## Absolute potential of the Fermi level of isolated single-walled carbon nanotubes

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Electrochemical potential dependence of Raman intensity of isolated single-walled carbon nanotubes (SWNT) on gold electrode in aqueous solution was investigated employing in situ resonant confocal micro Raman spectroscopy. Absolute potential of the Fermi level of individual tubes was estimated from the potential dependence. Observations suggest that the work function of the tube becomes larger in a manner inversely proportional to the diameter of SWNT. The structural dependence of a metallic tube is larger than that of a semiconducting tube.

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Single-walled carbon nanotubes (SWNTs) should be among the best candidates for ultrasmall functional units in ultrasensitive, low-energy consumption nanodevices. Several characteristics of the electronic band structure of individual SWNT, such as the energy separation between van Hove singularities and the density of the states, have been obtained successfully employing recently developed experimental techniques in confocal micro Raman spectroscopy,<sup>1</sup> scanning tunneling microscopy,<sup>2</sup> and fluorescence methodology.<sup>3</sup> In addition to these band profiles, information regarding absolute potential of energy levels of the states is known to be essential to nanodevice fabrication. Work functions of individual SWNT affect various important factors with respect to optimized device performance, such as the Schottky barrier height of SWNT-metal junctions,  $^{4} p$ - and n-type behavior of semiconducting SWNT with various dopants,<sup>5</sup> and selectivity of molecules as chemical sensors.<sup>6</sup> Several estimations of energy levels derived from measurements of work function were attempted in vacuums<sup>7</sup> and in electrolyte solution;<sup>8</sup> however, all of these measurements utilized bulk bundle SWNT, which display certain distributions with respect to size. Generally, the Fermi level of individual SWNT with different diameter is considered to be at the same potential energy relative to the vacuum level. However, careful examination based on the molecular orbital calculation showed slight diameter dependence of the work function of individual SWNT.<sup>9</sup> Estimated difference in the work function of metallic SWNT with diameters ranging from 0.57 to 1.65 nm was rather small, less than 0.14 eV. The diameter-dependent absolute potential of the Fermi level in individual isolated tubes has not been observed experimentally. The present report reveals that the energy position of the Fermi level of individual SWNT relative to the vacuum level is dependent upon tube diameter significantly, based on measurements of resonance Raman intensity of individual SWNT under electrochemical potential control.

In situ resonant confocal micro Raman spectroscopy was employed in order to detect the potential dependent change in the Raman intensity of isolated SWNT on gold (Au) electrodes under electrochemical potential control in aqueous solution. Adsorption of isolated SWNT onto cleaned polycrystalline Au surfaces was conducted via dropwise introduction of highly dispersed SWNT solutions containing sodium dodecyl sulfate (SDS).<sup>3</sup> Atomic force microscopy measurements demonstrated a concentration of <1.0 SWNT/ $\mu$ m<sup>2</sup> with tube lengths from 200-2000 nm on the Au substrate. Observation of the sample at a single spot with 785 nm  $(E_{ex} = 1.58 \text{ eV})$  excitation provided a typical Raman spectrum of isolated single SWNT.<sup>1,10</sup> Spectra at different spots afforded distinct RBM peaks. Experimentally determined linewidth [full width at half maximum (FWHM)] values through a Lorentzian fit of the RBM peaks of metallic and semiconducting tubes were approximately  $9 \text{ cm}^{-1}$  and  $3 \text{ cm}^{-1}$ , respectively. These values are in agreement with previously reported values of isolated single SWNT.<sup>10</sup>

Peak intensity of the RBM was dependent upon the electrode potential. Figure 1 displays the spectra of the RBM of a metallic tube at  $157 \text{ cm}^{-1}$  and a semiconducting tube at 234 cm<sup>-1</sup> observed at different electrode potentials. The me-



FIG. 1. RBM Raman spectra of isolated individual metallic tube with  $\omega_{RBM} = 157 \text{ cm}^{-1}$  (a), and semiconducting tube with  $\omega_{RBM}$  $= 234 \text{ cm}^{-1}$  (b) on polycrystalline Au electrode in 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution under electrochemical potential control. From top to bottom, the potential was changed from +0.4 V to -0.8 V in 0.1 V increments.



