Field Emission Properties of Carbon Nanotube Arrays with Defects and Impurities

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ABSTRACT

It has been found experimentally that the results related to the collective field emission performance of carbon nanotube (CNT) arrays show variability. The emission performance depends on the electronic structure of CNTs (especially their tips). Due to limitations in the synthesis process, production of highly pure and defect free CNTs is very difficult. The presence of defects and impurities affects the electronic structure of CNTs. Therefore, it is essential to analyze the effect of defects on the electronic structure, and hence, the field emission current. In this paper, we develop a modeling approach for evaluating the effect of defects and impurities on the overall field emission performance of a CNT array. We employ a concept of effective stiffness degradation for segments of CNTs, which is due to structural defects. Then, we incorporate the vacancy defects and charge impurity effects in our Green's function based approach. Simulation results indicate decrease in average current due to the presence of such defects and impurities.

Keywords: carbon nanotube, field emission, electron-phonon, defect, impurity, transport.

1 INTRODUCTION

From the time field emission from carbon nanotubes (CNTs) was reported in 1995 [1],[2], their applications in devices, such as field emission displays, gas discharge tubes, electron microscopes, cathode-ray lamps and x-ray tube sources have been demonstrated successfully [3], [4]. In recent years, studies on field emission from CNTs have been growing. CNTs in the form of arrays or thin films give rise to several strongly correlated processes of electromechanical interaction and degradation. Such processes are mainly due to (1) electron-phonon interaction (2) electromechanical force field leading to stretching of CNTs (3) ballistic transport induced thermal spikes, coupled with high dynamic stress, leading to degradation of emission performance at the device scale [5]. Fairly detailed physics based models of CNTs accounting for aspects (1) and (2) above have already been developed, and numerical results indicate good agreement with experimental results [6]-[9]. These studies are based on the electronic structure of an ideal CNT where a CNT is metallic or semiconducting depending on whether $n - m$ is a multiple of three or not. Here n and m are two integral components of the chiral vector. Although studies have reported defects in CNTs in general [10], [11], not much is known as to how these defects affect the field emission property of CNTs. For a better understanding of the field emission phenomenon, a system level modeling approach incorporating structural defects, vacancies or charge impurities is currently missing. This is a practical and important problem due to the fact that degradation of field emission performance is indeed observed in experimental I-V curves. What is not clear from these experiments is whether such degradation in the I-V response is due to dynamic reorientation of CNTs or due to the defects or due to both of these effects combined. Non-equilibrium Green's function based simulations using a tight-binding Hamiltonian for a single CNT segment demonstrate the localization of carrier density at various locations of the CNTs. About 11% decrease in the drive current with steady difference in the drain current in the range of 0.2-0.4V of the gate voltage was reported in [12] when negative charge impurity was introduced at various locations of the CNT over a length of $\approx$ 20nm. In the context of field emission from CNT tips, a simple estimate of defects have been proposed by introducing a correction factor in the Fowler-Nordheim formulae [13]. However, it is clear that a more detailed physics based treatment is required for a better understanding of processes at the device-scale level. The goal of this paper is to develop a model to analyze the effects of defects and impurities on the field emission performance of CNT arrays. This paper is structured as follows: in Section 2, a physics based model is proposed that incorporates structural, vacancy and charge impurity defects. Numerical simulations comparing longitudinal strains and field emission current histories for CNT arrays with and without defects and impurities are presented in Section 3. Section 4 contains concluding remarks.

2 MODEL FORMULATION

The physics of field emission from metallic surfaces is fairly well understood. The current density (J) due

to field emission from a metallic surface is usually obtained by applying the Fowler-Nordheim (FN) approximation [14]

$$J = \frac{BE^2}{\Phi} \exp\left[-\frac{C\Phi^{3/2}}{E} \right] , \quad (1)$$

where E is the electric field, Φ is the work function of the cathode material, and B and C are constants.

Based on our previously developed model [6], which describes the degradation of CNTs and the CNT geometry and orientation, the decreased surface area can be expressed as

$$\pi d_t \Delta h = V_{\text{cell}} n_1(t) \left[s(s-a_1)(s-a_2)(s-a_3) \right]^{1/2} , \quad (2)$$

where d_t is the diameter of the CNT, Δh is the decrease in the length of the CNT (aligned vertically or oriented as a segment) over a time interval Δt due to degradation and fragmentation, V_{cell} is the representative volume element, n_1 is the concentration of carbon cluster in the cell, a_1, a_2, a_3 are the lattice constants, and $s = \frac{1}{2}(a_1 + a_2 + a_3)$ (see Fig. 1). The chiral vector for the CNT is expressed as

