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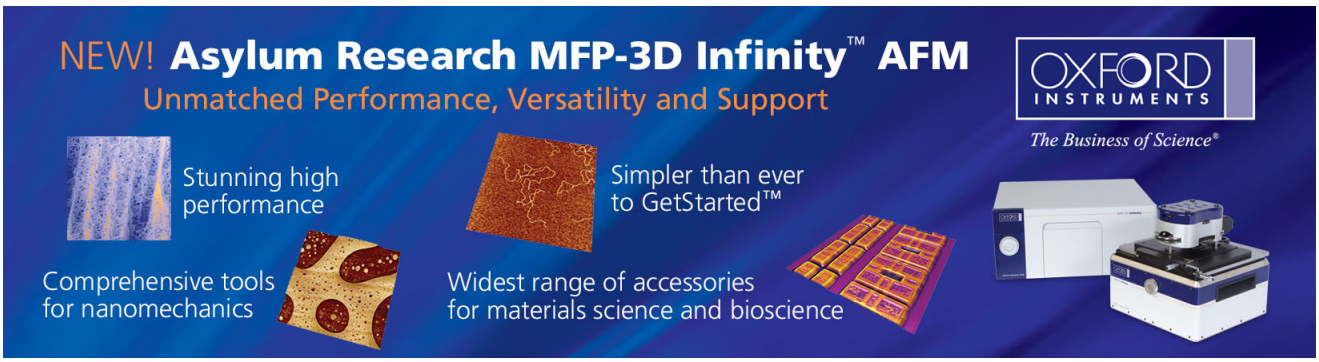

On the enhancement of field emission performance of ultrananocrystalline diamond coated nanoemitters

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Ultrananocrystalline diamond (UNCD) nanoemitters were synthesized by a microwave plasma enhanced chemical vapor deposition process using silicon nanowires (SiNWs) as the template. Preseeding markedly enhances the nucleation of diamond on the SiNW templates, resulting in UNCD grains of smaller size and uniform distribution, which leads to significantly improved electron field emission (EFE) properties. The EFE for UNCD nanoemitters can be turned on at $(E_0)_{\text{UNCD-NE}}$=4.4 V/μm, achieving large EFE current density, $(J_e)_{\text{UNCD-NE}}$=13.9 mA/cm^2 at an applied field of 12 V/μm, which is comparable with that of carbon nanotubes, but with much better processing reliability. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2768880]

Diamond films have been extensively investigated for applications as electron field emitter in vacuum microelectronic devices owing to the negative electron affinity with low effective work functions.[1,2] However, the electron field emission properties of these materials are inferior to those of carbon nanotubes due to the large electric field required for turning on the electron field emission process.[3] How to reduce the turn-on field for diamond films is thus urgently required. Several methods have been proposed to enhance the electron field emission properties of the diamond films,[4–7] including the synthesis of aligned silicon tip arrays as templates for fabricating diamond emitters.[7–9] However, conformal coating of diamond films on silicon nanowires (SiNWs) is extremely difficult. In this letter, we grew ultrananocrystalline diamond (UNCD) films on aligned SiNWs in order to synthesize UNCD nanoemitters that possess electron field emission (EFE) properties comparable with those of the carbon nanotubes but with markedly better processing reliability.

The SiNWs were fabricated by an electroless metal deposition (EMD) process, which is described elsewhere.[10] SiNWs were thus formed on the Si substrate via a self-aligned galvanic anisotropic etching process. Furthermore, some of the SiNWs were preseeded by ultrasonication in nanodiamond (~30 nm) slurry for 30 min to facilitate the formation of diamond nuclei on the Si surface. UNCD films were deposited on either unseeded or preseeded SiNWs by microwave plasma enhanced chemical vapor deposition (MPECVD) (IPLAS, Cyrannus) for 2 h under an Ar-plasma environment in which the gas flow was 1 and 99 SCCM (SCCM denotes cubic centimeter per minute at STP) for methane and argon respectively, and the total pressure was 100 torr. The microwave power was 600 W (2.45 GHz) and the substrate temperature was 673 K.

The morphologies of the SiNWs and diamond coated SiNWs were examined using scanning electron microscopy (SEM) (JEOL JSM-6500F), whereas the crystal structure of these nanowires was investigated using high-resolution transmission electron microscopy (TEM) (JEOL JEM-4000EX). The structure of the diamond coated SiNWs was examined by Raman spectroscopy (Renishaw, 632.8 nm) and near-edge x-ray absorption fine structure (NEXAFS) in synchrotron radiation. The EFE properties of the diamond coated SiNWs were measured with a tunable parallel plate setup, in which the sample-to-anode distance was varied using a micrometer. The current-voltage (I-V) characteristics were measured using an electrometer (Keithley 237) under pressures below 10^{-6} torr and were analyzed by the Fowler-Nordheim model.[11]