FIG. 2. Potential dependence of RBM Raman intensity of metallic [(a),  $\omega_{RBM} = 156 \text{ cm}^{-1}$  (circle),  $162 \text{ cm}^{-1}$  (triangle), and  $167 \text{ cm}^{-1}$  (square)] and semiconducting [(b),  $208 \text{ cm}^{-1}$  (circle),  $228 \text{ cm}^{-1}$  (triangle), and  $235 \text{ cm}^{-1}$  (square)] isolated individual SWNT. Intensities were monitored at the cathodic scanning of the electrode potential at a rate of  $10 \text{ mV s}^{-1}$ . Lines serve as visual guides.

tallic tube revealed stronger Raman intensity at more positive potential than a semiconducting tube. Figure 2 shows potential dependence of Raman intensity of metallic and semiconducting tubes present at distinct frequency of the RBM,  $\omega_{RBM}$ . The potential dependence of the Raman intensity broadened in both the metallic and the semiconducting tubes with larger  $\omega_{RBM}$ . As  $\omega_{RBM}$  increases, the potential at which the Raman intensity is at a maximum,  $\phi_0$ , becomes increasingly positive. The  $\phi_0$  of metallic tubes demonstrates relatively positive values with respect to those of semiconductor tubes.

The electrochemical potential dependence of Raman intensity, reported originally by Kavan *et al.*, involved bulk bundle SWNT samples.<sup>11</sup> They proposed that electrochemical anodic and cathodic polarization of SWNT caused depletion of the valence band and the filling of the conduction band in SWNT, respectively. These changes in electron density, which lead to bleaching of the electronic transition between van Hove singularities in visible and near-infrared regions, produce decreases in resonant Raman intensity. The potentials where bleaching began were considered to reflect the energy levels of van Hove singularities. Reversible bleaching of the optical transition of bulk bundle SWNT in the vis-NIR region utilizing controlled electrochemical doping was also confirmed by Kavan *et al.*<sup>11</sup> and Kazaoui *et al.*<sup>8</sup>

Based on the aforementioned model of electrochemical doping of SWNT, the FWHM of the potential dependence of the Raman intensity should reflect an energy separation between van Hove singularities,  $E_{ii}$ , of the isolated SWNT in the present system. As depicted in Fig. 2, the FWHM estimated from the potential dependence displayed significant tube-dependence. The values varied from approximately 0.6 V ( $\omega_{RBM}$ =156 cm<sup>-1</sup>) to 0.9 V (167 cm<sup>-1</sup>) at metallic tubes, and from 0.3 V (208 cm<sup>-1</sup>) to 0.7 V (235 cm<sup>-1</sup>) at semiconducting tubes. If the FWHM are assumed to reflect

apparent energy separation between van Hove singularities,  $E'_{ii}$ , the values of  $E'_{ii}$  are 0.6 eV ( $\omega_{RBM} = 156 \text{ cm}^{-1}$ ) and 0.9 eV (167 cm<sup>-1</sup>) at metal tubes, and 0.3 eV (208 cm<sup>-1</sup>) and 0.7 eV (235 cm<sup>-1</sup>) at semiconducting tubes. This dependence of the values of  $E'_{ii}$  on the tubes appears to reflect increments in the values of  $E_{ii}$  of the isolated SWNT estimated from  $\omega_{RBM}$  of each tube [ $E_{ii}=1.54 \text{ eV} (\omega_{RBM}$ = 156 cm<sup>-1</sup>), 1.72 eV (167 cm<sup>-1</sup>) at metallic tubes, and 1.37 eV (208 cm<sup>-1</sup>) and 1.60 eV (235 cm<sup>-1</sup>) at semiconducting tubes].<sup>12</sup> However,  $E'_{ii}$  are smaller than those of corresponding  $E_{ii}$ . It is noteworthy that the differences between  $E'_{ii}$  and  $E_{ii}$  occurred in the range of 0.8 eV to 1.1 eV.

Observed relatively sharp and sensitive dependence of the Raman intensity on the electrode potential is a characteristic of the isolated SWNT. Previously documented behavior of the potential dependence of the Raman intensity employing bundle samples showed rather broad potential dependence with FWHM of 1.0-2.0 V,<sup>11</sup> which were much larger compared with the present values. Isolated SWNT highly dispersed lying on an Au electrode in the present system should form an ideal junction with the Fermi-level alignment.<sup>13</sup> It is expected that the Fermi level of isolated SWNT in solution matches the potential of the Fermi level of an Au electrode without significant contribution of capacitive charging effect. Thus, the relatively sharp potential dependence may reflect characteristics of the distribution of the electronic states in isolated SWNT on an Au electrode in solution.

