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Multi-Mode Phonon Controlled Field Emission from Carbon Nanotubes: Modeling and Experiments

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Abstract

The main idea proposed in this paper is that in a vertically aligned array of short carbon nanotubes (CNTs) grown on a metal substrate, we consider a frequency dependent electric field, so that the mode-specific propagation of phonons, in correspondence with the strained band structure and the dispersion curves, take place. We perform theoretical calculations to validate this idea with a view of optimizing the field emission behavior of the CNT array. This is the first approach of its kind, and is in contrast to the the conventional approach where a DC bias voltage is applied in order to observe field emission. A first set of experimental results presented in this paper gives a clear indication that phonon-assisted control of field emission current in CNT based thin film diode is possible.

Keywords: Field emission, carbon nanotube, electrodynamics, hydrodynamics, phonon, dispersion.

I. Introduction

In order to understand the electron-electron interactions and electron-phonon interactions in carbon nanotubes (CNTs), the study of collective excitations is very important. For mathematical modeling of the complex dynamics during field emission from CNTs in the form of a thin film, the deformation of the CNTs and the related couping with the electrodynamics should be taken into account. Under the continuum type assumption for the CNTs as elastic nano-wire, the displacement can be decomposed into two parts: one is the displacement due to electromechanical forces in the slow scale (i.e., due to conduction current induced force under electrostatic potential etc.), and the other is the displacement due to fluctuation of the CNT sheet due to electron flow in the CNT and ballistic transport of electron from the tip to the anode. The displacement due to electromechanical forces has been modeled by these authors (see Ref. [1], [2] for details). The focus of this paper is to extend the previously developed model to include the deformation due to the fluctuation of the CNT sheet under electron flow. In this paper, we develop a systematic approach, starting from the unit cell of a generally oriented CNT to the interacting array of CNTs under realistic quantum-mechanical boundary conditions. A hydrodynamic model with mechanical coupling is used to model the CNTs, which assumes a thin layer of electron gas at the surface of the CNTs. Theoretical and experimental studies on quantum thermal transport suggest that the electronic transport (and hence the field emission current) is coupled with the thermal transport [3]. Therefore, thermodynamics of electron-phonon interaction has also been considered. Expressions for dispersion relations are obtained by solving all the governing equations simultaneously.

II. Model Formulation

The surface electron density of CNTs ($\tilde{n}$) can be decomposed into a steady (unstrained) part ($\tilde{n}_0$) and a fluctuating part ($\tilde{n}_0$). Therefore, $\tilde{n} = \tilde{n}_0 + \tilde{n}_1$, where the steady part $\tilde{n}_0$ is the surface electron density corresponding to the Fermi level energy in the unstrained CNT, and it can be approximated as in [4] $\tilde{n}_0 = \frac{kT}{\pi b^2 \Delta}$, where k is Boltzmann's constant, T is the temperature, b is the interatomic distance and Δ is the overlap integral ($\approx 2eV$ for carbon). The fluctuating part $\tilde{n}_1$ is inhomogeneous along the length of the CNTs. Actually, $\tilde{n}_1$ should be coupled nonlinearly with the deformation and the electromagnetic field [5]. However, in a simplified form, $\tilde{n}_1$ is primarily governed by one of the quantum-hydrodynamic equations, which will be illustrated later in this paper. The displacement of CNTs during field emission is the combined effect of the electromechanical forces in the slow time scale and the fluctuation of the CNT sheet due to electron flow in the fast time scale. Therefore, the total displacement vector $\mathbf{u_{total}}$ can be expressed as

$$\mathbf{u_{total}} = \mathbf{u^{(1)}} + \mathbf{u^{(2)}} \ , \tag{1}$$

where $\mathbf{u^{(1)}}$ and $\mathbf{u^{(2)}}$ are the displacement vectors due to electromechanical forces and fluctuation of the CNT sheet, respectively. The elements of displacement vector in the coordinate system (x', z') can be written as

$$\mathbf{u^{(1)}} = \left\{ \begin{array}{c} u_{x'}^{(1)} \\ u_{z'}^{(1)} \end{array} \right\} , \quad \mathbf{u^{(2)}} = \left\{ \begin{array}{c} u_{s}^{(2)} \\ u_{z'}^{(2)} \end{array} \right\} , \tag{2}$$

where $u_{x'}$ is the lateral displacement and $u_{z'}$ is the longitudinal displacement. The displacement $\mathbf{u^{(1)}}$, which is defined in the slow time scale, is calculated using the methodology previously developed by the authors [2]. To determine the displacement in the fast time scale ($\mathbf{u^{(2)}}$), a quantum-hydrodynamic formalism is used, which is discussed next.

