

Cesium-Filled Single Wall Carbon Nanotubes as Conducting Nanowires: Scanning Tunneling Spectroscopy Study

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Metal-filled single wall carbon nanotubes (SWCNTs) are examined for possible application to conducting wires in nanoelectronics architecture. The local electronic structure of SWCNTs partially filled with cesium atoms is studied with scanning tunneling spectroscopy. The conduction and valence bands are shifted downward with two localized states in the gap at the location where the Cs atoms are filled. From a first-principles calculation, we confirm that these two gap states are bound states originating from the two lowest conduction bands.

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Because of increasing technical difficulties in fabricating planar devices of sub 50 nm critical dimension, one-dimensional (1D) nanowire (NW) devices have been suggested as an alternative to achieving high stacking density [1]. Semiconducting NWs, not metallic NWs, were first studied to fabricate 1D-NW field effect transistors [1–3]. Once we successfully produce the 1D-NW active devices, conducting NWs are needed to interconnect them in nanoelectronics architecture. Elemental or alloy metal NWs reveal unique transport properties in the nanoscale and they may be used as interconnecting NWs [4]. However, the surfaces of the NWs can be highly reactive due to large surface to volume ratio in NW geometry. Nonreactive and hollow-cylindrical materials, like single wall carbon nanotubes (SWCNTs), may be used as the protective layer against unwanted chemical reaction. An alternative approach is to fill the inside of the hollow-cylindrical materials with metals, whereupon the complex may function as an interconnecting NW. Since carbon nanotubes (CNTs) are either semiconductors or conductors and less reactive than metal NWs [5], they can function as a protecting layer and as an alternate conducting path at the location where filled metals are locally missing.

Experimentally, it has been reported that the transport properties of CNTs can be controlled by the insertion of molecules [6], functionalization [7], and chemical doping [8]. Alkali metals (Li, K, Rb, and Cs) can function as *n*-doping materials for CNTs, as they are filled inside CNTs or placed between CNT bundles [8–11]. It was reported by Bockrath *et al.* that doping by potassium increases the conductivity of the CNT [10]. According to theory, there are two possible mechanisms for the change of CNT electronic structures caused by alkali metal doping [12–16]. One is a rigid band model in which there is a rigid band shift with charge transfer [12,13]. The other considers it due to the hybridization of the metal *s* band and CNT bands [14–16]. However, there is little experimental veri-

fication on the local electronic structural change of doped CNTs. In this study, we investigated the local electronic properties of SWCNTs filled with Cs metal using the scanning tunneling microscopy (STM) and spectroscopy (STS). We found that the conduction and valence bands are shifted downward with two localized states in the gap at the location where the Cs atoms are embedded. With this observation, it is suggested that Cs-filled SWCNTs (Cs-SWCNTs) may be applied to interconnecting NWs.

CNTs can be filled with several materials by placing both of them in a heated furnace. However, Cs ions can only be inserted into the SWCNTs by a plasma ion irradiation technique as reported earlier [12]. We obtained STM topographic images and spatially resolved scanning tunneling spectroscopy (SR-STs) maps by using the low temperature ultrahigh vacuum (UHV) STM which can be cooled down to ~ 10 K [17]. The clean and reconstructed Au(111) surface was obtained after repeated cycles of Ar ion sputtering and annealing in a UHV chamber. The clean substrate was transferred to a N₂-filled glove box for the deposition of Cs-SWCNTs and was transferred back to the STM chamber. Extremely low thermal drift (0.5 nm per hour) was needed to perform SR-STs measurement along a SWCNT over the range of 10 nm.

Figure 1(a) shows a typical STM topographic image of a Cs-filled SWCNT. After being exposed to the N₂-filled glovebox for ~ 5 min, the herringbone structure of the reconstructed Au(111) surface was visible after short annealing. As shown in an atomically resolved SWCNT image [Fig. 1(a)], a locally protruding area along a SWCNT, shown as a bright area in a gray scale image, suggests the existence of the embedded Cs atoms. The height change may have resulted from the local elastic deformation of the carbon nanotube or changes in the local density of states by embedded Cs atoms. But, to confirm the presence of Cs atoms, spatially resolved spectroscopic measurements are demanded.