To explain the observed sharp potential dependence of Raman intensity in the present system, additional effects should be considered with respect to causation of filling (depletion) of the conduction (valence) band at more positive (negative) electrode potentials. In the system of electrochemical interfaces, the effect of solvation is often considered as one of the most important factors in terms of alteration of the energy distribution of the electronic states at the interface.<sup>14</sup> Generally, an energy level of the electronic states of molecules in solution acquires a specific distribution due to the vibration-rotation interaction between these molecules and the surrounding solvent molecules.<sup>14</sup> Although precise estimation of the distribution of the energy state at the electrochemical interface is difficult, the Gaussian distribution associated with widths of approximately 0.5-1.0 eV often provides a rough estimation of the density of the electronic states of molecules at the electrochemical interface at room temperature.<sup>14</sup> If one assumes that the energy levels of SWNT on an Au electrode possess such distributions due to solvation, this broadened conduction (valence) band may allow the process of filling (depletion) of the electronic states at more positive (negative) electrochemical polarization, leading to relatively sharp potential dependence of the Raman intensity. In this case, the  $E'_{ii}$  depends on both  $E_{ii}$  and the widths of the energy distribution of the states in conduction and valence band,  $\lambda_C$  and  $\lambda_V$ . Considering significant contribution of van Hove singularities in conduction and valence band to the optical bleaching process, the  $E'_{ii}$  is expected to display a value smaller than  $E_{ii}$  by the sum of the half values of  $\lambda_C$  and  $\lambda_V$ :  $E'_{ii} = E_{ii} - (\lambda_C + \lambda_V)/2$ . Observed differences between  $E'_{ii}$  and  $E_{ii}$  in the present system were in



FIG. 3. Relation between observed  $\omega_{RBM}$  and  $\phi_0$  at metallic (circle) and semiconducting (triangle) SWNT. Closed and open marks correspond to results obtained at the cathodic and the anodic scanning, respectively.

the range of 0.8 eV to 1.1 eV, which demonstrated fairly good agreement with those expected from energy broadening as a consequence of solvation (0.5-1.0 eV). This result suggests that the potential dependence of the Raman intensity in the present system reflects the energy position of the electronic states of the individual SWNT on an Au electrode in solution.

Figure 3 presents a plot of  $\phi_0$  observed for different metallic and semiconducting tubes. The values of  $\phi_0$  were obtained through a Gaussian fit to the potential dependences of the Raman intensity. The  $\phi_0$  at negative and positive scan exhibited differences for approximately 0.1–0.2 V. Thus, both potentials were plotted in Fig. 3. A linear relation between  $\phi_0$  and  $\omega_{RBM}$  was detected in both metallic and semiconducting tubes. The  $\omega_{RBM}$  of isolated SWNT can be correlated to tube diameter,  $d_t$ , according to the equation,  $d_t = c/\omega_{RBM}$ , where c is a constant.<sup>12,16</sup> The present result suggests that the potential showing maximum Raman intensity becomes positive in a manner inversely proportional to the diameter of SWNT. The diameter-dependent shift at the metallic tube is more apparent than that at the semiconducting tube.

The  $\phi_0$  is expected to correspond to the energy level at the center between van Hove singularities in conduction and valence bands of individual SWNT. The origin of the difference in  $\phi_0$  at negative and positive scan remains unclear. Reversible morphological change of SWNT on an Au electrode at different potentials presumably contributes to this hysteresis.<sup>17</sup> In the present study, we propose that average values of  $\phi_0$  at negative and positive scan can reflect the energy level of the center position between van Hove singularities, i.e., the Fermi level of isolated SWNT. The work function of SWNT can be correlated to the absolute potential as proposed by Kazaoui *et al.*<sup>8</sup>

It is known that electrochemical potential measured with respect to a reference electrode is related to absolute potential relative to the vacuum level.<sup>18</sup> Potential scale versus the vacuum level using the values,  $V_{abs}$  (vs vacuum level) = V (vs NHE)+4.44 V, derived by Trasatti,<sup>18</sup> and V (vs Ag/AgCl) = V (vs NHE)-0.197 V is also exhibited



FIG. 4. (a) Relation between assigned energy separation,  $E_{ii}$ , and  $\phi_0$  at metallic (circle) and semiconducting (triangle) SWNT. Closed and open marks correspond to results obtained at the cathodic and the anodic scanning, respectively. Solid lines were derived from the average of the dotted lines at the metallic and the semiconducting tubes, indicating the proposed Fermi levels of SWNT. (b) Potential diagram of the electronic state for several SWNT (Ref. 15). From left to right, (9, 7), (11, 4) semiconducting nanotubes and (13, 10), (15, 6) metallic nanotubes.

