Institute of Physics Publishing Nanotechnology

Nanotechnology **17** (2006) 1564–1567 doi:10.1088/0957-4484/17/6/005

Local measurement of secondary electron emission from ZnO-coated carbon nanotubes

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Received 23 November 2005
Published 21 February 2006
Online at stacks.iop.org/Nano/17/1564

Abstract
The secondary electron emission (SEE) of ZnO-coated carbon nanotubes (CNTs) was measured using a biasing technique in a scanning electron microscope. The SEE yield of the ZnO-coated CNTs is higher than that of the ZnO film deposited on Si substrates. Direct observation of the variation in SEE from tip-end and non-CNT positions was demonstrated. Local measurement reveals that the SEE yield at the tip-end of the ZnO-coated CNTs is much higher than that of non-CNT positions. The enhancement of SEE is attributed to the strong local field generated at the tip of the CNTs.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], one-dimensional (1D) nanostructures (nanotubes, nanowires, nanoneedles etc) have attracted a great deal of interest because of their high aspect ratio, diverse functionalities and surface cleanliness [2–5]. Among these novel properties, electron field emission from 1D nanomaterials has attracted extensive attention because of its potential application in flat panel displays and compact x-ray devices [6–8]. However, only a few reports have investigated the effect of 1D nanostructures on secondary electron emission (SEE) [9, 10]. In fact, SEE processes under primary electron bombardment play an essential role in vacuum electronic devices [11, 12].

The use of CNTs as a template in the formation of nanostructures is very effective and rewarding: examples include enzyme-coated CNTs as single-molecule biosensors [13], CNTs coated with wide-bandgap materials for field emission [8] and high SEE from MgO-coated CNTs [9]. As ZnO is a wide-bandgap semiconductor, ZnO nanostructures have been extensively investigated as electron field emitters [14]. In this study, we report the measurements of SEE from ZnO-coated CNTs using a biasing technique in a scanning electron microscope (SEM). The local measurement of SEE from the ZnO-coated CNTs provides direct experimental evidence of SEE enhancement due to the strong local field generated at the tips of the CNTs.

2. Experimental details

Aligned CNTs on Si were synthesized by thermal chemical vapour deposition using Fe–N as the catalyst layer. The deposition details have been described elsewhere [15]. The ZnO thin films were deposited on the aligned CNTs using the filtered cathodic vacuum arc technique [5]. The topographical microstructure of the CNT template and ZnO-coated CNTs was observed by SEM (JEOL, JSM-5910LV). A detailed study of the microstructure was also carried out using transmission electron microscopy (TEM; JEOL JEM-2010) operating at 200 kV. The TEM sample was prepared by scratching the CNTs and depositing them on a carbon-coated copper grid.

The measurement of SEE yield (σ) was carried out in the SEM by measuring the specimen current after biasing the specimen in two separate experiments [16, 17]. A schematic diagram of the experimental setup is shown in figure 1. A 45 V-battery box was used to bias the sample. The sample to ground current was measured by a low-noise current preamplifier (Stanford Research Systems, SR570). An electron beam was generated using the electron gun of the SEM. The beam current was measured by a Faraday cup attached to the SEM system and fixed to 100 pA by adjusting the spot size while the electron beam energy was varied from 0.8 to 20 keV. In the first measurement the sample was positively biased (+45 V) and the sample to ground current (I_0) was measured for a selected primary beam energy. The positive bias is adequate to ensure complete electron collection, so that I_0 is the total incident

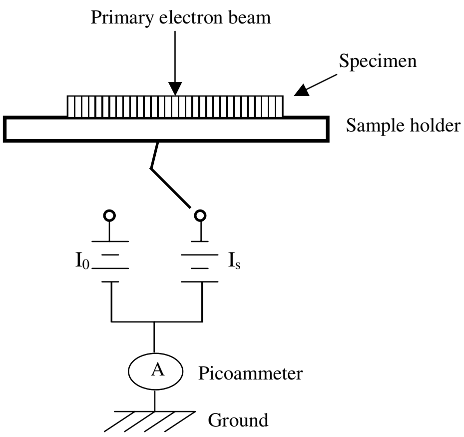

Figure 1. Schematic diagram of the SEE experimental setup.

