SIMULATION OF SEMICONDUCTOR PROCESSES AND DEVICES Vol. 12 429
Edited by T. Grasser and S. Selberherr - September 2007

Ab Initio Calculations of the Transport Through Single Molecules and Carbon Nanotubes

Kenji Hirose[1,4], Nobuhiko Kobayashi[2,4], and Hiroyuki Ishii[3]

[1] Nano Electronics Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan
hirose@frl.cl.nec.co.jp

[2] Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennohdai, Tsukuba, Ibaraki 305-8573, Japan
nkoba@bk.tsukuba.ac.jp

[3] National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
ishii@bk.tsukuba.ac.jp

[4] CREST, Japan Science and Technology (JST) Agency,

Abstract

We present calculations for the transport properties of single molecules and carbon nanotubes (CNT) bridged between electrodes. Here we use two calculation methods. One is the recursion-transfer-matrix (RTM) method, which is a reliable tool to calculate accurate scattering waves in plane-wave expansions. Combined with the NEGF method and density-functional formalism, we perform calculations of transport properties through single molecules. The other is the time-dependent wave-packet approach. Based on the linear-response Kubo formula, we perform O(N) calculation for the transport of large systems. We apply the method for the CNT-FET device and find that the control of the contact to electrodes are crusial for the device performance.

1 Introduction

Recently much effort has been focused to measure the transport properties of single molecules and carbon nanotubes (CNT) bridged between electrodes for the molecular electronics. Since it is still difficult to construct well-characterized nanometer-scale device system between electrodes, theoretical approaches based on the first-principles calculations become important to characterize the transport properties of such nanometer-scale devices.

For such purposes, we developed two calculation methods. One is to use the recursion-transfer-matrix (RTM) method, which is a reliable tool to calculate accurate scattering waves in plane-wave expansions, combined with non-equilibrium Green's functional (NEGF) method. Based on the density-functional formalism, we can perform ab initio calculations for the transport through nanometer-scale structures. We show calculated results for the single molecule conduction between electrodes.

The other is the time-dependent wave-packet approach. We calculate the time-dependent wave-packet for the electron diffusion and use the linear-response Kubo formula to calculate the conductance. This O(N) method enables us to treat transport properties for very large systems. We apply this method for the transport through CNT. We show the results on the electron-phonon coupling and contact effects to electrodes on the device performance of CNT-field effect transistor (CNT-FET).

2 Calculation Method

2.1 RTM/NEGF Method

First we show briefly an *ab initio* calculation method based on the scattering-wave approach for the quantum transport. This method is suitable for accurate calculations of the atomic and molecular-scale transport problems. We expand the wavefunctions in Laue representation

$$\Psi_{E,i}^{L/R}(\mathbf{r}) = \sum_m u_{E,i}^{L/R}(\mathbf{g}_\parallel^m, z) e^{i(\mathbf{k}_\parallel + \mathbf{g}_\parallel^m)\mathbf{r}_\parallel} \tag{1}$$

where the z axis is in the direction the current flows. Then we obtain the coupled-channel differential matrix equation of the Kohn-Sham equation and the transfer matrix defined on the neighboring mesh points z_p, z_{p+1} such as

$$\hat{S}^{L/R}(z_p) = \hat{U}^{L/R}(z_{p+1})\hat{U}^{L/R}(z_p)^{-1} \tag{2}$$

follows the recursive relation. Giving the boundary conditions deep in the electrodes, we obtain the scattering-states flowing between electrodes [1]. On the basis of these states, the non-equilibrium Green's function is constructed from the retarded and advanced Green's functions with the coupling constant to the electrodes $\Gamma_{L/R}$ by

$$\hat{G}^< = i\hat{G}^r(f_L\hat{\Gamma}^L + f_R\hat{\Gamma}^R)\hat{G}^a \tag{3}$$

where $f_{L/R}$ is the Fermi distribution function of each electrode and the applied bias voltage eV is the difference of chemical potentials $\mu_{L/R}$ at each electrode. Then charge density is obtained through density matrix as a sum over the occupied states

$$\hat{\rho} = -\frac{1}{\pi}\mathrm{Im}\int_C \hat{G}^r dZ + \frac{1}{2\pi i}\int_{\mu_R}^{\mu_L} \hat{G}^< dE \tag{4}$$

where integration of G^r is done in the complex upper plane C, which avoids singularity due to localized nature of the states, van Hove singularities, and others [2].

This charge density is utilized to construct the effective potential based on the density-functional formalism and these procedures are iterated until self-consistent solutions are obtained. Finally, the current flowing between electrodes is calculated from the Fisher-Lee relation

$$I = \frac{2e}{h}\int_{-\infty}^{\infty}(f_L - f_R)Tr\{\Gamma^L G^r \Gamma^R G^a\}dE \tag{5}$$

2.2 Time-Dependent Wave-Packet Approach

Second we show the O(N) transport calculation method based on the tight-binding approach [3]. We calculate the time evolution operator using the expansion of the Bessel function and Chebychev polynomials such as

$$U(t+\Delta t)=\sum_{n=0}^{\infty} h_n i^n J_n(\Delta t)\times T_n(H(t)) \tag{6}$$

Here due to a tiny amount of time evolution, we need only small terms n for the expansion of Bessel function. We calculate the conductance using the Kubo formula in the real time domain

$$G(E)=\frac{2e^2}{L}\rho(E)D(E,\tau(L))=\lim_{t->\tau(L)}\frac{2e^2}{L}Tr\left[\frac{\delta(E-H)}{L}\frac{(X(t)-X(0))^2}{2t}\right] \tag{7}$$

where D is the diffusion coefficient and the time evolution is $X(t)=U^{+}(t)X(0)U(t)$. This O(N) calculation method is suitable to treat the conductance of large systems.

