Alkaline metal-doped *n*-type semiconducting nanotubes as quantum dots

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A 0.4 μm long semiconducting single-walled carbon nanotube is doped into *n* type by potassium (K) vapor. Electrical measurements of the doped nanotube reveal single-electron charging at temperatures up to 160 K. The K-doped sample manifests as a single quantum dot or multiple quantum dots in series depending on the range of applied gate voltage. This is explained by an inhomogeneous doping profile along the nanotube length. Similarities between K-doped nanotubes and silicon-based quantum dots and the possibility of room-temperature nanotube single-electron transistors are discussed. © *2000 American Institute of Physics.* [S0003-6951(00)01950-1]

The electrical properties of carbon nanotubes are of significant fundamental and practical interest.[1] Nanotubes could be utilized for molecular scale electronic devices including single-electron transistors (SETs).[2] Previously, single-electron charging has been observed in individual metallic single-walled carbon nanotube (SWNT) samples with high contact resistance at low temperatures.[2–5]

This letter reports the results of electrical measurements of alkaline metal-doped semiconducting SWNTs and observation of Coulomb blockade at temperatures up to 160 K. Our work was intended to elucidate chemical doping effects to the electrical properties of individual SWNTs. SWNT doping with electron withdrawing (Br_2,I_2) and donating species (K, Cs) were carried out earlier with bulk SWNT mats[6,7] and individual ropes.[8,9]

Samples of individual SWNTs are obtained as described earlier.[10–12] Figure 1 shows our *in situ* alkaline-metal doping setup and the nanotube sample used in this study. The SWNT has a diameter ~2.5 nm and length=0.4 μm between the edges of two Au/Ti electrodes. Potassium doping of the SWNT is carried out inside a cryostat insert designed for variable temperature electrical measurements by using a ''potassium dispenser'' (SAES Getters USA Inc., Colorado Springs, CO). The dispenser consists of a potassium salt and resistive heater, and is placed at about 1 cm away from the sample surface (Fig. 1). Resistive heating of the dispenser causes the metal salt to decompose into atomic potassium. The potassium evaporates from the dispenser and absorbs onto the SWNT. During doping, the vacuum inside the insert is maintained at 1×10^{-6} Torr by a turbo pump. The current passed through the dispenser for resistive heating is 4.5 amperes and the time duration for the doping is 2.5 h.

Figure 2(a) shows the evolution of sample conductance as a function of time during K doping. Prior to K doping, the nanotube exhibited *p*-type semiconducting characteristics[13–16] as positive gate voltage caused the Fermi level shifting away from the valence band into the band gap, and turned the system into insulating states [Fig. 2(b) inset]. After K doping, the system became *n* type with the Fermi level close to the conduction band due to electron donation by K [Fig. 2(b)]. The sharp conductance drop followed by recovery [Fig. 2(a)] corresponds to the *p*-type to intrinsic and to *n*-type transitions of the system.

The *n*-type semiconducting behavior of the doped SWNT is clearly seen in the conductance (G) versus gate voltage (V_g) curves (Fig. 3) recorded under a bias $V=1$ mV (incremental step in $V_g=25$ mV) at various temperatures. The conductance of the sample increases nearly monotonically with V_g, although noise-like fluctuations exist. The conductance G under a given V_g at various temperatures appears to follow $G\sim\exp(-E_a/k_BT)$ (Fig. 3 inset), with an activation barrier $E_a\sim32$ meV for $V_g=0$ for T between 290 and 40 K. This result points to thermally activated transport[15] and energy barriers existing in the system.

Conductance oscillations in V_g is observed in Fig. 3 for $T\leqslant160$ K. We have focused on the oscillation region and recorded $G-V_g$ curves with a small incremental step (6 mV) in V_g under a bias $V=0.5$ mV (Fig. 4). Several features are seen over various V_g regimes. In regime I (V_g between -1 and ~0.75 V), oscillation peaks in V_g is reasonably periodic and evenly spaced at $\Delta V_g\sim0.45$ V. In regime II, the oscillations are periodic with $\Delta V_g\sim0.45$ V at high temperatures but some of the peaks split into doublets at low temperatures ($T<110$ K). In regime III, periodic oscillations are observed only at $T<90$ K with a small period of $\Delta V_g\sim0.15$ V.

