Metal Induced Intershell Coupling and Conductance Enhancement in Multiwalled Carbon Nanotubes

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ABSTRACT

Using two different metal (platinum and Tungsten) depositions on the individual multiwalled carbon nanotubes bridging the spacing between two gold electrodes, we segregate the contributions of change in nanotubes inherent properties and contact-improvement in total conductance enhancement caused by metal deposition. In these experiments, the metals were deposited precisely at the desired locations on the tubes using gas injection system available in the Raith150-Two direct write setup with 3 KeV electron beam induced deposition using organometallic precursor trimethyl-methylcyclopentadienyl-platinum (for Pt) and tungsten hexacarbonyl (for W). Typical increment up to 140% to 540% in conductance has been observed after Pt and W metal depositions on the MWNTs. The change in conductance is explained in terms of change in the density of states at Fermi level, due to charge transfer between metal atoms and nanotube as well as by radial stress created on the tube. HRTEM investigation of the metal deposited tubes suggests that metal atoms diffuse within the deep shells of the tube causing increased intershell interactions and hence improved electrical conductance.

Keywords: multiwalled carbon nanotubes, electron beam lithography, electron beam induced deposition, density of states, current-voltage characteristics

1 INTRODUCTION

Electrical characterization of individual carbon nanotubes is generally carried out either in side-contact or in end-contact geometry.[1-4] In end contact, the nanotubes ends are considered buried in metal leads while in side contact approach the natube is considered to lie on the bottom contacts so just the side of the nanotubes touch the bottom contacts. Theoretical studies suggest less contact resistence hence better electrical conduction in end contact approach.[1-2] Experimentally the comparison of the electrical properties of the same tube in both contact geometries is difficult and is subjected to the repeatability of experiments before and after any experimental alterations. However in one of our previous studies we have shown an easy approach to convert side contact geometry of individual multiwalled carbon nanotubes (MWNT) devices to end contact one.[5] This is achieved by first dispersing the tubes on the prepared bottom electrodes and measuring electrical characteristics of the tubes in this geometry and then depositing metal including the ends of the nanotubes and again obtaining the elctrical characteristics. However in this conversion, as the top metal is deposited at the part of the nanotubes which are already making side contact with bottom electrodes, hence any observed improvement in the current is attributed to the contact improvement. Nevertheless the increased density of states (DOS) as a result of the metal deposition may also contribute to the observed improvement in conductance. We here report the contributions of different metal induced effects in increased electrical conduction through individual MWNTs.

2 EXPERIMENTAL

The multiwalled carbon nanotubes used in this study were prepared by thermal chemical vapor deposition technique. a mixture of ferrocene (0.2 gm) and toluene (10 ml) has been used to synthesize the tubes. At the deposition temperature of 850^0C the mixture has been introduced in the heating furnace. A flow of 75 sccm carrier gas (hydrogen) was maintained during the growth. The so obtained vertically aligned tubes have been detached from the substrate, ultrasonicated in isopropyl alcohol for several hours for their seperation and were dispersed on the gold electrodes for electrical charaterization.

A Chromium and Gold (Cr/Au) layer of total thickness 200 nm was deposited on Si/SiO_2 (200 nm) wafer for patterning the bottom gold electrodes. The patterns for square contact pads (100μmx100μm) with typical spacing of about 2 μm were obtained by direct writing the spacing lines using electron beam lithography (EBL), on the pre-deposited Cr-Au layer and using PMMA 950 kA 4% as photoresist. Using wet etching of Cr/Au, the desired spacing between the pads has been fixed. The MWNTs were transferred on the so achieved patterns in order to have them suspended between the two pads. Positions of nanotubes on the gold

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electrodes were noted down carefully in SEM (Raith 150-TWO from Raith GmBH) instrument for the further steps.
The platinum metal has been deposited on the tubes using gas injection system available in the Raith150-Two direct write setup. Electron (3 KeV) beam induced deposition of platinum is achieved using organometallic precursor trimethyl-methylcyclopentadienyl-platinum IV $(CH_3)_3(CH_3C_5H_4)Pt$. For tungsten deposition, tungsten hexacarbonyl $[W(CO)_6]$ precursor has been used. Current-voltage characteristics of these individual tubes have been obtained using Keithley 4200 source meter using two probe configuration. HRTEM of the tubes after metal deposition has been performed using JEOL 2100 F TEM machine operated at 200 keV.

3 RESULTS AND DISCUSSION

The metal deposition locations on the tube are demonstrated by schematic shown in figure 1 (a-c). In figure 1a, a nanotube which is bridging the spacing between two bottom gold electrodes is shown. At the second step, the platinum metal deposition at the part of the tubes lying between the spacing is shown [1b] while at the third step [1c], Pt deposition at the part of the tube, touching the bottom gold contact is demonstrated.