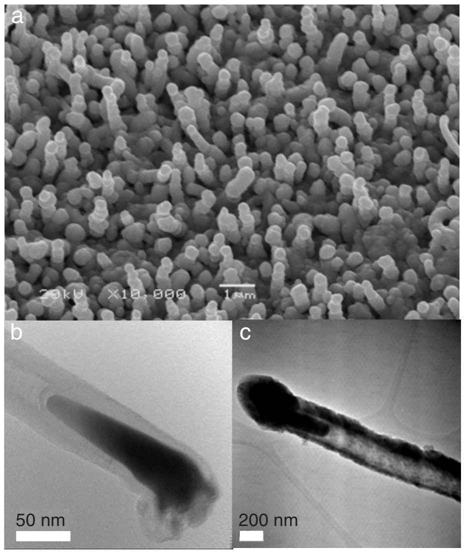

Figure 2. (a) SEM image of the topography of the ZnO-coated CNTs. (b) and (c) TEM images of the as-grown CNTs and ZnO-coated CNT, respectively.

electron current. Subsequently, the sample to ground current (I_s) was then measured as the sample was biased at a negative voltage (−45 V) in order to repel the secondary electrons from the sample surface. The difference in sample to ground current measured under the two biasing conditions is taken as the secondary electron emission current. Thus, the yield of SEE (σ) is defined as $\sigma = (I_0 - I_s)/I_0$. The current I_0 is always negative, while I_s can be positive or negative depending on the SEE strength of a material.

For the local measurement of SEE, a 10 000× magnification of the SEM image was first obtained with an electron beam energy of 2 keV and a beam current of 70 pA at a negative bias of 45 V. Then the SEE-related current (I_s) was automatically recorded as the incident electron beam was set to the selected positions in the SEM image by using the electron beam spot-scan and line-scan functions of the SEM.

3. Results and discussion

Figure 2(a) shows the SEM image of the topography of the aligned CNT template after being coated with a 200 nm thick ZnO film. It is observed that a protuberant feature hundreds of nanometres high is formed where the CNTs are encapsulated by the ZnO. Figure 2(b) shows the TEM image of a single CNT; a metal catalyst can also be observed near the tip of the CNT. An as-grown CNT is around 50 nm in diameter. ZnO is coaxially coated on the CNT, where the thickness of ZnO on the tip and sidewalls, respectively, is ∼200 nm and ∼125 nm (see figure 2(c)).

Figure 3 shows σ as a function of primary electron energy (PEE) for the ZnO-coated CNTs, ZnO film and CNT template. The curves follow the trend of a typical PEE dependence on SEE yield [11]. In general, after σ reaches a maximum value, σ will decrease as PEE increases. The secondary electrons generated by the primary electrons in the film first move to the surface with relatively weak e–e scattering in a wide-bandgap material, and then escape from the surface if they have enough energy to overcome the work function of the material. The secondary electrons generated near the surface can escape from the solid given the true negative electron affinity of the surface. However, as the PEE increases, the majority of secondary electrons are excited deeper into the solid and have more time

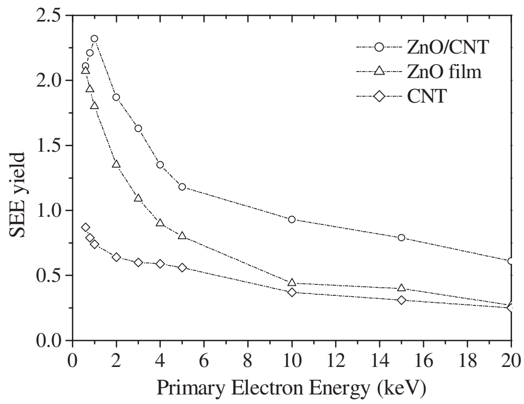

Figure 3. The dependence of σ on primary electron energy from the ZnO-coated CNTs, ZnO film on an Si wafer and CNT template.

to thermalize to the bottom of the band. Regardless of whether they are generated in or beyond the depletion region, diffusion towards the surface is impeded by the depletion field which pushes the carriers back towards the bulk. As a result, the total yield decreases rapidly with increasing PEE.

The SEE yield of the CNT template is less than 1, which is in good agreement with the result for graphitic carbon (σ_{max} is 1.0) [18]. But it is interesting to note that the σ of the ZnO-coated CNTs is much higher than that for the ZnO film on Si substrate. The peak value for ZnO-coated CNTs at a low primary electron beam energy of 1 keV is 2.32, which is only slightly larger than 2.07, the peak value of ZnO film deposited on Si wafer at a primary electron beam energy of 0.6 keV. However, it is worth mentioning that the enhancement in σ is more apparent at higher primary electron energies (>5 keV). These results suggest that the SEE yield of ZnO-coated CNTs is enhanced significantly by the nanostructured surface from the CNT templates compared with the ZnO film on Si substrates. Generally, the nanostructured surface is

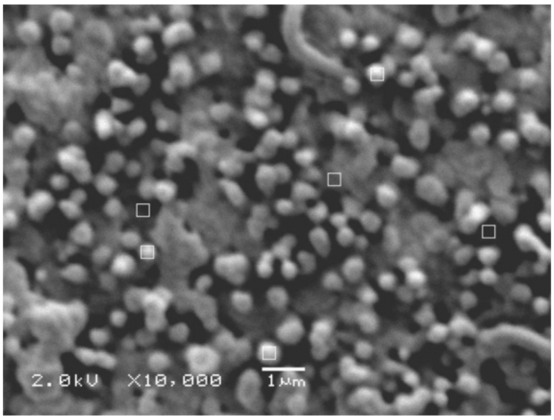

Figure 4. A typical SEM image of the ZnO-coated CNTs, taken under 2 kV and an electron beam current of 70 pA at a negative bias of 45 V.