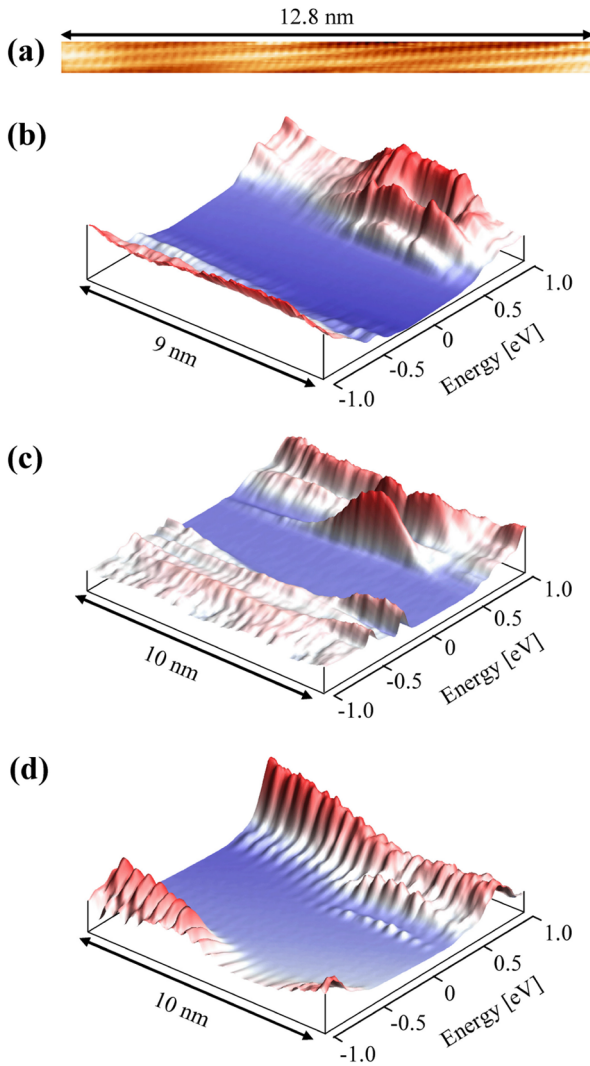


FIG. 1 (color online). (a) A typical STM topographic image of a Cs-SWCNT. The image is 12.8 nm long and the sample bias voltage is -1.5 V. (b)–(d) 3D plots of various SR-STs maps measured along the tube axes of 3 different Cs-SWCNTs.

As shown in Figs. 1(b)–1(d), local variations in the electron density can be observed in the SR-STs results of three different Cs embedded SWCNT samples. Although the details are different, the general trends of the local electronic structures are very similar. First, the conduction and valence are shifted downward. Second, new, localized gap states are observed near the conduction band. In the SR-STs results, the size of the band shift varies with different samples. As observed earlier in the TEM images [12], this may be due to the difference in embedded sites in the middle of the SWCNT and the amount of charge transfer. In the case of the rigid band model, the downward shifts of valence and conduction bands have been predicted in theoretical studies of alkali metal doped carbon nanotube systems [12,13]. However, as shown in Figs. 1(b)–1(d), the downward shift cannot be explained by the simple rigid band model; by Cs filling the conduction band is

slightly shifted and the electron density is reduced while the shift of the valence band is obvious. It is confirmed that the total number of electronic states from valence bands to conduction bands is conserved despite the shift [18].