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 , \quad (3)$$

where n and m are integers ($n \geq |m| \geq 0$) and the pair (n, m) defines the chirality of the CNT. The following properties hold: $\vec{a}_1.\vec{a}_1 = a_1^2$, $\vec{a}_2.\vec{a}_2 = a_2^2$, and $2\vec{a}_1.\vec{a}_2 = a_1^2 + a_2^2 - a_3^2$. With the help of these properties the circumference and the diameter of the CNT can be expressed as, respectively [15],

$$|\vec{C}_h| = \sqrt{n^2 a_1^2 + m^2 a_2^2 + nm(a_1^2 + a_2^2 - a_3^2)} , \quad (4)$$

$$d_t = \frac{|\vec{C}_h|}{\pi} . \quad (5)$$

Let us now introduce the rate of degradation of the CNT or simply the burning rate as $v_{\text{burn}} = \lim_{\Delta t \to 0} \Delta h / \Delta t$. By dividing both side of Eq. (2) by Δt and passing to the limit, we have

$$\pi d_t v_{\text{burn}} = V_{\text{cell}} \frac{dn_1(t)}{dt} \left[s(s-a_1)(s-a_2)(s-a_3) \right]^{1/2} , \quad (6)$$

By combining Eqs. (4)-(6), the rate of degradation of CNTs is finally obtained as

$$v_{\text{burn}} = V_{\text{cell}} \frac{dn_1(t)}{dt} \left[\frac{s(s-a_1)(s-a_2)(s-a_3)}{n^2 a_1^2 + m^2 a_2^2 + nm(a_1^2 + a_2^2 - a_3^2)} \right]^{1/2} . \quad (7)$$

Therefore, at a given time, the length of a CNT can be expressed as $h(t) = h_0 - v_{\text{burn}} t$, where h_0 is the initial average height of the CNTs and d is the distance between the cathode substrate and the anode.

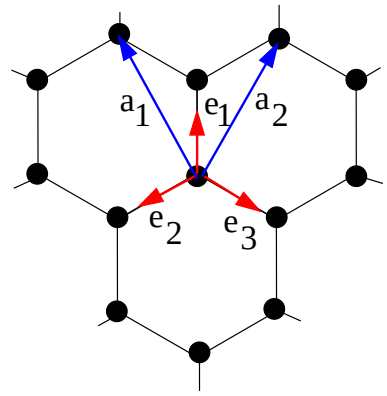

Figure 1: Schematic drawing showing hexagonal arrangement of carbon atoms in a CNT.

We follow the same procedure as in [5] to obtain the effective electric field component for field emission calculation with Eq. (1). The effective electric field component is expressed as

$$E_z = -e^{-1} \frac{d\mathcal{V}(z)}{dz} , \quad (8)$$

where e is the positive electronic charge and $\mathcal{V}$ is the electrostatic potential energy. The total electrostatic potential energy can be expressed as

$$\mathcal{V}(x, z) = -eV_s - e(V_d - V_s)\frac{z}{d} + \sum_j G(i, j)(\hat{n}_j - n) , \quad (9)$$

where V_s is the constant source potential (on the substrate side), V_d is the drain potential (on the anode side), $G(i, j)$ is the Green's function [16] with i being the ring position, and $\hat{n}_j$ denotes the electron density at node position j on the ring. Here, ring is assumed as per unit length of a CNT. The field emission current (I_{cell}) from the anode surface associated with the elemental volume V_{cell} of the CNT array is obtained as

$$I_{\text{cell}} = A_{\text{cell}} \sum_{j=1}^{N} J_j , \quad (10)$$

where A_{cell} is the anode surface area and N is the number of CNTs in the volume element. The total current is obtained by summing the cell-wise current (I_{cell}). This formulation takes into account the effect of CNT tip orientations and one can perform statistical analysis of the device current for randomly distributed and randomly oriented CNTs.

The novelty of our present approach is twofold. Firstly, we employ a concept of effective stiffness degradation for segments of CNTs, which is due to structural defects, by modifying the chiral vector in Eq. (3). The effective stiffness degradation is modeled by introducing an effective chiral vector $\alpha\vec{C}_h$, where $0 < \alpha < 1$ describes

the extent of structural defects over the tube circumference at a particular cross-section of a CNT in the array. Secondly, we incorporate the vacancy defects and charge impurity effects in our Green's function based approach. This is done by computing the effective electric potential energy as

$$\mathcal{V}(x,z) = -eV_s - e(V_d - V_s)\frac{z}{d} + \sum_j G(i,j)(\hat{n}_j - n \pm \overline{m}_l + \delta_{kj}) \ , \qquad (11)$$

where $\overline{m}_l$ denotes the charge due to impurity at coordinate l, and δ_{kj} denotes the vacancy at atom position k. The effective electric field is subsequently calculated by Eq. (8) and current density is obtained by using Eq. (1).

