Ab initio study of field emission from carbon nanotubes

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Abstract An *ab initio* computational method has been developed to simulate the field emission from nanostructures based on the time-dependent Schrödinger equation. Electronic structures of realistic systems are calculated within the *ab initio* pseudopotential formalism and emission currents are obtained through a direct integration of the electron dynamics under external field for both singlewall and multiwall carbon nanotubes. In each nanotube, three distinct states are identified to contribute to the current: π, π^*, and localized states. For most conventional metallic tips, extended states (like π or π^* states) are the main source of the current. For carbon nanotubes, however, our quantum-mechanical calculation indicates that the currents associated with the localized state account for most of the total emission current.

1 Introduction

The classic theory of field emission was developed by Fowler and Nordheim in 1928 [1]. In this theory, the system is simplified as a one-dimensional structure along the direction of the external field. The emission tip is modelized as a semi-infinite quantum well and the local electric field is approximated as a linear potential. The resulting current is basically an exponential function of the bias voltage as follows:

$$I \propto V^2 \exp[-\beta \Phi^{3/2}/V], \quad (1)$$

where Φ is the work function and β is a constant including the field enhancement factor. When I/V^2 is logarithmically plotted against $1/V$, the data lie on a straight line, which is so-called the Fowler-Nordheim (F-N) plot. In most of the experiment with the micronsize tip, I-V curves follow the form of Eq. (1), which is usually taken as evidence that the emission is driven by the field, not by the thermally excited hot-electrons. The local electric field is obtained from the slope of the F-N plot, assuming a certain reasonable value for the work function.

Theoretical estimation of the emission current was usually done in a semi-classical fashion with improvements over the F-N theory. The potential around the tip region was obtained by solving the classical electrostatics with the Laplace equation. The transmission functions were then evaluated by using the one-dimensional semi-classical approach (e.g., WKB approximation) along a specific line in the emission direction. The electronic structure of the emitter was reflected in the supply function, as a form of the density of state.

Such a simple picture, however, is not appropriate for the nanostructures. For instance, the boundary of the tip is not a well-defined physical quantity at the atomic scale and the potential obtained through the Laplace equation would not be valid for nanosize systems. In addition, the one-dimensional WKB calculation neglects any spatial variation of the wave function in the xy-plane (the emission is in the z-direction). Even for the flat metal plane, the suppression of current from the d band compared to the s band is well addressed in many works. (See Ref. [2] and references therein.) The situation becomes more complicated in the nanotip where the xy-dimension of the tip is order of nanometers. It is also well-known that the total current is changed significantly by the localized states induced by the adsorbates at the tip. The importance of the localized states increases for the nanotip where the atomic size of the tip restricts the number of channels for the metallic states. The consideration of the localized states is difficult in the semi-classical approach because they are not normally the current-carrying states.

2 Computational Method

In our analysis of the field emission process, we do not make any simplifying assumptions on the tube shape, the potential distributions, or the electronic states. We calculate the electronic structures of carbon nanotubes (under a given applied electric field) using the standard *ab initio* pseudopotential method with the local density approximation. Troullier-Martins pseudopotentials in the separable form are used with a cutoff energy 40 Ry to ensure the reliable computational results. At first, electronic states are expanded with the localized basis set on the nanotube side. Upon converting the localized basis set into plane waves, electronic states start to leak out to the vacuum (anode) side over the tunneling barrier. Then the transmission rate of the individual electronic states to the vacuum side is obtained by solving the time-dependent Schrödinger equation with the Suzuki-Trotter type split-operator method. We implement the Suzuki-Trotter method into the pseudopotential formalism by modifying the work by Sugino et al. [3] and the time increment Δt in the calculation is 0.1 atomic unit (1 a.u. = $2.42 \times 10^{-17} s$). As will be presented in more detail below, for a (10,10) capped carbon nanotube, we find that the emission current contributed from the states localized at the tip of the tube dominates the direct contribution from the extended metallic states (π and π^* states in this case), accounting for anomalously large emission current of the carbon nanotube.

3 Results and Discussion

Figure 1 shows the snapshot of the electronic configuration for a localized state associated with the pentagon

defect of a (10,10) capped nanotube. The state is at the Fermi level and the snapshot is taken 60 a.u. ($\approx$ 1.5 fs) after the field is turned on. In this particular carbon nanotube, this kind of localized states turn out to contribute 95% of the total current. Figure 1(a) is the charge density distribution of the state and Fig. 1(b) shows the equipotential lines (separation between successive lines is 1 Volt) and the current density indicated by arrows. Electrons leaking out of the tunneling barrier demonstrates a characteristic shapes of the states and the flow pattern in space. When the electron arrives at the phosphor screen of a field emission display, it exhibits a cross section of a pair of asymmetric lobes. When two localized states, mutually orthogonal, are degenerate in energy (as usually the case unless a symmetry-breaking distortion or adsorbate exists), the pattern would be a ring. (An open multiwall nanotube of a large diameter would give a ring as well.) Another possibility is a spot pattern generated by a constructive interference of a coherent emission from an open singlewall nanotube. All these patterns have been observed experimentally.