Figure 1 shows that well aligned SiNWs about 90 μm in

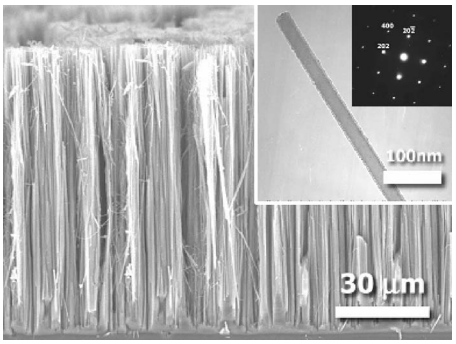

FIG. 1. SEM micrographs of SiNWs fabricated by EMD process using (100) Si substrates. The inset shows the TEM micrograph of an independent SiNW and the corresponding SAD patterns.

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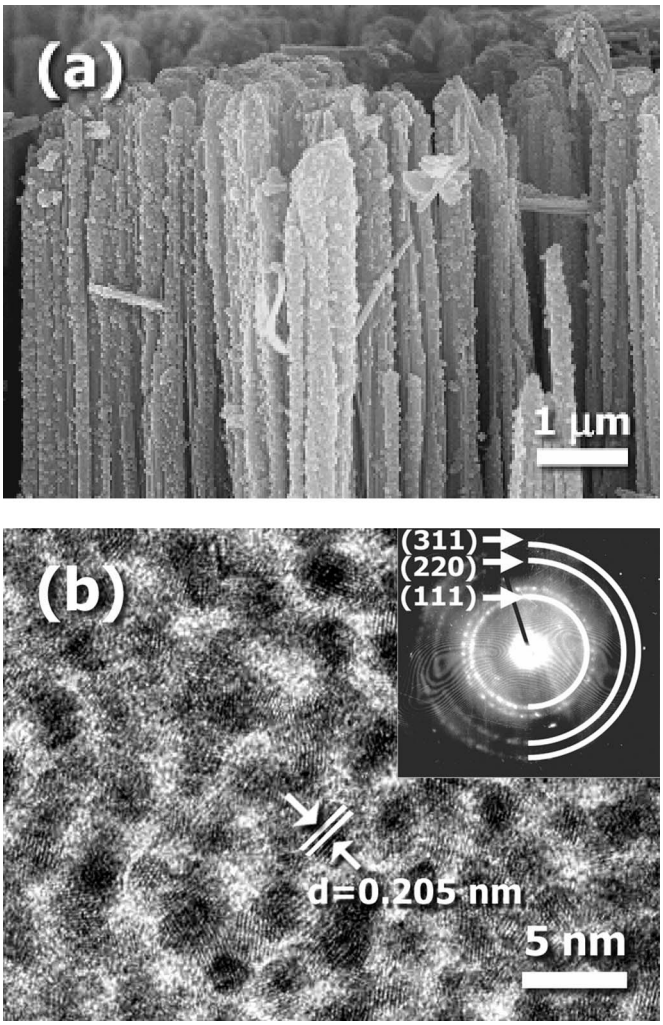

FIG. 2. (a) SEM and (b) TEM micrographs of UNCD nanoemitters fabricated on preseeded SiNWs by MPECVD process for 2 h. The inset in (b) shows the SAD patterns of UNCD films.

length are uniformly formed on the Si substrates by the EMD process. The SiNWs formed bundles with diameters of hundreds of nanometers. The inset in Fig. 1 reveals that the SiNWs are about 35 nm in diameter and are [100] oriented. The UNCD films can grow directly on these SiNW templates even when they are not subjected to the seeding process. Such a growth behavior is markedly better than that of UNCD on planar Si substrates.[12,13] This result infers that the as-etched SiNWs surface already contains abundant active sites, which readily react with carbon species in the plasma, forming diamond nuclei. However, the coating of UNCD on these unseeded SiNWs is not uniform. In some areas, the UNCD grains fully cover the SiNWs, forming a continuous film, while in others only discrete and sparse UNCD grains are observed.

Figure 2(a) shows that the UNCD grains are densely coated on SiNWs, when they are preseeded. The TEM micrograph shown in Fig. 2(b) indicates that the grain size of UNCD films obtained by this method is about 5 nm and the grain size distribution is very uniform. The selective area diffraction (SAD) pattern in the inset of Fig. 2(b) demonstrates that the grains are diamonds. Most importantly, the UNCD grains conformably cover the SiNWs. Restated, the seeding process dramatically increases the density of diamond nuclei, resulting in conformal coating of diamond

