# $LaB_6$ tip-modified multiwalled carbon nanotube as high quality field emission electron source

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An effective field emitter has been developed by modifying an individual multiwalled carbon nanotube (MWCNT) tip with $LaB_6$. The modified emitter possesses the merits of both the MWCNT and $LaB_6$, which presents a significant low turn-on voltage, good emission properties, and long lifetime. As a result, a total current of 70 $\mu$A has been reached at a very low electric field of only 1.2 V/$\mu$m for an individual modified MWCNT emitter, which is also expected to have advantages of high brightness and coherence, clearly indicating great promise for practical applications such as electron guns or cathodes for field emission flat panel display. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2388862]

Carbon nanotubes (CNTs) are currently considered as promising field emission electron sources (FEESs) for use in many applications such as field emission flat panel displays (FEFPDs),[1] field emission (FE) electron guns,[2] x-ray sources,[3] and parallel electron beam lithography.[4] Owing to the nanometer-sized tip and high aspect ratio, CNTs present an ideal shape as well as excellent electrical properties and structural stability for FE.[5]

Recently, de Jonge *et al.* have demonstrated that an individual multiwalled carbon nanotube (MWCNT) can serve as an FEES with high brightness and excellent coherence.[2] However, their highest current was 20 $\mu$A above which breaking occurs due to Joule heating by the current or mechanical stress by the electric field ($E$ field). For practical application, a current of 40–50 $\mu$A was expected for a FEES in a high-resolution transmission electron microscope (HRTEM) (e.g., Tecnai F20, FEI).

According to the Fowler-Nordheim (FN) equation,

$$j_0 = \frac{1.54\times10^{-6}\varepsilon^2}{\phi}\exp\left[-\frac{6.83\times10^{7}\phi^{3/2}}{\varepsilon}\theta\left(3.79\times10^{-4}\frac{\sqrt{\varepsilon}}{\phi}\right)\right], \quad (1)$$

the FE current density $j_0$ is fully determined by the work function of the cathode $\phi$ and the local $E$ field $\varepsilon$. Reducing the work function will greatly benefit the emission current at the same $\varepsilon$. The CNTs innately possess a high aspect ratio and a correspondingly large enhancement factor which can induce a high local $E$ field during FE, whereas they have a moderate work function as tungsten.[6] As is well known, however, $LaB_6$ is a traditional thermionic emission material with extremely low work function, good conductivity, chemical stability, and high melting point. In this letter we report a high quality FEES possessing the merits of both MWCNT and $LaB_6$ having been achieved by modifying an individual MWCNT's tip with $LaB_6$. As a result, a total current of 70 $\mu$A has been reached at a very low electric field of only 1.2 V/$\mu$m for an individually modified MWCNT emitter, which is also expected to have the advantages of high brightness and coherence. Additionally, a practical method for accurate work function measurement will be provided subsequently in this letter.

The MWCNTs we used in this study were synthesized on a 4 in. silicon wafer by low pressure chemical vapor deposition. A tungsten probe attached with a single MWCNT was fabricated using a scanning tunneling microscope inside a HRTEM [Fig. 1(a)].[7] A 2-nm-thick layer of $LaB_6$ was coated on the MWCNT by a sputtering coating system (Gatan, PECS682). The MWCNT was placed normal to the sputtering target in the deposition chamber, and as a result most of the $LaB_6$ was deposited on the MWCNT's tip (tip modification) rather than its sidewall [Fig. 1(b)]. Figure 1(c) is the energy dispersive x-ray (EDX) analysis spectrum of the MWCNT's tip.

The experiment was carried out in a high vacuum chamber ($10^{-5}$ Pa). An original or tip-modified MWCNT-tungsten probe served as the cathode, and a square piece of indium tin

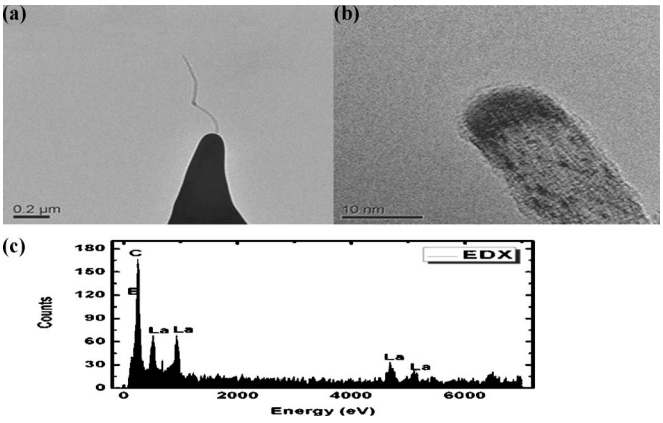


FIG. 1. (a) TEM images for $LaB_6$ tip-modified MWCNT emitter; (b) high magnification image for the emitter's tip showing that most of $LaB_6$ was deposited on the tip of the MWCNT (dark area); (c) EDX spectrum of the emitter's tip.