Another interesting observation distinct from the case of the micronsize metallic tips is that there is a narrow and strong peak in the emission energy spectrum and the peak shifts down in energy almost linearly in the applied field. [4] We have performed the same quantum-mechanical calculations as a function of the applied field and probed the energy distribution of the emitted electron current. The localized states begin to be occupied after a certain threshold voltage and the occupation of the localized states near the Fermi level is found to be linear in the applied field until occupation is completed. This behavior may simply be understood in terms of the energy minimization as follows. Let f be the occupation number of the localized states. The total energy change U by adding a charge $-nef$ (n is the number of localized states including the spin degeneracy and $-e$ is the electron charge) for a given applied field ($E_{\rm appl}$) is

$$U(f) = -nef\alpha E_{\rm appl} + \frac{(-nef)^2}{2C_{\rm eff}}, \qquad (2)$$

where $\alpha E_{\rm appl}$ is the effective electric potential shift experienced by the localized state w.r.t. the potential deep inside the tube. This term originates from a finite field penetration depth and is obviously linear in the applied field. $C_{\rm eff}$ is the effective capacitance. The contribution of the finite energy width of the density of the localized states can be included in this capacitance term because both terms are quadratic in charge ($-nef$). Minimizing U with respect to f, we have

$$f = \alpha E_{\rm appl} C_{\rm eff}/ne, \qquad (3)$$

proving that f is linear in $E_{\rm appl}$. Since the local field at the nanotube edge is linear in the applied field, we can rewrite the potential shift $\alpha E_{\rm appl} = \gamma E_{\rm local}$. The value of γ estimated from the calculation is ~ 0.2 Åand it indicates roughly the field penetration depth divided by the dielectric constant. Once f reaches 1, the energy level

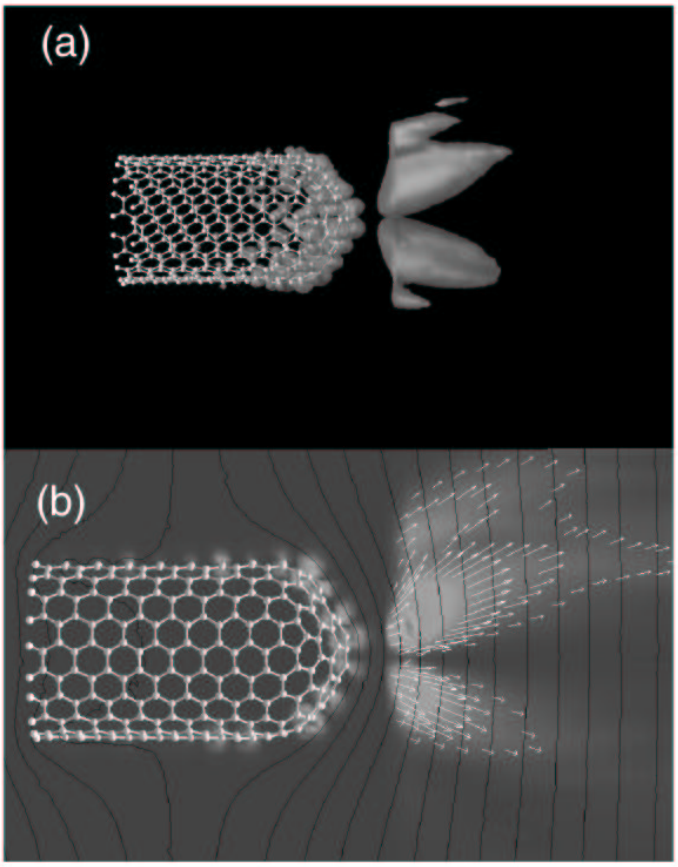

Fig. 1 Snapshot of electron emission from a nanotube as described in the text.

of the localized states shifts down rapidly by a further increase in the applied bias because the screening is less complete. The linear shift of the localized state level is the result of the potential bending (due to incomplete screening) near the edge which is proportional to the applied field. We have also obtained actual values of the emission current for different nanotubes at different bias voltages.

References

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