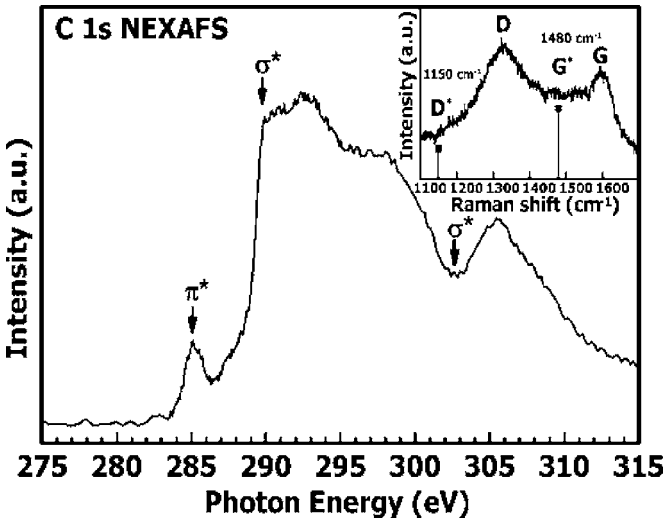

FIG. 3. Typical NEXAFS and Raman (inset) spectra for UNCD nanoemitters.

grains in SiNW templates. It should be noted that the parameters in the seeding process are quite critical.

Typical NEXAF spectrum shown in Fig. 3, displays a sharp rise near 289.7 eV and a deep valley near 302.5 eV (labeled as σ^* band). These results confirm the sp^3-bonded nature of the UNCD grains, which is in agreement with the SAD patterns observed in the TEM micrographs [insets in Fig. 2(b)] and is strong evidence of the diamond structure. The Raman spectroscopy, shown as inset in Fig. 3, is not able to unambiguously identify the characteristics of UNCD films, as the Raman peaks are too broad, which can be attributed to both the smallness of diamond grains and the formation of *trans*-polyacetylene surrounding the nanosized grains.[14,15]

The EFE properties and the corresponding Fowler-Nordheim (*F-N*) plot of the SiNWs and UNCD nanoemitters are illustrated in Fig. 4 and the corresponding inset, respectively. The important EFE parameters extracted from these *J-E* curves are listed in Table I. The turn-on field was designated as the interceptions of straight lines extrapolated from the low-field and high-field segments of the *F-N* plots. The

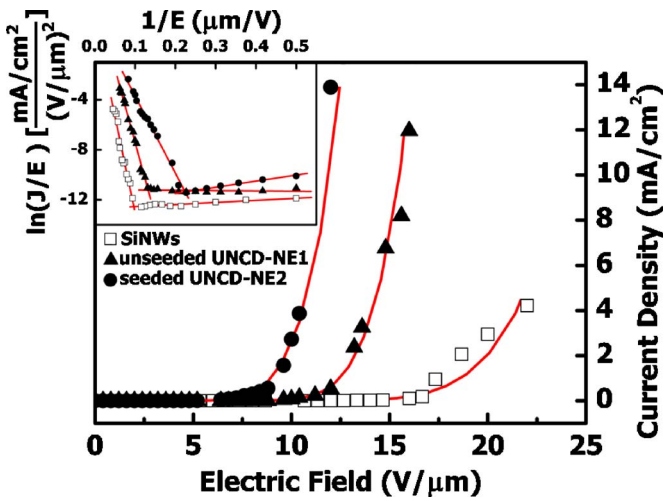

FIG. 4. Electron field emission properties and current density–field (*J-E*) plots of SiNWs and UNCD nanoemitters, which were prepared on unseeded or preseeded SiNWs using the MPECVD process for 2 h (the insets are the corresponding Fowler-Nordheim plots).

TABLE I. Electron field emission properties of the SiNWs and UNCD nanoemitters.

	SiNWs	UNCD-NE1	UNCD-NE2
J_e (mA/cm^2)[a]	<0.01	0.5	13.9
E_0 (V/μm)[b]	8.6	7.4	4.4
Φ (eV)[c]	4.10	3.43	2.23

[a]J_e is the electron field emission current density achieved at 12.0 V/μm applied field.
[b]E_0 is the turn-on field estimated from Fowler-Nordheim plots, as the interceptions of straight lines extrapolated from the low-field and high-field segments of the *F-N* plots.
[c]ϕ is the work function and field enhancement factor deduced from *J-E* curves by using the *F-N* model.

SiNWs require a very large turn-on field, $(E_0)_{\mathrm{SiNW}}=8.6$ V/μm, to induce EFE and can attain only $(J_e)_{\mathrm{SiNW}}=4.2$ mA/cm^2 EFE current density at an applied field of $(E_a)_{\mathrm{SiNW}}=22.0$ V/μm (open squares, Fig. 4), even though they are nanosized and possess large field enhanced factors (β). The UNCD-NE1 (solid triangles, Fig. 4) possess better EFE properties than the bare SiNWs, $(E_0)_{\mathrm{UNCD\text{-}NE1}}=7.4$ V/μm and $(J_e)_{\mathrm{UNCD\text{-}NE1}}=12.0$ mA/cm^2 at 16 V/μm. However, the EFE properties of the UNCE-NE1 vary pronouncedly among different samples, which is presumably due to the inconsistency of the UNCD coverage on the SiNWs.

