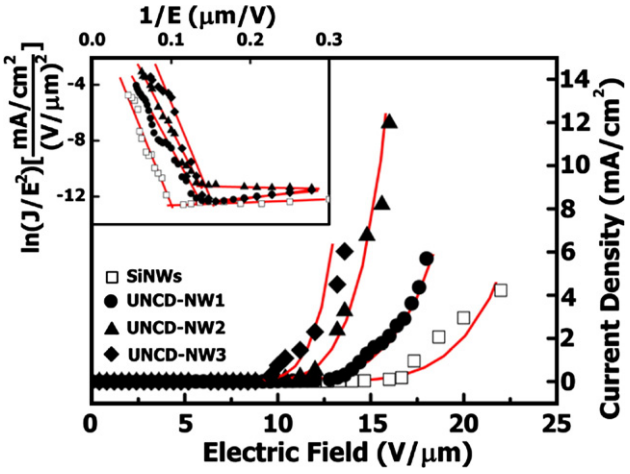

Fig. 4. The electron field emission properties, the current density-field (J–E) plots, of SiNWs and UNCD nanowires, which were coated on SiNWs by MPECVD process for 1–3 h (the insets are the corresponding Fowler–Nordheim plots).

Table 1
The electron field emission properties of the SiNWs and UNCD nanowires

UNCD depositon time (h)	0	1	2	3
J_e (mA/cm^2) [a]	<0.01	0.8	3.2	6.0
E_t (V/μm) [b]	>22.0	18.0	14.2	13.6
E_0 (V/μm) [c]	8.6	7.6	7.4	6.4

[a] J_e: the electron field emission current density achieved at 13.6 V/μm applied field.
[b] E_t: the electric field necessary for attaining J_e=6.0 mA/cm^2.
[c] E_0: the turn-on field derived from Fowler–Nordheim plots.

Fig. 4 indicates that, for UNCD–NW1 (closed circles, Fig. 4), the electron field emission can be turned on at $(E_0)_{UNCD-NW1}$= 7.6 V/μm and electron field emission current density achieves $(J_e)_{UNCD-NW1}$=6 mA/cm^2 at 18 V/μm applied field. The turn-on field decreases markedly for UNCD nano-emitters, which were MPECVD for longer time interval (>2 h). The E_0 decreases from 7.6 V/μm for UNCD–NW1 to 7.4 V/μm for UNCD–NW2 (Closed triangles, Fig. 4) and then to 6.4 V/μm for UNCD–NW3 (Closed diamonds, Fig. 4). The applied field required for inducing 6 mA/cm^2 EFE current density reduces from 18 V/μm for UNCD–NW1 to 13.6 V/μm for UNCD–NW3. The electron field emission for UNCD nano-emitters can be turned on at markedly smaller field, attaining pronouncedly larger electron field emission current density, as compared with those for SiNWs. Presumably, the improvement in electron field emission properties for UNCD–NWs synthesized by longer MPECVD process is due to better coverage of the UNCD grains over the SiNWs, which enhances the transport efficiency of electrons from Si to UNCD materials. The electron field emission properties of these UNCD–NWs are summarized in Table 1. It should be noted that for an applied field of E_a=13.6 V/μm, the SiNWs are hardly emitting, whereas the UNCD–NWs can emit large current density, viz. $(J_e)_{UNCD-NW2}$=3.2 mA/cm^2 for UNCD-NW2 and $(J_e)_{UNCD-NW2}$=6.0 mA/cm^2 for UNCD–NW3.

Since, both UNCD grains are densely populated, fully covering the SiNWs for UNCD–NW2 and UNCD–NW3, the characteristics of the emitting surface, the nanocrytalline diamond grains, should be the same. Therefore, the superior electron field emission properties of the UNCD–NW3 nanowires over the UNCD–NW2 ones must arise from the better UNCD-to-Si electrical contact, facilitating the transport of electrons from the Si to the emitting sites, which will be discussed shortly. In the growth of UNCD on planar Si-substrates[18], large UNCD clusters of nuclei are resulted and are scarcely distributed on the Si surface due to the fact that too few nuclei were available. The UNCD clusters grew laterally to completely cover the Si surface after long time MPECVD process, resulting in large UNCD grains. In such a growth process, voids between the large UNCD grains will be resulted, especially in the vicinity of UNCD-to-Si interface. Although nucleation took place much more easily on the SiNWs, as compared with that on Si-planar surface, resulting in more densely populated UNCD nuclei on the SiNWs. Similar kind of defects is expected to occur also for UNCD nano-emitters, especially near the UNCD-to-SiNWs interfaces, resulting in large resistance for electron transport. Some proportion of the voltage drop will occur at the UNCD-to-Si interface, such that the apparent turn-on field is larger. Smaller electron field emission current density will be resulted, as the actual electric field experienced by UNCD nano-emitters is smaller than the applied field due to the poor UNCD-to-Si electrical contact. Therefore, even though the UNCD nano-emitters are of high aspect ratio and large field enhancement factor (β), the turn-on field for these UNCD nano-emitters is still large, as compared with those for carbon nanotubes. Nevertheless, the electron field emission properties attainable for the UNCD nano-emitters ($(E_0)_{UNCD-NW}$=6.4 V/μm and $(J_e)_{UNCD-NW}$=6.0 mA/cm^2) is significantly better than those for UNCD films coated on a planar substrates, which require $(E_0)_{UNCD}$=8.3 V/μm to turn-on the electron field emission phenomenon and the electron field emission current density is only $(J_e)_{UNCD}$=0.2 mA/cm^2 at 13 V/μm[18].

4. Conclusion

The UNCD nano-emitters were successfully fabricated by MPECVD process using silicon nanowires (SiNWs) as templates. TEM analysis indicates that the grains, about 5 nm in size, are uniformly distributed, whereas SAED confirms that the films coated on the SiNWs are diamonds. The densely populated granular structure of thus obtained UNCD nanowires exhibit good electron field emission properties of the nanowires, which possess turned-on field of $(E_0)_{UNCD-NW}$=6.4 V/μm and electron field emission current density of $(J_e)_{UNCD-NW}$= 6.0 mA/cm^2 at 13.6 V/μm applied field. These electron field emission properties are superior to those for SiNWs, ($(E_0)_{SiNW}$= 8.6 V/μm, $(J_e)_{SiNW}$=<0.1 mA/cm^2) and planar UNCD films ($(E_0)_{UNCD}$=8.3 V/μm, $(J_e)_{UNCD}$=0.2 mA/cm^2) at the same applied field.

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