Figures 2(a) and 2(b) show the STM topographic image and the SR-STs map of a Cs-filled SWCNT corresponding to Fig. 1(d). The dashed line is the contour drawn along the edge of a valence band and the dotted line indicates the appropriate parallel shift of this contour toward a conduction band. The amount of shift is nearly identical to that of the conduction band. Two localized gap states, clearly shown as two peaks in the STS data of Fig. 2(c), were

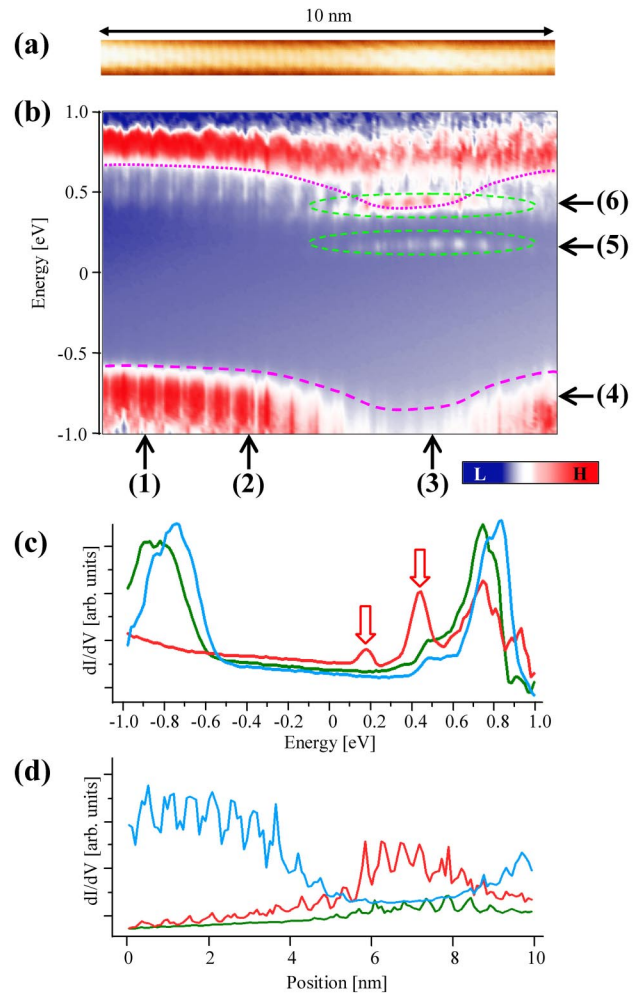


FIG. 2 (color online). (a) The STM topographic image of a Cs-SWCNT corresponding to Fig. 1(d). The image length is 10 nm. The sample bias voltage is 1.0 V. (b) The SR-STs map of a Cs-SWCNT corresponding to Fig. 1(d). (c) STS data which are the selections of vertical line profiles from (b). Blue, green, and red curves are sampled from the spatial positions indicated with the vertical arrows (1), (2), and (3) in (b), respectively. Two arrows indicate the appearance of localized states. (d) Horizontal line profiles sampled from the SR-STs map in (b). Blue, green, and red curves correspond to the energy levels indicated with the horizontal arrows (4), (5), and (6) in (b), respectively.

observed at ~ 0.18 and ~ 0.44 eV near the conduction band of the Cs-SWCNT. The SR-STs also reveals atomically resolved localized gap states and the decay of the states away from the proposed location of the encapsulated Cs atoms with a decay length scale of ~ 3 nm, very similar to the decay of donor and acceptor states [5,18]. The upper state of the two gap states at ~ 0.44 eV is more intense than the lower state at ~ 0.18 eV. It is quite unusual to induce two gap states in the gap, and the detailed electronic nature will be discussed with the following theoretical results. Since there are two states at the same spatial location, there is a possibility that these two states are charged simultaneously during the tunneling process of the STM operation, experiencing the Coulomb repulsion similar to double donor states in some semiconductors [19,20]. But we could not find any intergap variation or individual gap width variation with the tunneling current in STS data.