The conductance oscillations are due to single-electron charging[17,18] through a doped nanotube quantum dot system. Conductance versus V_g (in regime I) and V shown in Fig. 5(a) recorded at $T=80$ K exhibits diamond structures that are

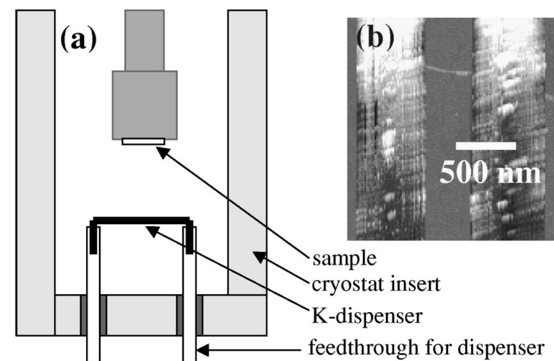

FIG. 1. (a) Schematic K-doping setup. (b) Tapping mode atomic force microscopy image of a Ti/Au contacted SWNT.

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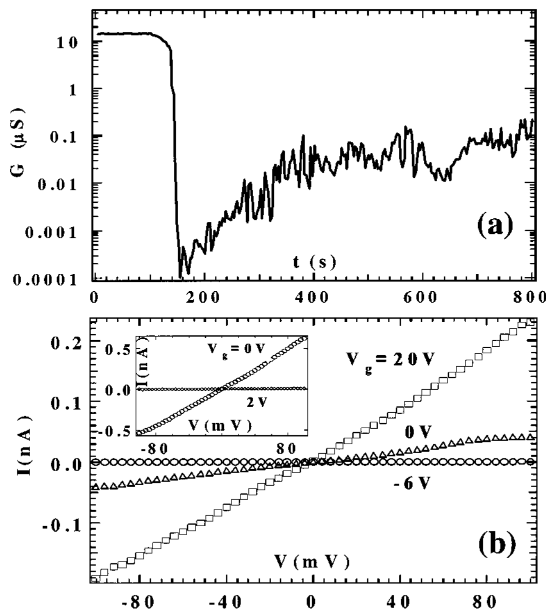

FIG. 2. (a) G vs time (t) during K doping. Data obtained with bias $V=100$ mV under $V_g=0$. (b) $I-V$ curves recorded at various gate voltages after K doping. Inset: $I-V$ curves recorded prior to K doping.

signatures of Coulomb blockade.[18] In this regime, we can consider the system as dominant by a single quantum dot. The change of ΔV_g by $\sim$0.45 V causes one electron addition or removal from the dot, the gate capacitance is therefore $C_g=e/\Delta V_g=0.35$ aF. The two boundaries of a diamond exhibit different slopes (dV_g/dV) because $C_1 \neq C_2$ where C_1 and C_2 are the capacitances at the source and drain sides of the quantum dot. C_1 and C_2 can be estimated from the slopes of dV_g/dV lines at the diamond boundaries.[18] We find $C_g/C_1=0.28$, $-C_g/C_2=-0.17$ and thus $C_1=1.25$ aF, $C_2=2.12$ aF. The total capacitance of the system is $C_\Sigma = C_1+C_2+C_g=3.72$ aF, which yields a charging energy of $U=e^2/C_\Sigma=43$ meV. The charging energy can also be estimated from the Coulomb blockade $I-V$ curve shown in Fig. 5(b) to be $\sim$50 meV, close to the value obtained from total capacitance estimate. Figure 5(b) shows that Coulomb blockade is completely lifted at a certain gate voltage. Coulomb