1) Quantum-hydrodynamic formalism: In this study, following assumptions have been made for the quantum-hydrodynamic formalism:

(i) CNTs deform due to electrodynamic forces, thus changing the atomic coordinates leading to change in energy band structure;

(ii) The valence electrons flow as uniformly distributed electron gas over the cylindrical surface; and

(iii) An electromagnetic wave propagates along the CNT axis and perturbs the homogeneous electron gas density.

By combining the continuity equation and the momentum conservation equation (that contains $\mathbf{u^{(2)}}$), the hydrodynamic model for electron density on the CNT surface can be expressed as

$$\frac{\partial^2\tilde{n}_1}{\partial t^2}-\frac{e\tilde{n}_0}{m_e}\frac{\partial E_{z'}}{\partial z'}-\alpha\frac{\partial^2\tilde{n}_1}{\partial z'^2}+\beta\frac{\partial^4\tilde{n}_1}{\partial z'^4}+\frac{\beta}{r^2}\frac{\partial^2}{\partial z'^2}\left(\frac{\partial^2\tilde{n}_1}{\partial\theta_0^2}\right)+\frac{n_0}{m_e}\frac{\partial f_{lz'}}{\partial z'}-\frac{e\tilde{n}_0}{m_e}\frac{1}{r}\frac{\partial E_{\theta_0}}{\partial\theta_0}-\frac{\alpha}{r^2}\frac{\partial^2\tilde{n}_1}{\partial\theta_0^2}+\frac{\beta}{r^4}\frac{\partial^4\tilde{n}_1}{\partial\theta_0^4}+\frac{\beta}{r^2}\frac{\partial^2}{\partial\theta_0^2}\left(\frac{\partial^2\tilde{n}_1}{\partial z'^2}\right)+\frac{n_0}{m_e}\frac{1}{r}\frac{\partial f_{l\theta_0}}{\partial\theta_0}-\frac{en_0}{m_e}\frac{\partial E_r}{\partial r}+\frac{n_0}{m_e}\frac{\partial f_{lr}}{\partial r}=0\ , \quad (3)$$

where e is the electronic charge (positive), m_e is the mass of the electron, α is the speed of propagation of density disturbances, β is the single electron excitation in the electron gas, f_l is the Lorentz force, f_p is the ponderomotive force, and $E_{z'}$, E_{θ_0} and E_r are the axial, circumferential and out-of-plane components of the electromagnetic field, respectively. The effect of temperature on $\tilde{n}$ is not directly taken into consideration. Instead, the thermodynamics of electron-phonon interaction is modeled separately later in a decoupled manner through quantum thermal conductance. In order to introduce coupling between the quantum fluctuation and the eletromagnetic field, we consider the Maxwell's equations in general form, which is combined to the following form:

$$\nabla^2 E-\mu\sigma\frac{\partial E}{\partial t}-\mu\epsilon\frac{\partial^2 E}{\partial t^2}=\mu\frac{\partial J}{\partial t}\ , \quad (4)$$

where μ, σ, ϵ, and J are permeability, conductivity, permittivity, and current density, respectively. Magnetic field fluctuation is neglected for simplicity. In the present case, the current density in the CNT sheet is given by $J=e\tilde{n}\partial u^{(2)}_{z'}/\partial t$. Therefore, by simplifying Eq. (4) further, one can obtain the equations in (z',θ_0,r) coordinate system as

$$\frac{\partial^2E_{z'}(r)}{\partial z'^2}+\frac{1}{r^2}\frac{\partial^2E_{z'}(r)}{\partial\theta_0^2}+\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial E_{z'}(r)}{\partial r}\right)-\mu\sigma\frac{\partial E_{z'}(r)}{\partial t}-\mu\epsilon\frac{\partial^2E_{z'}(r)}{\partial t^2}=\mu\frac{\partial}{\partial t}\left(e\tilde{n}\frac{\partial u^{(2)}_{z'}}{\partial t}\right)\ , \quad (5)$$