On the other hand, UNCD-NE2 shows markedly superior EFE properties to the other two nanoemitters. The turn-on field is only $(E_0)_{\mathrm{UNCD\text{-}NE2}}=4.4$ V/μm and EFE density is as large as $(J_e)_{\mathrm{UNCD\text{-}NE2}}=13.9$ mA/cm^2 at 12 V/μm. It should be noted that the UNCD nanoemitters fabricated on unseeded SiNWs can only attain $(J_e)_{\mathrm{UNCD\text{-}NE1}}=0.5$ mA/cm^2 and the SiNWs can reach only $(J_e)_{\mathrm{SiNW}}=0.01$ mA/cm^2 under the same conditions. These EFE characteristics are summarized in Table I to illustrate the superiority of UNCD nanoemitters fabricated on seeded SiNWs over UNCD nanoemitters made on unseeded SiNWs, not to mention plain SiNWs.

The work function (ϕ) of the UNCD nanoemitters was evaluated using the Fowler-Nordheim model. We first fit the *J-E* curves with an exponential function to extract the preexponential and exponent constants in the *F-N* model, i.e., Eq.

$$J(E)=AE^2\exp\left[\frac{-B\phi^{3/2}}{E}\right], \tag{1}$$

where $A\equiv e^3/16\pi^2\hbar\phi t^2(y_0)$ and $B\equiv(4/3e)(2m/\hbar^2)^{1/2}v(y_0)$ and ϕ is the work function of the emitting material. The results of fitting are shown as solid curves in Fig. 4, illustrating that the electron field emission data fit the *F-N* model very well. Assuming that the work function of SiNWs is the same as that of planar silicon materials, i.e., $\phi_{\mathrm{Si}}=4.1$ eV,[16] the β value of SiNWs can be estimated from the effective work function ($\phi_e=\phi^{3/2}/\beta$) of SiNWs, which is proportional to the slope of *F-N* plots, and the result is $(\beta)_{\mathrm{Si}}=367$. The value of $(\beta)_{\mathrm{Si}}$ obtained from this is higher than that of planar Si materials, but is much lower than the β value expected for nanowires with such a large aspect ratio. Low β value for SiNWs is presumably due to "screening effect" of too densely populated SiNWs. Simple calculation[17] shows that the β value is around 5000 for a nanowire of the geometry about $35\times90\,000$ nm^2. The screening factor is thus estimated to be around $a=0.07X$. Coating UNCD on SiNWs could markedly reduce the field enhancement factor (β value) of the nanowires owing to the increase in diameter (a factor of $0.3-0.5X$). However, large screening effect due to densely populated nanowires ($a\sim0.07X$) is expected to predominate the effective field enhancement factor (β value). The effective β value for the UNCD-coated SiNWs was thus assumed to be the same as that for uncoated ones. Therefore, the effective work function ($\phi_e=\phi_{\mathrm{UNCD}}^{3/2}/\beta$) of the UNCD-NEs was again estimated from the slope of the corresponding *F-N* plots by assuming that $(\beta)_{\mathrm{UNCD\text{-}NEs}}=(\beta)_{\mathrm{SiNW}}=367$ for UNCD nanoemitters, and the work function of the UNCD nanoemitter was calculated to be $(\phi)_{\mathrm{UNCD\text{-}NE2}}=2.23$ eV, which is listed in Table I.

For the unseeded SiNWs, large UNCD clusters resulted due to fewer nuclei available and the SiNWs were not fully covered by UNCD grains. The electrons are most probably transported along the SiNWs and emitted from the tip, either through UNCD grains or the Si material. Therefore, the EFE current density is only moderately larger than that of SiNWs. In contrast, nucleation took place much more easily for the seeded SiNWs, resulting in densely populated UNCD grains on the SiNWs. The electrons are presumed to travel only through UNCD grains coated on SiNWs and are emitted at the tip of UNCD nanoemitters leading to a superior EFE current density compared to that of SiNWs.

In summary, UNCD nanoemitters were fabricated using MPECVD process with SiNWs as a template. TEM analysis indicates that UNCD nanoemitters are composed of 5 nm sized grains, which are uniformly distributed. SAD and NEXAF analyses confirm that the films coated on the SiNWs are diamonds. The denser granular structure markedly improves the EFE properties of the nanoemitters, which possess a turned-on field of $(E_0)_{\mathrm{UNCD\text{-}NE2}}=4.4$ V/μm and an electron field emission current density of $(J_e)_{\mathrm{UNCD\text{-}NE2}}=13.9$ mA/cm^2 at 12 V/μm applied field.

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