

# ENHANCED FIELD EMISSION PROPERTIES OF CARBON NANOTUBES BY COATING DIAMOND-LIKE CARBON LAYER

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## ABSTRACT

Diamond-like carbon (DLC) coated carbon nanotubes (CNTs) can obtain dramatically enhanced properties of field emission compared to the pristine CNTs. After coated the DLC layer, the threshold field and current density can be improved remarkably. When the current density arrived at 5mA/cm<sup>2</sup>, the electric field of DLC-coated CNTs was 1.88V/μm, much smaller than the value of pristine CNT arrays which was 3.03V/μm. And compared to the pristine CNTs, the field emission current density from the DLC-coated CNTs was much larger at electric field 4.0V/μm. The current density of the DLC-coated CNT arrays was 80mA/cm<sup>2</sup>, while that of the pristine CNT arrays was 51mA/cm<sup>2</sup>.

## INTRODUCTION

Since Iijima reported the electronic microscopy studies on the carbon nanotubes (CNTs) in 1991 [1], CNTs have been attracting much attention for various electronic applications [2][3]. Due to their unique geometry, chemical and physical properties, such as high aspect ratio, excellent conductivity, CNTs have become the research focus in the field of electron field emission (EFE) [3] [4]. For example, as field emission X-ray source, CNTs can generate x-ray radiation with temporal resolution up to nanoseconds [5]. However, the threshold field should be further reduced in the actual applications. Heterostructure, such as modifying CNT surface by introducing nanoscale thin layer (such as Ta [6] and BaO/SrO [7]), is an efficient method to reduce the threshold field and achieve high field emission performance. Among many materials, diamond-like

carbon (DLC) films, due to the negative electron affinity (NEA), have also attracted great attentions in the field of EFE. NEA means that the conduction band of DLC is beyond the vacuum level hence electrons in DLC are much easier to transit to the vacuum, and so that DLC layer can reduce the threshold field of emitters. Although many reports studying the properties of DLC electron field emission [8] [9] have been published, combination of DLC and CNT in EFE has been rarely discussed.

In this paper, we used CVD and magnetron sputtering to fabricate the CNTs and DLC layer respectively, and discussed the enhanced field emission properties of vertically aligned carbon nanotubes by coating a layer of DLC.

## EXPERIMENT

In the experiment, silicon was used as the substrate and 100nm Ti was covered on the silicon by magnetron sputtering in order to increase the conduction of the substrate. CNTs' catalyst pattern was prepared using e-beam lithography technology. 20nm Copper/10nm aluminum/2nm iron acted as catalyst layers. All the metal catalysts were prepared by e-beam evaporation. The substrate covered catalyst patterns was placed on a graphite heater. The pressure of the system was kept as 15mbar during pre-treatment and growth. Then the substrate was treated in the H<sub>2</sub> at 665°C for 1min. After that, C<sub>2</sub>H<sub>2</sub> flew into the chamber at the rate of 40sccm, and 15 seconds was given to synthesize CNTs. After CNTs growth, DLC layer was covered onto the surface of samples by direct current magnetron sputter for 7200s. The thickness of the DLC layer was 20nm.

Scanning Electron Microscope (SEM) (Hitachi-S4800) was used to observe the morphology of the CNTs. Raman Spectrometer was used to study the structure of the production. The EFE properties could be compared by the JE curve.

## RESULTS AND DISCUSSIONS

Figure 1 shows the SEM pictures of our samples tilted by 45°. From Figure 1 (a) and (b), we could see that all aligned CNTs had a good vertical shape and almost uniform height at 8 micrometers. This height, 8 micrometers, is an optimized value, and has been verified by our previous experiment that it can enhance the property of electron field emission when taken the period of each CNT unit and electric field shielding effect into consideration. If the growth CNTs is taller, electron field shielding effect may decrease the properties of EFE; whereas if the height is shorter, insufficient high aspect ratio of growth CNTs will lead to poor EFE results. After adding the DLC layer onto the CNTs, we could observe that DLC layer was coated onto the top and even middle of CNTs from Figure 1(c) and (d). As shown in the Figure 1 (c), the diameters of CNTs became a little larger than those without DLC layer. And meanwhile, there is no obvious degeneration of vertical CNT shape after coating DLC and the verticality of CNTs is still maintained.

Raman spectrum was employed to measure the structure of CNTs. In the Figure 2, the DLC-coated CNTs Raman spectra was depicted in red line, while the Raman spectra of the pristine CNTs was plotted in black line. The peaks at  $1349\text{cm}^{-1}$ ,  $1592\text{cm}^{-1}$  and  $2675\text{cm}^{-1}$  corresponded to the D-band, G-band and G'-band of pristine CNTs. The original graphite features of CNTs was signified by the G-band and the D-band was originated by the defects in CNTs. After sputtering DLC layer onto CNTs, D-band dramatically rose most possibly due to the formation of  $\text{sp}^3$  introduced by DLC layer and the damages on the CNT during sputtering. Besides those main peaks, several low peaks (RBM peaks) at low wavenumbers could be also observed, however,

these were usually observed in single-wall nanotubes. As show in the Figure 2(b), the RBM peaks of DLC-coated CNTs moved to the low wavenumbers mainly because after sputtering the DLC layer, the diameters of CNTs became larger, which is corresponded to the change from pristine CNTs to DLC-coated CNTs shown in the SEM pictures.

