Three-dimensional carbon nanowall field emission arrays

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(Received 17 September 2009; accepted 5 January 2010; published online 26 January 2010)

This letter reports on the fabrication of regular arrays of three dimensional graphite structures, by growing carbon nanowalls on forests of conical Si microspikes. The high field enhancement achieved by this hierarchical growth process indicates a potential for electron emission applications. Experiments show that the field emission performance and long-term stability of the structures is far superior to that of planar carbon nanowall mats and comparable to that reported for optimized carbon nanotube based emitters. The improved field emission properties of the fabricated arrays are attributed to the dual micro and nanomorphology of the emitters, involving a two-scale enhancement process. © 2010 American Institute of Physics. [doi:10.1063/1.3298648]

In the last decade intensive research effort has been devoted to the design and fabrication of cold cathode electron emitters having low turn-on voltage, high current emissivity, and increased durability under poor vacuum conditions. Potential applications include vacuum microelectronic devices, such as electron guns and microwave power amplifiers, and field emission (FE) electronic devices, such as flat panel FE displays (FEDs).1

Owing to their unique geometries of small curvature radius, one-dimensional graphitic nanostructures like carbon nanotubes (CNTs) and nanofibers have attracted significant interest for their potential FE applications.2–4 Two-dimensional carbon nanostructures such as carbon nanowalls (CNWs) have also been grown and used as FE materials.5,6 However, there is a growing research effort to develop three-dimensional (3D) graphitic FE structures and good FE properties have been obtained.7–9 Those results indicate that the emission performance might be effectively improved by a hierarchical development of field emitters starting from microstructured substrates and subsequently growing graphitic nanostructures onto them.

Here, we report on the hierarchical fabrication and FE performance of large scale regular arrays of 3D CNW field emitters produced by growing CNWs on forests of microconical Si spikes (CNW/μSi). The results indicate that the FE performance and stability of 3D CNW structures is by far superior to that of planar CNW mats and comparable to that reported for optimized CNT-based emitters.

CNW mats were grown by Hot Filament CVD (HFCVD) as described previously.9 All the CNW samples were grown for 20 min in 30 mbar CH4/He atmosphere, substrate temperature of 700 °C and gaseous precursors’ ratio of 3/100. In particular, for FSi sample, CNW mats were grown over planar n-type Si substrates, while for (CNW/μSi) samples HSi and LSi, CNW mats were grown on laser etched Si substrates comprising 3D arrays of high- and low-aspect ratio microspikes respectively. For the production of spikes arrays, Si wafers (resistivity of 1–20 Ω cm) were subjected to femtosecond (fs) laser irradiation in a SF6 atmosphere as described previously.10 Samples were characterized by scanning electron microscopy (SEM) and micro-Raman spectroscopy. The latter revealed typical spectra (not shown) of nanocrystalline CNWs with the ordered graphitic G peak at 1584 cm−1 and the disorder-induced D peak at 1362 cm−1. The intensity ratio of the two peaks is IG/ID ~ 1.3 for all samples indicating that the quality of the deposited CNWs is similar.11