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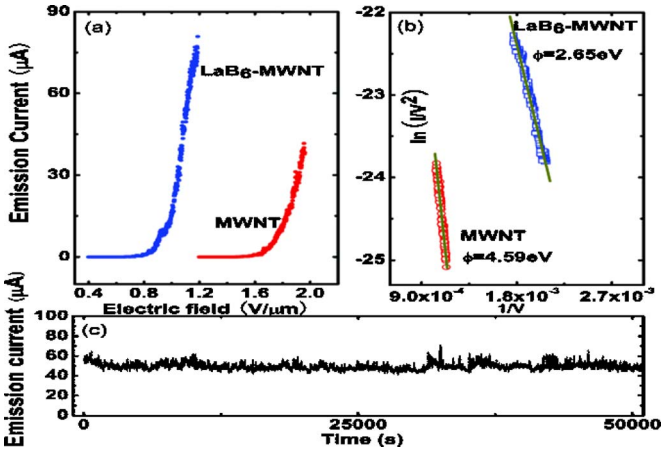


FIG. 2. (Color online) (a) Comparison of *I-V* curves of a MWCNT emitter before and after $LaB_6$ tip modification at an anode-cathode distance of 500 $\mu$m. The turn-on E field decreased significantly after tip modification. (b) Corresponding FN curves above 10 $\mu$A with work function calculation of MWCNT emitters before and after tip modification. (c) Modified MWCNT emitter kept emitting for 50 000 s.

oxide glass served as the anode. The *I-V* curves could be recorded when the source meter (Keithley 2410) swept a range of voltages between the two electrodes.

Figure 2(a) shows a comparison of FE measurements of MWCNTs taken at a fixed interspace between two electrodes of about 500 $\mu$m before and after tip modification. As expected, the turn-on $E$ field of the $LaB_6$ tip-modified MWCNT was significantly decreased due to its low work function, and it consequently achieved a high emission current density of $4.4\times10^7$ A/cm$^2$ at only 1.2 V/$\mu$m. The low turn-on $E$ field provides great potential for the modified MWCNT to work in a high current regime because the field-induced failures of CNT emitters frequently happen during FE due to the oversized electrostatic force born on the CNTs by the $E$ field.[5,8] Clearly, a reduction of the turn-on $E$ field will decrease the force born on the CNTs and, consequently, the likelihood of the failure of the emitters. Moreover, no obvious degradation was observed when the $LaB_6$ tip-modified MWCNT emitter kept emitting about 50 $\mu$A current within 50 000 s [Fig. 2(c)], clearly indicating its high reliability and long lifetime.

For further confirmation of exactly which component contributes to the FE on the tip-modified MWCNT, we designed a method to accurately measure the work function of the cathodes. As the distance between the two electrodes was fixed, ignoring the tiny variation of the MWCNT's geometrical shape before and after $LaB_6$ tip modification, the field enhancement factor ($\beta$) stayed the same. According to the FN equation [Eq. (1)], the ratio of the slopes of FN curves,

$$\frac{d\ln(I_1/V_1^2)/d(1/V_1)}{d\ln(I_2/V_2^2)/d(1/V_2)} = \left(\frac{\phi_1}{\phi_2}\right)^{3/2}. \tag{2}$$

With regard to the work function of MWCNT $\phi_1$, we gain accurate value ($\phi_1$=4.59 eV by average) by analyzing thermionic emission data of MWCNT yarns from our previous work.[6] Thus if we could measure the slopes of FN curves before and after tip modification, we will obtain the work function of the deposited material according to Eq. (2).

However, in a high vacuum (around $10^{-5}$ Pa) chamber, the field emission *I-V* curves of CNTs deviated from a straight line in FN plot due to the adsorption of residue gas on the emission sites of CNTs' tips. Therefore, to accurately determine the work function of the deposited material based on Eq. (2), the emitter has to be adsorbate-free. Our previous results indicate that intrinsic field emission *I-V* curve from CNTs, which is a straight line in FN plot, can be obtained at temperatures above 1000 K, in which case full desorption of adsorbates occurs.[9] In the case of individual CNT emitters, the emission current will heat the tip to high temperatures at which desorption of adsorbate may occur.[10–12]

In our experiments, the FE *I-V* curves at the initial sweeps deviated from FN equation and were intensely fluctuated, which was induced by the adsorption of residue gas. However, if a fixed voltage was applied to the individual CNT emitter to maintain an emission current about 10–20 $\mu$A for about 10 min, the FE *I-V* curves became more smooth and the corresponding FN curves became a straight line. We believe that this phenomenon might correspond to the desorption process because our theoretical calculation indicates that the tip of CNT emitter will be heated to 1300 K at an emission current of 10 $\mu$A.[13] We therefore recorded the FE *I-V* curves exclusively right after the aforementioned desorption process in our experiments.