To elucidate experimental findings, we perform *ab initio* electronic structure calculations using a density functional theory (DFT) with an OPENMX package [21,22]. For the exchange-correlation energy, we adopt the Ceperley-Alder [23] form of the LDA potential. The relativistic effects important in heavy elements such as Cs are taken into consideration. For Cs, 9 valence electrons ($5s^25p^66s^1$) are taken as valence electrons since the $5s$ and $5p$ orbitals are essential in describing the interactions with the CNT. The wave functions are expanded using a numerical pseudo-atomic orbital basis set and an energy cutoff of 120 Ry is used.

An approximately 7-nm-long (16, 0) carbon nanotube, including more than 1000 atoms, is chosen to understand the experimental observations. To describe such a long CNT unit cell, a minimal basis set, which allocates 4 basis orbitals (1 for $2s$, 3 for $2p$) for a carbon atom and 5 basis orbitals (1 for $5s$, 3 for $5p$, 1 for $6s$) for Cs, is used. We determine the equilibrium geometry by relaxing the position of the Cs atom inside the CNT. The equilibrium distance between Cs and the wall of the CNT is about 3.2 Å, which is consistent with the literature [12].

The theoretical STS map of the Cs-encapsulated carbon nanotube is constructed using the density of states projected to the carbon atoms along a straight line parallel to the tube axis as shown in Fig. 3(a). The carbon atoms are located at the opposite side of the wall to where the Cs atom resides nearby. Here we use $\exp\{\text{DOS}^2\}$ scale for visual clarity. The two bound states are observed in the gap at the location where the Cs atom is embedded; the peak height of the upper bound state near the conduction band minimum (CBM) is higher than the lower one. The decay length of each state (~ 3 nm) and the energy spacing (0.22 eV) between these two agree well with our experimental results. The bound character of the two bound states is shown in the isosurface plot of the wave function in Figs. 3(b) and 3(c).

The Mulliken population analysis shows that about one electron is transferred from Cs to the CNT. The potential

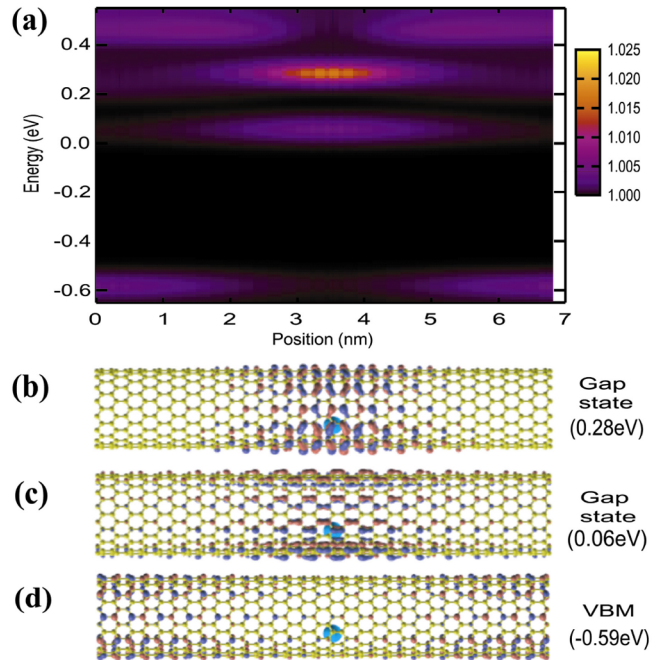


FIG. 3 (color online). (a) Theoretical STS map of a Cs atom encapsulated (16,0) carbon nanotube. The wave functions of two gap states located at 0.28, 0.06 eV in (b), (c) and the valence band maximum at -0.59 eV in (d), respectively. For the visual clarity, we use $\exp\{\text{DOS}^2\}$ scale in the two-dimensional STS map.

well made by the Cs^+ ion induces two bound states in the gap. The wave functions of these two bound states are identical to those of conduction band states with respect to their angular momentum character; the lower bound state has $m = 5$ and the upper has $m = 6$. Here $m = k$ indicates k nodes due to phase variation over the perimeter of the CNT. Therefore, we can realize that the two localized states in the gap originate from conduction band states in the pristine CNT.