Figure 1(a) shows the high-aspect ratio spike array obtained after the laser structuring process, showing a forest of Si spikes, which are well-separated and perpendicular to the substrate surface, forming a highly aligned array. Figures 1(b)–1(f) depict the corresponding SEM images after the CVD process for the HSi and LSi samples respectively. It is observed that nanowalls follow the surface and decorate the microspikes forming a flower-like coating. As a result the final surface exhibits a 3D structure comprising arrays of CNW-spikes with hierarchical micro and nanomorphology. The nanowalls on the LSi sample are slightly larger than those on HSi, because the respective Si tip morphologies were different and locally the effect of the electric field induced plasma is different, even though the process parameters are kept constant. Structural features for both CNW/μSi samples are summarized in Table I. The spike tip radius, r, represents the best fitting sphere radius, as measured by 45° tilted SEM images and the spike height, h, was measured from the base of the spike’s cone using cross-sectional SEM micrographs. The spike density, measured from top view SEM images, is ~5 × 106/cm² for both CNW/μSi samples. FE measurements were performed under 5 × 10−6 mbar vacuum, using the samples as cold cathode emitters in a planar diode system. Current-voltage (I-V) curves were taken...
at a sample-to-anode distance, $d$, equal to $d=200$ μm. Details for the setup can be found elsewhere.\textsuperscript{12,4} Figure 2(a) shows a plot of the current density-field (J-E) emission characteristic curves. Several emission cycles were taken in order for the J-E curves to become relatively stable and reproducible. Error bars are a measure of the emission stability in each case. The threshold field, $E_{\text{th}}$, which we define as the macroscopic field where the emission current is 60 pA/cm$^2$, is measured to be lowest for the HS$_i$—CNW/μSi, sample, reaching a value of $\sim$0.9 V/μm. This value is more than four times lower from that measured on the FSi sample prepared at identical growth conditions. Interestingly, the FE performance is greatly improved, when the CNW mat is deposited on top of the 3D structured substrate compared to the same mat on planar substrate. On the other hand, for the lower aspect ratio sample, LS$_i$, $E_{\text{th}}$ increases to 2.4 V/μm indicating that as the spike aspect ratio decreases, $E_{\text{th}}$ becomes higher. Increase of bias voltage above the threshold dramatically increases the FE current according to a Fowler–Nordheim (FN) tunneling process, until saturation is reached. A similar saturation behavior was observed in other graphitic emitters and attributed to a large voltage drop along the emitter and/or at the emitter/substrate interface.\textsuperscript{13,14} On the contrary, Wang et al.\textsuperscript{15} measured current densities of up to 10 mA/cm$^2$ without observing any saturation, probably due to the much lower resistivity of the substrates used and thus the absence of a substantial voltage drop (low contact resistance) at the emitter/substrate interface. At high fields current tends to saturate at about the same level for all samples, possibly because it becomes limited by the CNW/substrate contact resistance. The latter should be equal among samples, considering that the CNW quality is similar and the deposition conditions and substrate types were kept constant. In analyzing our FE data, we adopted the FN analysis\textsuperscript{16} of field-assisted tunneling, which is widely used to describe the relationship between the current density $J$ and the local field at the emitter $E_{\text{loc}}$, which is related to the average field $E$ as follows:

$$E_{\text{loc}} = \beta E = \beta \frac{V}{d},$$

where $\beta$ is the geometric field enhancement factor. Within this frame the FN law is expressed as

$$J = A(\beta E)^2 \exp \left(- \frac{b_{\text{FN}}}{\beta E} \right),$$

where $A=1.54 \cdot 10^{-6}$ A V$^{-2}$ eV, $b_{\text{FN}}$=0.94$B\Phi^{3/2}$, with $B=6.83 \cdot 10^7$ V cm$^{-1}$ eV$^{-3/2}$, while $\Phi$ is the work function in electron volt. Figure 2(a) (inset) shows FN plots $\ln(J/E^2)$

### Table I. Morphological characteristics and FE properties of the planar and CNW/μSi emitters. The ± values denote the standard deviation of each measured or estimated quantity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spike height, $h_i$ (μm)</th>
<th>Spike tip radius, $r_i$ (nm)</th>
<th>$E_{\text{th}}$ (V/μm)</th>
<th>$\beta$</th>
<th>$\beta \times E_{\text{th}}$ (V/μm)</th>
<th>$\beta_{\text{single}}$</th>
<th>$\beta_{\text{exp}}$</th>
<th>$\beta_{\text{single}}/\beta_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSi</td>
<td>...</td>
<td>...</td>
<td>3.8</td>
<td>800</td>
<td>3040</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>HS$_i$</td>
<td>20.8 ± 3.0</td>
<td>590 ± 100</td>
<td>0.9</td>
<td>3533</td>
<td>3180</td>
<td>35.2</td>
<td>4.4</td>
<td>8.0</td>
</tr>
<tr>
<td>LS$_i$</td>
<td>10.9 ± 2.0</td>
<td>1010 ± 300</td>
<td>2.4</td>
<td>1221</td>
<td>2930</td>
<td>10.8</td>
<td>1.5</td>
<td>7.2</td>
</tr>
</tbody>
</table>
versus $E^{-1}$] of the FE data. The corresponding $\beta$ values (also shown in Table I) are determined by fitting the linear part of the data, following Eq. (2), assuming a typical work function for graphite of 5.0 eV.