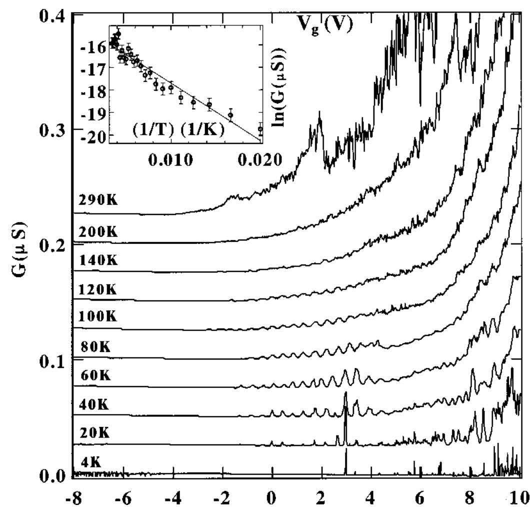

FIG. 3. G vs V_g at various temperatures. Inset: ln G vs $1/T$ for $V_g=0$ and T between 290 and 40 K. For clarity, the curves recorded at the temperatures shown are shifted successively along the G axis by 0.025 μS.

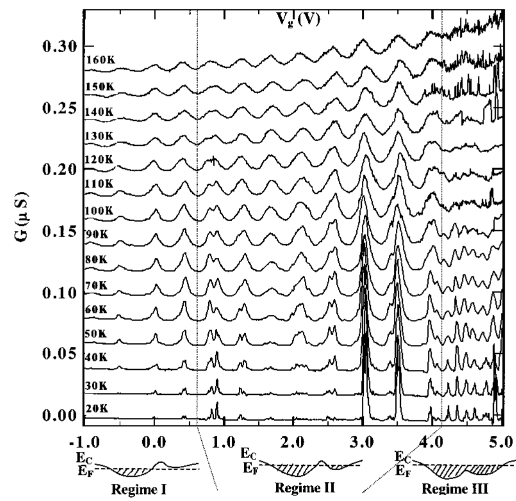

FIG. 4. G vs V_g recorded at various temperatures to show the details of Coulomb oscillations. The curves recorded at the temperatures shown are shifted successively along the G axis by 0.02 μS. Lower panel: possible band diagrams in various gate voltage regimes.

oscillations typically become smeared out by thermal energy at $T=U/4K_B$,[19] which appears to be true in our case since $U/4K_B \sim 160$ K.

For $U\sim50$ meV, the size of the quantum dot seen in regime I appears smaller than the tube length $L=0.4$ μm between the edges of metal electrodes. Previous work by Tans *et al.* observed $U=2.6$ meV for $L=3$ μm,[3] while Nygard *et al.* found $U\sim5$ meV/L (μm).[5] Comparison with these results suggests that the dot in regime I has an effective length of $L_{\text{eff}}\sim0.1-0.15$ μm, about one third of the actual geometry of the nanotube. This can be explained by an inhomogeneous K-doping profile along the nanotube. Fluctuations in the amount of K atoms deposited at various positions along the nanotubes can cause the conduction band (E_c) to fluctuate relative to the Fermi level (E_F) (Fig. 4). In regime

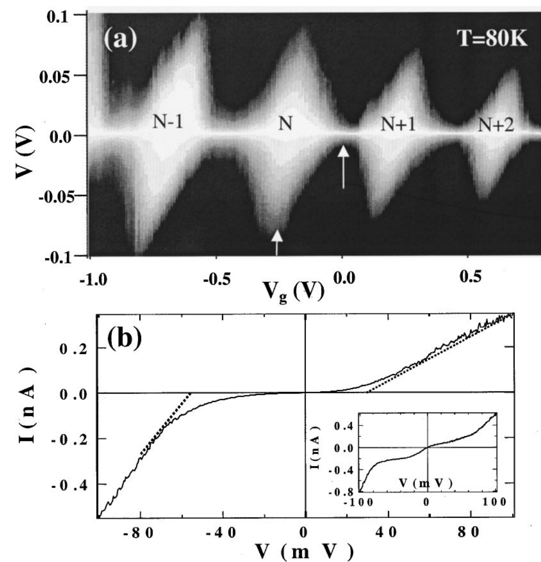

FIG. 5. (a) Grayscale plots of current vs bias V and V_g. Bright areas correspond to Coulomb blockade regions and black areas are conducting regions. ''N'' refers to the electron count in a Coulomb diamond. Left and right arrows point to two gate voltages under which $I-V$ curves are shown in (b) and inset, respectively.