3 Calculation Results

3.1 Transport Properties Through Single Molecule

Figure 1 shows the I-V characteristics for the transport properties through benzene-dithiolate (BDT) molecule between jellium electrodes. The left panel shows that the BDT molecule is sandwiched to both left and right electrodes with an appropriate distance (d=0). We see that non-linear behaviour of the current and the resonance peaks in the differential conductance in the inset panel. It is at present difficult in experiments to fabricate the nanometer-scale gap structure with high precision. So we expect that the molecules have imperfect contact to the electrodes. The right panel shows the I-V characteristic with d=8 (a.u.) separation. We see that the magnitude of the current decreases significantly, but similar non-linear behaviour is observed. This suggests that it is difficult from the I-V data to show that the contacts are good or not.

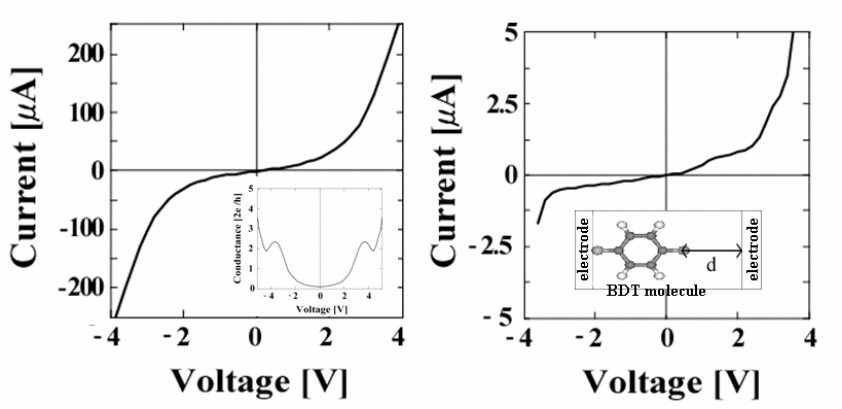

Figure 1: I-V characteristics of the BDT molecule sandwiched between electrodes.

3.2 Transport Characteristics Of The CNT-FET Device

Next we show the transport properties of CNT-FET devices. Single-walled CNTs are remarkable quasi-one-dimensional materials and recently they have been utilized for the channel of the FET devices [4]. It is reported that the mobility can be as high as 79000 cm^2/Vs. Here we study the CNT-FET device with 1 μm channel length by the time-dependent wave-packet approach. The effects of Schottky barrier and electron-optical phonon scattering are included in the calculations. The left panel of figure 2 shows the diffusion coefficient D as a function of time with various gate voltages. The right panel shows the mobility obtained from $\mu = e\tau/m^*$ ($\mu \propto dG/dV_G$). We see that the mobility becomes zero under the gate voltage of $V_G=0.7V$ with the semiconductor gap and it reaches up to 80000 cm^2/Vs. We find that the control of the contact to electrodes (Schottky barrier) becomes crucial for the device performance.

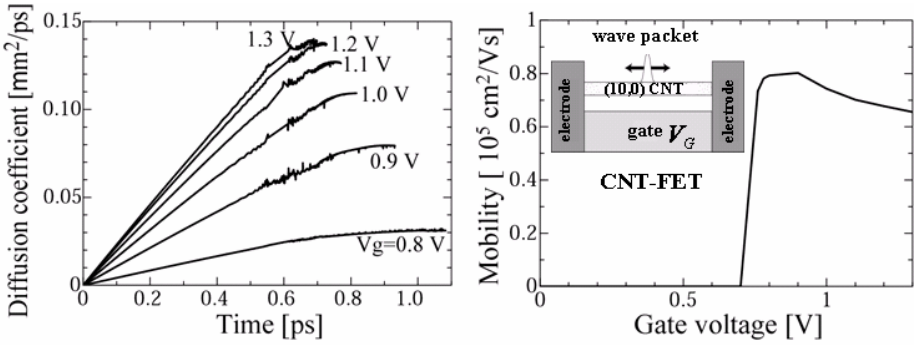

Figure 2: Calculation of the performance of CNT-FET device.

Acknowledgements

This work is supported by the CREST project on "Contact effects and transport properties of single molecules". The computation was carried out using the facilities of the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

References

[1] K. Hirose, N. Kobayashi, and M. Tsukada, "Ab initio calculations of transport properties of atomic wires by the RTM method", Physical Review, B69, pp. 245412-1-5, 2004.

[2] K. Hirose and N. Kobayashi, "Theory of electron hopping through nanometer-scale contacts –from tunneling to ballistic regimes –", Physica, E29, pp. 515-518, 2005.

[3] H. Ishii, N. Kobayashi, and K. Hirose, "Electron-phonon coupling effect on quantum transport in carbon nanotubes using time-dependent wave-packet approach", Physica E, to be published, 2007.

[4] For a recent review, see J.-C Charlier, X. Blasé, and S. Roche, "Electronic and transport properties of nanotubes", Review of Modern Physics, vol. 79, pp. 677-732, 2007.