in Fig. 3. The values of SWNT observed in the present investigation can be estimated from the dotted line in Fig. 3. The lines determined from the average of the values of anodic and cathodic scans at metallic and semiconducting tubes afforded a simple relation between  $\omega_{RBM}$  and the work function of metallic,  $\Phi_M$ , and that of semiconducting,  $\Phi_S$ , tubes, which are given by  $\Phi_M = |e| V_{abs}$ , as follows,

$$\Phi_M = 2.2 \times 10^{-2} \omega_{RBM} + 1.15,$$
  
$$\Phi_S = 1.2 \times 10^{-2} \omega_{RBM} + 1.59.$$

Structural-dependent shift of work functions can also be correlated to the energy separation  $E_{ii}$  of SWNT. Figure 4(a) illustrates the relation between the potential of the Fermi level of SWNT and  $E_{ii}$ . Although there are several assignments of observed  $\omega_{RBM}$  to  $E_{ii}$  and the tube diameter,  $d_t$ , available,<sup>12,16</sup> we tentatively assigned  $E_{ii}$  based on the report of Dresselhaus *et al.*<sup>12,19</sup> Relative ratios of the change in the potential of the Fermi level to that of  $E_{ii}$  are 1.96 V/eV for the metallic tubes and 1.20 V/eV for semiconducting tubes. These values imply that the change in the work function relative to that of  $E_{ii}$  is significantly large. Figure 4(b) shows selected potential diagrams of the electronic state of (9, 7), (11, 4) semiconducting SWNTs and (13, 10), (15, 6) metallic SWNTs.<sup>15</sup> This fact indicates that energy levels of both the conduction band and the valence band become deeper relative to the vacuum level as  $E_{ii}$  increases in the case of SWNT.

These values appear to be smaller than those of previous investigations. Although documented work functions of SWNT bundles determined by photoelectron spectroscopy in a vacuum exhibit some discrepancy, recent SWNT values can be regarded in the range of 4.8–5.1 eV.<sup>7</sup> Recent theoretical calculations employing the first-principles method revealed the positive shift of the work function due to the formation of bundles. The work function of metallic (12,12) tubes changed from 4.77 eV in the case of isolated tubes to 4.94 eV in the case of a bundle.<sup>9</sup> Relatively small work functions obtained in the current experiments may be partially explained by the effect of the isolation of single SWNT on the surface of the Au electrode.

Significant diameter-dependent shift of the work function is also a novel feature of isolated nanotube. Currently, we have no definitive explanation for this phenomenon; however, we may consider the effect of the  $\sigma-\pi$  hybridization at the tubes. The strength in the hybridization alters the density of the states and the carrier concentration of CNT.<sup>20</sup> Recent calculations reveal that  $\sigma-\pi$  mixing increases with decreasing CNT diameter, leading to the downward shift of the

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- <sup>1</sup>G. S. Duesberg, I. Loa, M. Burghard, K. Syassen, and S. Roth, Phys. Rev. Lett. **85**, 5436 (2000).
- <sup>2</sup>J. W. G. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) **391**, 59 (1998); T. W. Odom, J. L. Huang, P. Kim, and C. M. Lieber, Nature (London) **391**, 62 (1998).
- <sup>3</sup>M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. P. Ma, R. H. Hauge, R. B. Weisman, and R. E. Smalley, Science **297**, 593 (2002).
- <sup>4</sup>S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and P. Avouris, Phys. Rev. Lett. **89**, 106801 (2002).
- <sup>5</sup>L. Duclaux, Carbon **40**, 1751 (2002).
- <sup>6</sup>J. Kong, N. R. Franklin, C. W. Zhou, M. G. Chapline, S. Peng, K. J. Cho, and H. J. Dai, Science **287**, 622 (2000).
- <sup>7</sup>D. Lovall, M. Buss, E. Graugnard, R. P. Andres, and R. Reifenberger, Phys. Rev. B **61**, 5683 (2000); S. Suzuki, C. Bower, Y. Watanabe, and O. Zhou, Appl. Phys. Lett. **76**, 4007 (2000); M. Shiraishi and M. Ata, Carbon **39**, 1913 (2001); J. P. Sun, Z. X. Zhang, S. M. Hou, G. M. Zhang, Z. N. Gu, X. Y. Zhao, W. M. Liu, and Z. Q. Xue, Appl. Phys. A: Mater. Sci. Process. **75**, 479 (2002).
- <sup>8</sup>S. Kazaoui, N. Minami, N. Matsuda, H. Kataura, and Y. Achiba, Appl. Phys. Lett. **78**, 3433 (2001).
- <sup>9</sup>J. J. Zhao, J. Han, and J. P. Lu, Phys. Rev. B 65, 193401 (2002).
- <sup>10</sup>A. Jorio, C. Fantini, M. S. S. Dantas, M. A. Pimenta, A. G. Souza,