Comparing this theoretical model to the experimental STS, one of the differences in the calculations is that the Fermi level lies at the lower gap state. This can be explained by the charge transfer from the CNT to the gold substrate due to the difference in the work function between them. In Figs. 4(a) and 4(b), we plot a few horizontal STS cuts of Fig. 3(a). Figure 4(a) displays the calculated corrugation of the DOS similar to our experimental dI/dV data as shown in Fig. 2(d). In Fig. 4(b), smooth curves are shown for visual clarity. Vertical cuts of Fig. 3(a) are displayed in Fig. 4(c). We clearly see the difference in DOS profiles between the near-Cs site and the far-from-Cs site.

In summary, we observed local changes in the electronic structure of CNTs with embedded Cs atoms. In our STS study, two localized gap states, as well as a downward shift of electronic bands, were observed for the Cs embedded SWCNT system. Based on our theoretical analysis, these

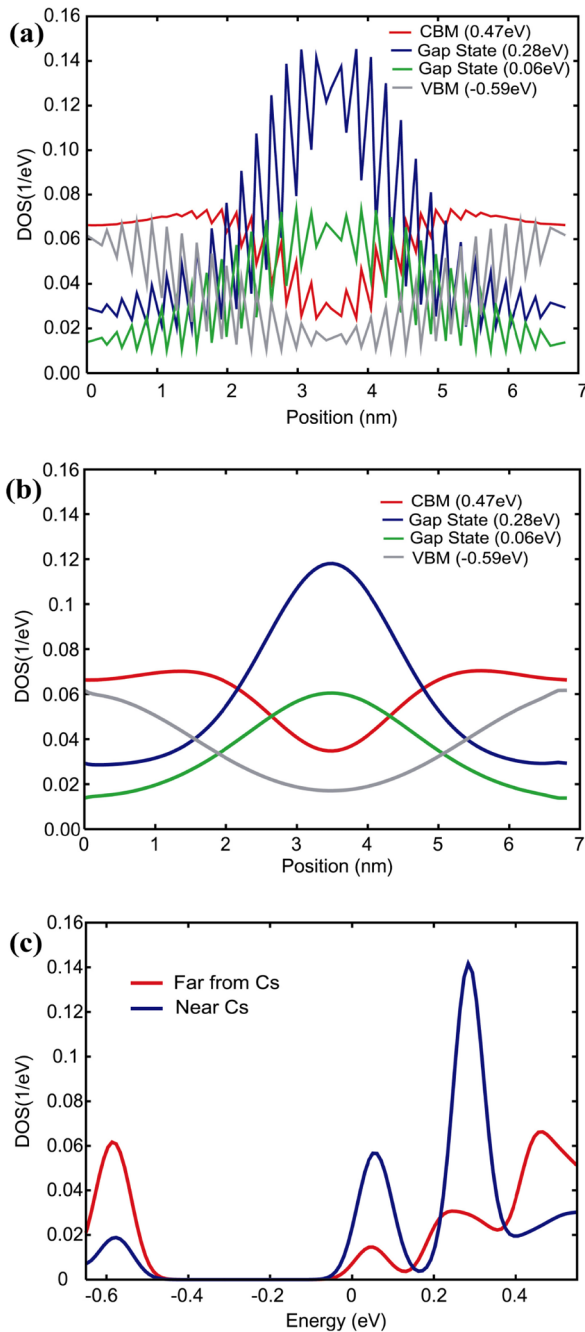


FIG. 4 (color online). The vertical and horizontal cuts of STS data shown in Fig. 3(a) are plotted. The horizontal cut in (a) is shown as smooth curve in (b) again. The PDOS of carbon atom which is located near the Cs atom and far from the Cs atom are shown in (c).

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