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I, a portion of the tube with length $\sim L_{\mathrm{eff}}$ is heavily doped and has E_c below E_F. Transport through the system is dominant by this portion acting as a quantum dot. At higher gate voltages in regime II, E_c of the other portion of the tube is shifted below E_F. The system behaves as multiple (possibly two) dots in series[20,21] in this regime. In regime III, periodic oscillation peaks in $G-V_g$ are closely spaced at $\Delta V_g \sim 0.15$ V (Fig. 4), about one third of the period in regime I. This could be due to E_c throughout the tube is shifted below E_F, and the nanotube merges into a large quantum dot with $L \sim 0.4$ μm. The gate capacitance coupled to this dot is $C_g' \sim 1.05$ aF, about three times of $C_g \sim 0.35$ aF in regime I.

The Coulomb oscillations in regime III disappear at $T > \sim 90$ K and become replaced by irreproducible noise-like fluctuations (Fig. 4). The charging energy of the large dot in this regime is estimated to be $U' = 4K_BT(T=90\text{ K}) = 21$ meV, which is one half to one third of that for the small dot in regime I. This confirms that the effective size of the dot in regime I is about one third of the tube length.

Interestingly, many of the single-electron transport phenomena observed here bear similarities with silicon quantum wires. A narrow silicon wire lithographically fabricated with doped Si can be made into a single quantum dot over certain gate voltage ranges.[22] Periodic Coulomb oscillation peaks have been observed in many Si wires, and the peaks split at low temperatures due to multiple dots in series.[23,24] The origin of the serial dots is attributed to inhomogeneous doping profile of the Si wires.[24,25] The active Si dot structure thus deviates from the wire geometry. Also, the Coulomb gap size appears to change with V_g similar to that shown in Fig. 5(a), because the gate voltage affects the size of the semiconducting dot.[22,26] A Si quantum wire may manifest as quantum dots of very different sizes in various gate voltage regimes.[23,25] These phenomena have all been observed with our K-doped SWNT.

We have measured a number of K-doped semiconducting SWNT samples with lengths ~ 0.4 μm. Some of the samples manifest as a single dot with length ~ 0.1–0.3 μm (charging energy ~ 50–20 meV) over certain gate voltage ranges, but show dots-in-series behavior under other gate voltages. Samples showing nonperiodic Coulomb oscillations (up to ~ 120 K) under the entire gate voltage range have also been seen. These results point to the need of controlling the homogeneity of dopants along tube lengths for reliably obtaining single quantum dots with semiconducting nanotubes.

Single-electron transistors operating at room temperatures have been pursued actively with Si and metal systems.[23,27–30] With nanotubes, room temperature single-electron charging will require a tube ''dot'' with length on the order of 10–50 nm, so that charging energy $U \geqslant 100$ meV$= 4K_BT(300\text{ K})$. It is shown here that inhomogeneous effect can lead to a high temperature SET due to the formation of a single quantum dot with its size smaller than the geometrical tube length. This can occur when the two barriers for the dot are located within the length of the tube. To obtain high temperature nanotube SETs reliably, it is desired to obtain samples with 10–50 nm tube lengths and have high chemical homogeneity along the lengths.