The FE results can be explained in the framework of the “two-step field enhancement (TSFE)” approach. According to this model, the emitting surface may be thought of as a number of primary structures (corresponding to Si spikes in our case) with height of $h_1$ and sharpness of $r_1$, decorated by tiny emitters, corresponding to CNWs [Fig. 2(c)]. The local field on the primary tip is $E_2 = \beta_2 E_1 (V/d)$ while that on the very end of the secondary protrusions is

$$E_2 = \beta_2 E_1 = \beta_2 \beta_1 (V/d).$$  \hspace{1cm} (3)

If the nature of emitting sites is the same in all samples measured, then according to Eq. (1), the local field at the threshold, $BE_{\text{th}}$, should be constant. As shown in Table I, $BE_{\text{th}}$ is indeed found constant among samples, indicating that CNW emission sites are of the same nature and thus $\beta_2 = 800$ in all samples; it also suggests that the small difference in the nanowall length does not have a significant impact on the $\beta_2$ value. By placing $\beta_2 = 800$ in Eq. (3) one can calculate the corresponding $\beta_1$ values experimentally in the framework of the TSFE approach, i.e., $\beta_1 \exp$. Assuming now a point-to-plane geometry, the farfield value of $\beta_1$ for a single isolated spike can be calculated, i.e., $\beta_1 \text{single} = h_1/r_1$, and compared with $\beta_1 \exp$. The results are presented in Table I and show that the enhancement effect of the primary tips, $\beta_1 \exp$, is lower than the farfield value predicted by geometrical considerations, $\beta_1 \text{single}$. This discrepancy can be attributed to the fact that the local field at one spike is considerably reduced due to the shielding effect by the neighboring ones.\(^{20,21}\) Screening effects are found to be substantial when the average distance of emitters is in the order of few microns,\(^{18}\) as it is in our case. As the ratio $\beta_1 \exp/\beta_1 \text{single}$ remains fairly constant, the TSFE model predicts that the $\beta$ reduction caused by screening effects is equal for the two CNW/µSi samples, which is reasonable considering that the respective spike densities are equal.

The stability of the FE current over time is crucial and of equal importance to $E_{\text{th}}$ and $\beta$ for practical device applications. Figure 2(b) presents the evolution of the saturated emission current density over a long period of continuous operation for the best emitting sample HSI. No degradation of emission performance was observed, even after four days of continuous operation. It should be noted that stable emission was in the saturated limit and was therefore controlled by the CNW/substrate resistance, not the emission process.

In conclusion, we have prepared a large scale Si-based graphitic cathode (CNW/µSi), exhibiting high FE performance, by a simple hierarchical growth process. CNWs were grown radially on the surface of laser fabricated Si microspikes to form a 3D regular array of micro/nano structured field emitters. The threshold field, enhancement factor and the remarkable stability of FE current is comparable to that of optimized CNT emitters,\(^{16}\) demonstrating that CNW/µSi is a promising FE cathode with potential applications in vacuum microelectronics and FEDs.

This work was supported in part by the Ultraviolet Laser Facility at IESL-FORTH through the access activities of the EC FP6 project “Laserlab-Europe”, Contract No. RI3-CT-2003-506350.