$$\frac{\partial^2E_{\theta_0}(r)}{\partial z'^2}+\frac{1}{r^2}\frac{\partial^2E_{\theta_0}(r)}{\partial\theta_0^2}+\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial E_{\theta_0}(r)}{\partial r}\right)-\mu\sigma\frac{\partial E_{\theta_0}(r)}{\partial t}-\mu\epsilon\frac{\partial^2E_{\theta_0}(r)}{\partial t^2}=0\ , \quad (6)$$

$$\frac{\partial^2E_{r}(r)}{\partial z'^2}+\frac{1}{r^2}\frac{\partial^2E_{r}(r)}{\partial\theta_0^2}+\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial E_{r}(r)}{\partial r}\right)-\mu\sigma\frac{\partial E_{r}(r)}{\partial t}-\mu\epsilon\frac{\partial^2E_{r}(r)}{\partial t^2}=0\ , \quad (7)$$

2) Thermodynamics of electron-phonon interaction: In order to arrive at the governing equation in temperature $T(z')$ (assuming the CNTs to be one-dimensional elastic nano-wire), a diffusive heat transport model in the ballistic regime is used to analyze the temperature rise in different CNTs in our present problem. In the ballistic regime, the heat flux carried by the phonons can be obtained by integrating the non-equilibrium phonon distribution associated with several phonon modes. Further simplification of this integral based on the analogy with the Landauer formula for ballistic conduction of electron leads to an approximate thermal conductance quantum $k_Q=\pi k^2T/(6\hbar)$. This temperature dependent thermal conductance is employed to derive the heat transport equation. By considering the Fourier heat conduction and thermal radiation from the surface of CNT, the heat transport equation using the energy rate balance principle can be written as

$$dQ-\frac{\pi d_t^2}{4}dq_F-\pi d_t\sigma_{SB}(T^4-T_0^4)dz'=\beta_{in}k\frac{\partial T}{\partial t}\ , \quad (8)$$

where dQ is the heat flux due to Joule heating, d_t is the diameter of the CNT, q_F is the Fourier heat conduction ($q_F=-k_Q\nabla T$), σ_{SB} is the Stefan-Boltzmann constant and β_{in} is a constant. By dropping the non-linear terms as a simplification, Eq. (8) can be written as

$$-k_Q\frac{\partial^2 T}{\partial z'^2}=\beta_{in}k\frac{\partial T}{\partial t}\ . \quad (9)$$

Solution branches of this equation couped with the temperature dependent charge density (derived next) represents the thermal phonon mode.

3) Computation of output current: The average conduction electron density ($\tilde{n}^{CNT}_{av}$) for a particular energy band i can be calculated by using the following relation:

$$\tilde{n}^{CNT}_{av}=\sum_{i=1}^{R}f^i(E_{FL},E_i,T)|\psi_i|^2\ , \quad (10)$$

where R is the total number of conduction bands, E_{FL} is Fermi level energy, E is the energy state and ψ is the wave function. The function $f^i(E_{FL},E_i,T)$ is expressed as

$$\sum_{i=1}^{R}f^i(E_{FL},E_i,T)=\frac{1}{1+\exp\left(\frac{\mathrm{E_{FL}-E_i}}{\mathrm{kT}}\right)}\ , \quad (11)$$

and this is the function which couples the quantum thermal conductance in Eq. (9) to the fluctuation of the CNT sheet and the related mechanics in the fast time scale. To obtain the energy state E, we solve the k.p band structure problem

$$H^c\psi=E^c\psi\ , \quad (12)$$

where the superscript c denotes the conduction band and H is the total Hamiltonian, which is expressed as

$$H=\nabla\frac{\hbar^2}{2m^*}\nabla+H(\varepsilon)+e(V+\phi)\ , \quad (13)$$

where m^* is effective mass, ε is the longitudinal strain (including thermal strain), V is the DC bias voltage and ϕ is the fluctuating in the electrical potential due to Maxwellian electromagnetics. Assuming the CNTs as one-dimensional elastic nano-wire (as in an Euler-Bernoulli beam) and subjected to small strain and small curvature, the longitudinal strain can be written as