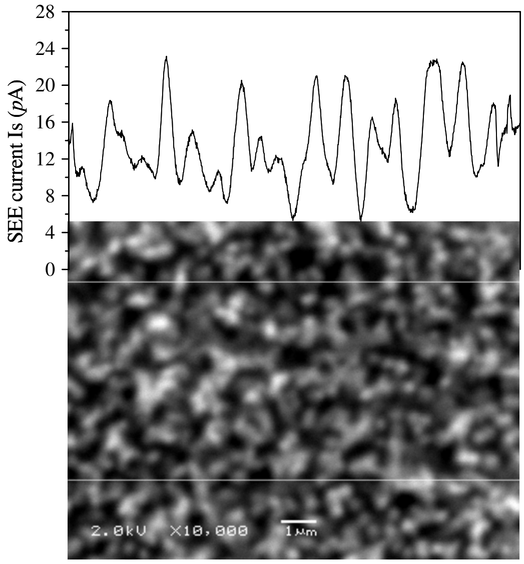

Figure 5. A line-scan of the SEE-related current (I_s) using the corresponding SEM image shown in figure 4.

rough and shadowing effects may also be expected, since an electron already emitted from a surface point may meet a solid asperity and change its trajectory so that the penetration depth is reduced which leads to the enhancement of SEE as well [12].

It is well known that the field emission properties of 1D nanostructures are dependent on a strong local field [6, 8]. But there is no experimental evidence of any local field effect on SEE properties. It should also be noted here that the measured SEE yield is an average effect, thus the local enhancement of σ at the tip-end of the CNT is not apparent. This may also lead to marginal enhancement of σ_{max}. In order to investigate the local field effect of the ZnO-coated CNTs, we employ the beam spot-scan function in the SEM to probe the individual tip-ends of the CNT and non-CNT region. The local measurement of SEE from the tip-ends of the ZnO-coated CNTs relies on a clear SEM image taken at the lower electron beam energy. Figure 4 shows a SEM image of the ZnO-coated CNTs which was taken under 2 kV and electron beam current of 70 pA at a negative bias of 45 V. The image is clear enough to distinguish between tip-end positions and non-CNT positions. Then, the incident electron beam was set to the selected positions in the SEM image by using the electron beam spot-scan function so as to measure the SEE-related current (I_s) from the tip-end of ZnO-coated CNTs and non-CNT positions, respectively. The SEE-related current (I_s) at the tip-ends of ZnO-coated CNTs is around 14 pA, which is three times greater than that for non-CNT positions. In order to further confirm the enhancement of SEE originating at the tip of ZnO-coated CNTs, the SEE-related current (I_s) has been mapped using the electron beam line-scan function in the SEM. Figure 5 shows the line-scan of the SEE-related current using the corresponding SEM image shown in figure 4. The line-scan mapping corresponds to the top white line in the SEM image as shown in figure 5. It is easier to identify the peak positions of I_s as they correspond to the tip-ends of the ZnO-coated CNTs. Hence, this study provides a direct observation of the variation in SEE for tip-ends and non-CNT positions of ZnO-coated CNTs. The higher SEE at the tip-ends of the ZnO-coated CNTs is derived from the local field generated by the CNT tips. We note that there are much lower values of I_s at non-CNT positions. This proves that the small diameter of the CNTs enhances the local field strength near the tip of nanotubes. The high local field will accelerate the primary electrons arriving at the tips and promote SEE.

These findings should shed light on how to develop high-efficiency electron emission devices such as radiation detectors based on the enhanced secondary electron effect of nanostructured materials. Nanomaterials with a potentially high SEE yield should have a wide band gap and preferably a negative electron affinity with regular high aspect ratio features.

4. Conclusions

In summary, the SEE yield of the ZnO-coated CNTs was higher than that of ZnO film deposited on an Si substrate. The local measurement revealed that the SEE enhancement was mainly at the tip-ends of the ZnO-coated CNTs rather than at the non-CNT positions. Our results provide direct evidence of the enhancement of SEE using nanostructures as a strong local field can be generated at the tips of the nanostructures.

Acknowledgment

This work was supported by the Agency for Science, Technology and Research, Singapore (project no 022 101 0020).

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