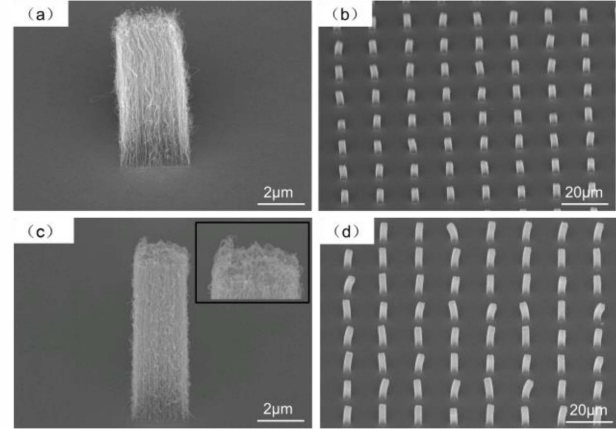


Figure 1: SEM pictures of pristine CNTs ((a) and (b)) and DLC-coated CNTs ((c) (The insert is the top of DLC-coated CNT) and (d)).

Figure 3 shows the JE curves based on FN theory which is always used to describe the properties of CNT field emission. In the FN theory, emission current density ( $J$ ) from the CNT surface can be expressed as a function of the electric field ( $E$ ), according to the F-N relation

$$J = A\beta^2 E^2 / \exp(-B\phi^{3/2}/\beta E) \quad (1)$$

where  $A = 1.54 \times 10^{-6} \text{AV}^{-2} \text{eV}$ ,  $B = 6.83 \times 10^3 \text{V}\mu\text{m}^{-1} \text{eV}^{-3/2}$  and  $\phi$  is the work function of the emitters [5]. As shown in the JE curves (Figure 3), the threshold electric field (the field value when the current density reached  $5\text{mA}/\text{cm}^2$ ) was improved significantly by the DLC-coating layer. The threshold field of pristine aligned CNT array was  $3.03\text{V}/\mu\text{m}$ , almost twice of the value of DLC-coated CNT arrays ( $1.88\text{V}/\mu\text{m}$ ). Comparing to other's result [3][6][9], this value is still much smaller (as shown in Table 1). For the applied electric field of  $4.0\text{V}/\mu\text{m}$ , the current density of the DLC-coated CNT arrays reached a significant value of  $80\text{mA}/\text{cm}^2$ , whereas the current density of the pristine CNT arrays was only  $51\text{mA}/\text{cm}^2$ . There was a dramatical enhancement of EFE properties

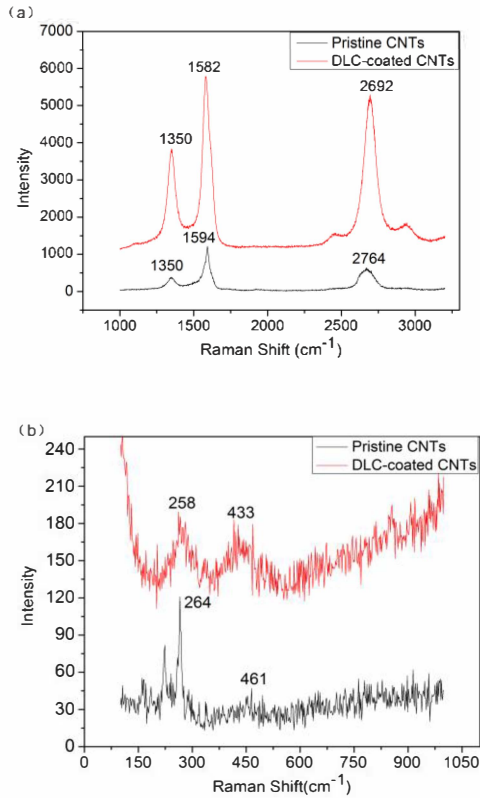


Figure 2: The Raman spectra of pristine and DLC-coated CNTs (a) and RBM peaks (b)

TABLE 1. EFE PROPERTIES COMPARISON

Authors	Electric field
N. A. Asli et.al.[3]	3.47 V/ $\mu\text{m}$ (at 0.1mA/cm <sup>2</sup> )
F. Jin et.al.[6]	4.4 V/ $\mu\text{m}$ (at 23.6 $\mu\text{A}$ )
S. Sridhar et. al.[10]	2.2 V/ $\mu\text{m}$ (at 10 $\mu\text{A}$ / cm <sup>2</sup> )
Our result	1.88 V/ $\mu\text{m}$ (at 5 mA/cm <sup>2</sup> )

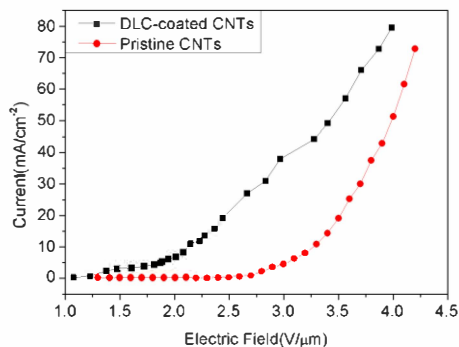


Figure 3: JE plot of pristine and DLC-coated CNTs

form pristine CNTs to DLC-coated CNTs due to the NEA effect of DLC layer covered on the CNTs.

## CONCLUSIONS

DLC-coated vertically aligned CNT arrays were deposited on 100nm Ti covered Si substrate. The DLC-coated CNTs dramatically improved the EFE properties compared with pristine CNTs by remarkably decreased the threshold field from 3.03V/ $\mu\text{m}$  to 1.88V/ $\mu\text{m}$  and increased the current density at the applied electric field from 51mA/cm<sup>2</sup> to 80mA/cm<sup>2</sup>. This enhancement could be mostly attributed to the negative electron affinity of DLC, which enhanced the electron emits from the top of CNTs and finally improved the EFE properties of vertically aligned CNTs. Hence, DLC-coated CNTs would be a potential material to fabricate EFE devices, such as electron field emission X-ray source.

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