$$\varepsilon_{zz} = \frac{\partial u_{z'0}^{(m)}}{\partial z'} - r^{(m)} \frac{\partial^2 u_{x'}^{(m)}}{\partial z'^2} + \alpha \Delta T(z') \,, \tag{14}$$

where the superscript (m) indicates the mth wall of the MWNT with $r^{(m)}$ as its radius and $u_{z'0}$ as the displacement of the center of the cylindrical cross-section, $\Delta T(z') = T(z') - T_0$ is the difference between the absolute temperature (T) during field emission and a reference temperature (T_0) and α is the effective coefficient of thermal expansion (longitudinal). The axial strain ε_{zz} is related to the bond elongation during field emission. For example, the relation between the axial strain and the bond elongation for an armchair nanotube is expressed as [6]

$$\varepsilon_{zz} = \frac{\Delta a_1 \sin(\alpha/2) + \frac{a_1}{2}\cos(\alpha/2)\Delta\alpha}{a_1 \sin(\alpha/2)} \,, \tag{15}$$

where a_1 is the bond length, α is the bond angle, Δa_1 is the bond elongation and $\Delta\alpha$ is the bond angle variance.

The electrostatic potential (V) is calculated using Greens' function approach [7]; that is,

$$V(z) = -eV_s - e(V_d - V_s)\frac{z - z_0}{L - z_0} + \sum_j G(i,j)(n_j - N) \,, \tag{16}$$

where V_s is the source potential, V_d is the drain potential, L is the length of the CNT, (i, j) are rings on different sections of CNT and N is denotes chirality in a $(N, 0)$ CNT. This potential changes slowly, depending on the globally deformed shape of the CNTs for a given condition of the thin film.

In Eq. (5), the fluctuating part of the electrical field is given by $E_{z'} = -\partial\phi/\partial z'$. By using Eq. (12)-(16), the energy state E is calculated. The value of E is plugged in Eq. (10) to obtain the fluctuating electron density $\tilde{n}_{av}^{CNT}$. By summing up the current density contribution from all the CNT tips within a volume element of the thin film, the total electron density ($\tilde{n}_{total}^{i'}$) is determined. Finally, the field emission current (I) in the anode is estimated as

$$I = \sum_{i'=1}^{S} \tilde{n}_{total}^{i'} \Delta A \,, \tag{17}$$

where S is the total number of CNTs in the volume element and ΔA is the area of the anode.

III. Results and Discussions

In the theoretical model of the electron-phonon interaction, we have eight partial differential equations, as discussed above. The variables here are $\{T\, \tilde{n}_1\, u_{z'}^{(2)}\, u_r^{(2)}\, u_{\theta 0}^{(2)}\, E_{z'}\, E_r\, E_{\theta 0}\}$. By applying Fourier transform from time domain to frequency domain and assuming periodic field distribution in terms of the wavevectors, and by substituing them into the eight governing equations, we get the dispersion equation. Fig. 1 shows the frequencies for various values of the CNT radius. The circles shows the frequencies (ω_k) at which there will be uniform flow of conduction electrons, that is for the zero waveneumebrs: $q_k = 0$, $m_k = 0$, where

$$\tilde{n} = \sum_k \tilde{\tilde{n}}_{1_k} e^{j(m_k\theta_0 + q_k z' - \omega_k t)} \,, \tag{18}$$

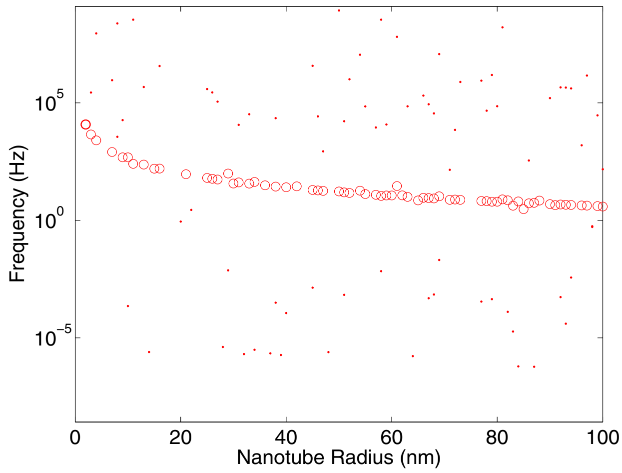

Fig. 1. Frequencies for zero longitudinal wavenumber and zero radial wavenumber and for various values of the CNT radius.

and similar transformation for the other variables hold. In Fig. 1, the dots indicate the various values of the frequencies at the which the acoustic phonons and the thermal phonons cease to exist; that is, at these frequencies the couples phonon modes are degenerate and the resulting effect is the same as in a ideal cylindrical CNT with no fluctuation in the CNT sheet.