3 RESULTS AND DISCUSSIONS

The CNT film considered in this study consists of randomly oriented multiwalled CNTs (MWNTs). The film was grown on a stainless steel substrate. The film surface area (projected on anode) is 49.93 mm^2 and the average height of the film (based on randomly distributed CNTs) is 10-14 μm. As in [5], in the simulation and analysis, the constants B and C in Eq. (1) were taken as $B = (1.4 \times 10^{-6}) \times \exp((9.8929) \times \Phi^{-1/2})$ and $C = 6.5 \times 10^7$. It has been reported in the literature (e.g., [17]) that the work function Φ for CNTs is smaller than the work functions for metal, silicon, and graphite. However, there are significant variations in the experimental values of Φ. The value of Φ depends on the structure, defect, types of CNTs (i.e., SWNT/MWNT), and surface state of CNTs (specifically, cap nature, the edge structure of graphene sheet in an open end). The type of substrate materials has also significant influence on the electronic band-edge potential. All these factors should be taken into consideration together. A comprehensive understanding about the work function of CNTs is still missing. The results reported in this paper are based on computation with $\Phi = 2.2eV$.

An array of 10 vertically aligned and each 12 μm long CNTs is considered for the device scale analysis. Defect regions are introduced randomly over the CNT length with $\alpha = 0.2$ and positive charge density of $\overline{m}_l = 10$. Figure 2 shows the decrease in the longitudinal strain due to defects. Contrary to the expected influence of purely mechanical degradation, this result indicates that the charge impurity, and hence weaker transport, can lead to a different electromechanical force field, which ultimately can reduce the strain. However, there could be significant fluctuations in such strain field due to electron-phonon coupling. The effect of such fluctuations (with defects) can be seen in Fig. 3 where we provide the plot of the field emission current history. The average current also decreases significantly due to such defects.

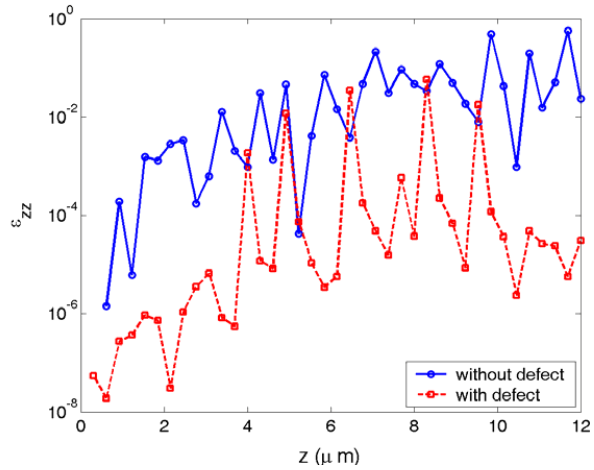

Figure 2: Cross-sectional average longitudinal strain distribution along the CNT at t=0.1s.

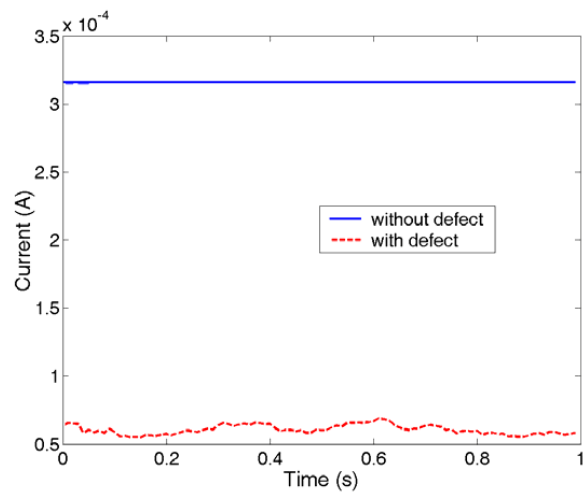

Figure 3: Field emission current history for gate voltage of 600V from an array of 10 CNTs with and without defects.

4 CONCLUSION

In this paper, a model incorporating defects and impurities in CNT based field emission cathodes has been developed from the device design point of view. The model has been incorporated by using a two-step procedure. Firstly, structural defects are considered by modifying the chiral vector. Secondly, vacancy defects and charge impurity effects are introduced in our Green's function based approach. Based on this procedure, the impact of the defects and impurities on the field emission current has been computed. It has been found that the average current decreases significantly due to such defects.

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