Fermi level.<sup>21</sup> The charge transfer from  $\pi$  to  $\sigma$  orbitals at smaller diameter CNT increases the carrier concentration in a manner inversely proportional to the diameter of SWNT. Although qualitative comparisons between the charge transfer and the shift of the Fermi level are not currently available, contribution of the  $\sigma$ - $\pi$  mixing at SWNT should be a major factor in terms of alteration of the work functions of the tubes. Differences in the mixing between the semiconducting and the metallic tubes may lead to distinct diameterdependence in the shift and values of the work functions observed in the present system.

In conclusion, the significant structural dependence of the Fermi level of isolated metallic nanotubes was clarified. The dependence of a metallic tube is larger than that of a semiconducting tube. The level of a metallic tube is deeper than that of a semiconducting tube characterized by comparable energy separation between the valence and conduction states. Further investigation is necessary in order to clarify the origins of the relatively large shift depending on the structure and the difference in the metallic and semiconducting tubes in terms of the energy levels. However, data obtained from the present experiments may be utilized to select desired SWNT with favorable electronic structure for construction of tailored "single-tube" devices.

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G. G. Samsonidze, V. W. Brar, G. Dresselhaus, M. S. Dresselhaus, A. K. Swan, M. S. Unlu, B. B. Goldberg, and R. Saito, Phys. Rev. B **66**, 115411 (2002).

- <sup>11</sup>L. Kavan, P. Rapta, and L. Dunsch, Chem. Phys. Lett. **328**, 363 (2000); L. Kavan, P. Rapta, L. Dunsch, M. J. Bronikowski, P. Willis, and R. E. Smalley, J. Phys. Chem. B **105**, 10764 (2001).
- <sup>12</sup>A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. Lett. 86, 1118 (2001).
- <sup>13</sup>F. Leonard and J. Tersoff, Phys. Rev. Lett. 84, 4693 (2000).
- <sup>14</sup>H. Gerischer, in Advances in Electrochemistry and Electrochemical Engineering, edited by P. Delahay and C. W. Tobias (Interscience, New York, London, 1961), Vol. 1; J. O. M. Bockris and S. U. M. Khan, Surface Electrochemistry: A Molecular Level Approach (Plenum, New York, 1993).
- <sup>15</sup>H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, and Y. Achiba, Synth. Met. **103**, 2555 (1999); S. Maruyama, http://www.photon.t.u-tokyo.ac.jp/~maruyama/kataura/kataura.html
- <sup>16</sup>S. Bandow, S. Asaka, Y. Saito, A. M. Rao, L. Grigorian, E. Richter, and P. C. Eklund, Phys. Rev. Lett. **80**, 3779 (1998); J. Körti, G. Kresse, and H. Kuzmany, Phys. Rev. B **58**, R8869 (1998); L. Henrard, E. Hernandez, P. Bernier, and A. Rubio, Phys. Rev. B **60**, R8521 (1999).
- <sup>17</sup> P. Kim and C. M. Lieber, Science **286**, 2148 (1999).
- <sup>18</sup>S. Trasatti, J. Electroanal. Chem. **52**, 313 (1974); R. Parsons, in *Standard Potentials in Aqueous Solution*, edited by A. J. Bard,

R. Parsons, and J. Jordan (Marcel Dekker, New York and Basel, 1985).

- <sup>19</sup>M. S. Dresselhaus, A. Jorio, A. G. Souza, G. Dresselhaus, and R. Saito, Physica B **323**, 15 (2002).
- <sup>20</sup>X. Blase, L. X. Benedict, E. L. Shirley, and S. G. Louie, Phys. Rev. Lett. **72**, 1878 (1994).
- <sup>21</sup> A. Rakitin, C. Papadopoulos, and J. M. Xu, Phys. Rev. B 67, 033411 (2003).