In this paper, we report the first set of experimental results, wherein the field emission current has been measured for various AC frequencies at 600V of bias DC voltage across the CNT substrate and the anode. The thin film sample has vertically aligned CNTs with average height of 12 μm and 200 nm diameter. Figure 2 shows the field emission current history (thin lines) and the applied AC voltage history (solid line) at frequency of $10HZ$. The field emission current is obtained for a steady-state oscillation of voltage with amplitude of 600V. A drop in the resistivity can be seen at the peak voltage, whereas at the minimum voltage, the field current is fluctuation dominated. Figure 3 shows the variation in the maximum field emission current obtained for 600V DC voltage as we vary the frequencies. Due to frequency limitation in the high voltage power supply, the present experiments have been restricted to 60Hz frequency. From Fig. 3, it seen that the field emission current drops by approximate 10 μA as the applied voltage is changed from 600V DC to 600V AC at 2 Hz. However, an amplification of field emission current at about $40Hz$ (voltage is kept at 600V) can be seen. Although a very low frequency as compared to the ballistic transport regime (see the frequency range in Fig. 1), the frequency variation seen in Fig. 3 is essentially an indication that phonon-assisted control of field emission current in CNT film device is possible.

IV. Conclusions

In this paper, we have developed a computational model to optimize the field emission behavior of a carbon nanotube thin film by applying a frequency dependent electric field. The idea behind the individual phonon mode excitation under AC field is that this will help in validating the overall model dynamics

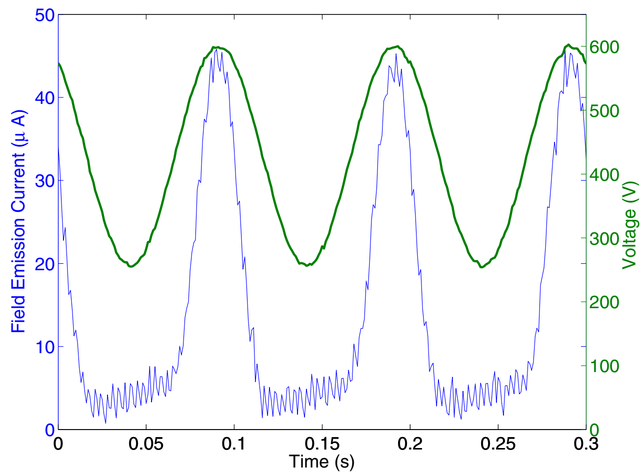

Fig. 2. Field emission current history for applied AC voltage at 600V and 10 Hz. Voltage history is shown by thick solid line.

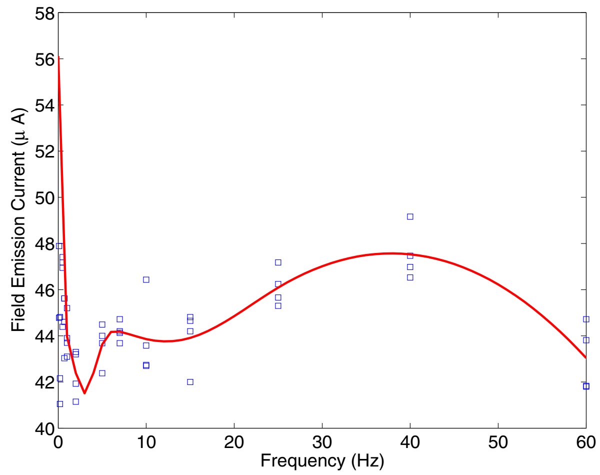

Fig. 3. Variation in the field emission current amplitude for various frequencies of applied AC voltage. Applied AC voltage amplitude is 600V for all the frequencies.

and in shaping the field emission versus time response. A first set of experimental results presented in this paper gives a clear indication that phonon-assisted control of field emission current in CNT based thin film diode is possible.

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