We have fitted the emitter's *I-V* curves above 10 $\mu$A with FN equation before and after $LaB_6$ tip modification for three samples. Using Eq. (2), a work function of 2.65±0.14 eV could be calculated and is shown in Fig. 2(b), which is very close to the work function of $LaB_6$ as compared with some prior reports.[14] The result indicates that the emission component is the $LaB_6$ deposited on the MWCNT's tip, as we expected. The good linear agreement of the FN curves also indicates that the high current emitters have no significant deviation from the classical Fowler-Nordheim behavior.

To compare with the CNT emitters modified by traditional transitional metals such as Ti, Zr, and Hf,[15] we used a 2-nm-thick Zr tip-modified single MWCNT to serve as a cathode and applied 100 times voltage sweep to record *I-V* curves [Fig. 3(a)]. The corresponding FN curves and work function were iterated and calculated in the same way we mentioned above [Fig. 3(b)]. It is interesting to note that the turn-on voltages and the slopes of the FN curves (present the work function of the cathode) gradually decrease and converge to a certain value with the voltage sweep. The ultimate value of the emitter's work function is about 3.34 eV, which is very close to that of zirconium carbide (ZrC) reported before.[16] This dynamic process vividly presents that Zr and the MWCNT gradually react with each other on the tip and finally form a stable ZrC. The reaction can take place thanks to the huge Joule heat in high current FE processes similar to the conventional annealing steps.[15] Similar phenomena were also observed in Ti tip-modified MWCNT cathodes but not in $LaB_6$, which does not react with MWCNTs and serves as the emission component itself from our foregoing results. For practical consideration, it is sometimes unfeasible for industrial application to anneal the FE cathodes at such high temperatures above 1200 K, as in Ref. 15. Thus $LaB_6$ is truly a better choice for modifying MWCNT emitters because it can perform well as a low work function emitter without annealing or other complex chemical treats. Through our observation, deposited $LaB_6$ tends to wet well the surface of the MWCNT as Ti and Zr rather than form discrete particles on nanotubes as Au and Pt.[17] Moreover, because $LaB_6$ modification does not change the nanoscale emission size of the

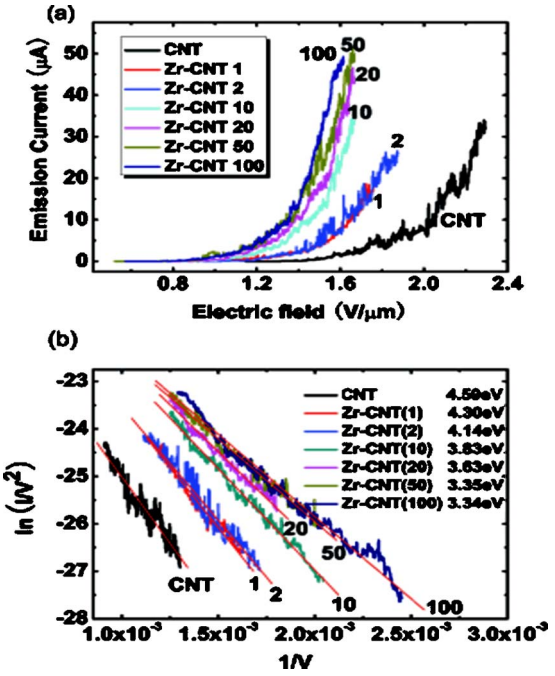


FIG. 3. (Color online) (a) *I-V* and (b) FN curves and corresponding emitter's work function calculations in the FE process for repetitive emission of Zr tip-modified MWCNT emitter. The numbers shown in the legends of the figures represent the times of applying voltage sweep. Through repeated sweeping, the *I-V* and FN curves gradually converge to constant, representing the chemical reaction process during FE and the formation of a stable ZrC on the MWCNT.

MWCNT, the modified emitter also possesses a low energy spread associated with electron emission and high reduced brightness.[2] It emits most current into a single narrow beam which leads to a high brightness and a good coherence electron beam. Combined with its high emission current density and long lifetime, $LaB_6$ modified MWCNT emitters do have a great potential to serve as electron sources in high-resolution electron beam instruments.

In conclusion, through tip modification, we combined the good geometrical shape of nanotubes and the good emission properties of $LaB_6$ to achieve a low turn-on *E* field, high emission current density, high brightness, and good coherence FEES, indicating its great promise to serve as FEES of HRTEM or cathodes of FEFPD. We also observed that the emission current of the $LaB_6$ modified MWCNT suffered a fluctuation of about 20% in our experiment, which needs further work to solve. Through accurate measurement of the work function of the cathodes, we gained knowledge of the exact component which contributes to FE, and additionally we found that we could use any conductive material to modify the MWCNT's tip, whose work function can be accurately given out through our FE measurement.

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