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[1] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
[2] C. Dekker, Phys. Today **52**, 22 (1999).
[3] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, and C. Dekker, Nature (London) **386**, 474 (1997).
[4] M. Bockrath, D. H. Cobden, P. L. McEuen, N. G. Chopra, A. Zettl, A. Thess, and R. E. Smalley, Science **275**, 1922 (1997).
[5] J. Nygard, D. H. Cobden, M. Bockrath, P. L. McEuen, and P. E. Lindelof, Appl. Phys. A: Mater. Sci. Process. **69**, 297 (1999).
[6] R. S. Lee, H. J. Kim, J. E. Fischer, A. Thess, and R. E. Smalley, Nature (London) **388**, 255 (1997).
[7] L. Grigorian, K. A. Williams, S. Fang, G. U. Sumanasekera, A. L. Loper, E. C. Dickey, S. J. Pennycook, and P. C. Eklund, Phys. Rev. Lett. **80**, 5560 (1998).
[8] R. S. Lee, H. J. Kim, J. E. Fischer, J. Lefebvre, M. Radosavljevi, J. Hone, and A. T. Johnson, Phys. Rev. B **61**, 4526 (2000).
[9] M. Bockrath, J. Hone, A. Zettl, P. L. McEuen, A. G. Rinzler, and R. E. Smalley, Phys. Rev. B **61**, R10606 (2000).
[10] J. Kong, H. Soh, A. Cassell, C. F. Quate, and H. Dai, Nature (London) **395**, 878 (1998).
[11] H. Soh, C. Quate, A. Morpurgo, C. Marcus, J. Kong, and H. Dai, Appl. Phys. Lett. **75**, 627 (1999).
[12] H. Dai, J. Kong, C. Zhou, N. Franklin, T. Tombler, A. Cassell, S. Fan, and M. Chapline, J. Phys. Chem. **103**, 11246 (1999).
[13] S. Tans, A. Verschueren, and C. Dekker, Nature (London) **393**, 49 (1998).
[14] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and P. Avouris, Appl. Phys. Lett. **73**, 2447 (1998).
[15] C. Zhou, J. Kong, and H. Dai, Appl. Phys. Lett. **76**, 1597 (1999).
[16] J. Kong, N. Franklin, C. Zhou, M. Chapline, S. Peng, K. Cho, and H. Dai, Science **287**, 622 (2000).
[17] M. A. Kastner, Phys. Today **46**, 24 (1993).
[18] *Single Charge Tunneling*, edited by H. Grabert and M. H. Devoret (Plenum, New York, 1992).
[19] H. V. Houten, C. W. J. Beenakker, and A. A. M. Staring, in *Single Charge Tunneling*, edited by H. Grabert and M. H. Devoret (Plenum, New York, 1992), p. 167.
[20] I. M. Ruzin, V. Chandrasekhar, E. I. Levin, and L. I. Glazman, Phys. Rev. B **45**, 13469 (1992).
[21] F. R. Waugh, M. J. Berry, D. J. Mar, R. M. Westerwelt, K. L. Campman, and A. C. Gossard, Phys. Rev. Lett. **75**, 705 (1995).
[22] R. Augke, W. Eberhardt, C. Single, F. E. Prins, D. A. Wharam, and D. P. Kern, Appl. Phys. Lett. **76**, 2065 (2000).
[23] H. Ishikuro, T. Fujii, T. Saraya, G. Hashiguchi, T. Hiramoto, and T. Ikoma, Appl. Phys. Lett. **68**, 3585 (1996).
[24] R. A. Smith and H. Ahmed, J. Appl. Phys. **81**, 2699 (1997).
[25] A. Irvine, Z. A. K. Durrani, and H. Ahmed, Appl. Phys. Lett. **73**, 1113 (1998).
[26] Y. Takahashi, H. Namatsu, K. Kurihara, K. Iwadate, M. Nagase, and K. Murase, IEEE Electron Device Lett. **43**, 1213 (1996).
[27] H. Ishikuro and T. Hiramoto, Appl. Phys. Lett. **71**, 3691 (1997).
[28] L. Zhuang, L. Guo, and S. Y. Chou, Appl. Phys. Lett. **72**, 1205 (1998).
[29] K. Matsumoto, M. Ishii, K. Segawa, Y. Oka, B. J. Vartanian, and J. S. Harris, Appl. Phys. Lett. **68**, 34 (1996).
[30] Y. A. Pashkin, Y. Nakamura, and J. S. Tsai, Appl. Phys. Lett. **76**, 2256 (2000).

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