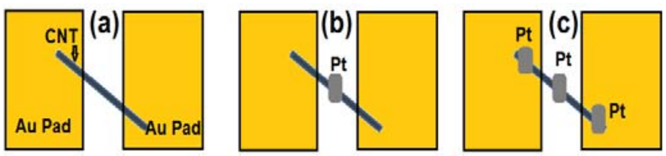

Figure 1. (a) schematic of MWNT lying in side contact geometry between two metal electrodes (b) MWNT with metal (Pt) deposition at middle (c) MWNT with Pt deposition at bottom contacts.
The scanning electron microscope (SEM) images of the tube corresponding to situations a,b and c in figure 1, are shown in figure 2(a,b,c). The current-voltage characteristics for the metal deposition steps are shown in figure 3.

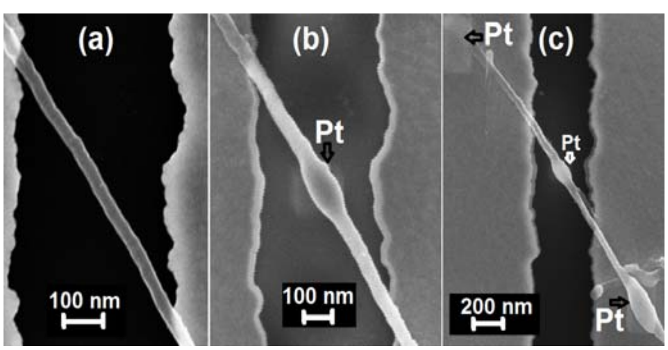

Figure 2. (a) MWNT bridging the gap between two metal electrodes (b) MWNT with metal(Pt) deposition at middle between the two bottom electrodes (c) MWNT with Pt deposition at bottom contacts.

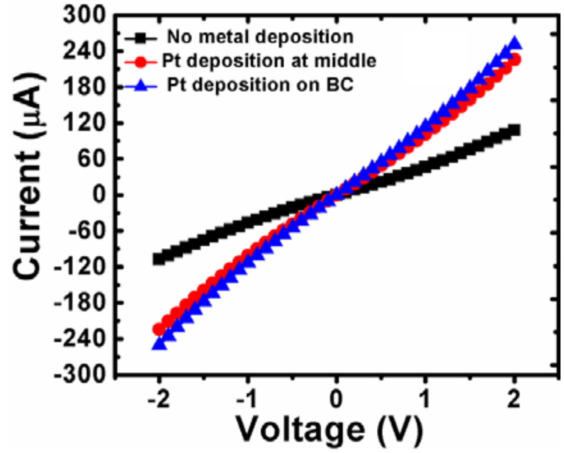

Figure 3. I-V curves of the tube corresponding to three situations of metal depositions.

Initially without any metal deposition the current through the tube is about 107 µA. After the metal deposition in middle, current increases to 224 µA and increases further to only 250 µA, at the third step of metal deposition. In case when Pt metal is deposited at the part of the tube lying in the dielectric spacing between the two contact electrodes, since there is no metal underneath, the overall improvement in current, if any, after Pt deposition is due to the increased intershell coupling and change in the local density of states available for the conduction.
The calculated zero bias conductances for the above three situations also give a clear idea about the change in the intrinsic properties of nanotubes rather than the contact improvement.Without any metal deposition the conductance of the tube is 40µS. While after the second step of Pt metal depostion in the middle, a 140% of incresed value of conductence has been noticed, the value of conductance being about 95 µS. While a negligible improvement in zero bias conductance has been observed corresponding to third Pt metal deposition step. Hence in the overall improved electrical conductance of tube the major contribution comes from increased intershell interaction and increased density of states (DOS) of the tubes due to metal deposition and not by the contact improvement.
Change in the elctrical characteristics after deposition of the Pt and tungsten (W) metals on some tubes in the middle of the spacing between the bottom contact electrodes was also studied. On some tubes first the W metal was deposited and then the Pt was deposited, while on some other tubes Pt metal was deposited first. The SEM images of a tube on which the W metal was deposited first are shown in figure 4 [a-d]. The electrical characteristics of the tubes were obtained after every metal deposition. The maximum change in zero bias conductance, obtained for a tube (not shown here) from 31.8 µS to 135.6 µS and 161.8 µS after Pt and W metal depositions comapred to the no top metal deposition, respectively indicate an overall increment in conductance after both the metal depositions to be 544 % (calculated by the initial conductance vs. conductance after

deposition of metal at bottom contacts). However conductance improves by 326 % after first metal (Pt) and just 19.3 % after second metal (W) deposition. Metal (Pt) deposition at contacts leads to 26.6 % improvement (each one is calculated with respect to the previous value of conductance).

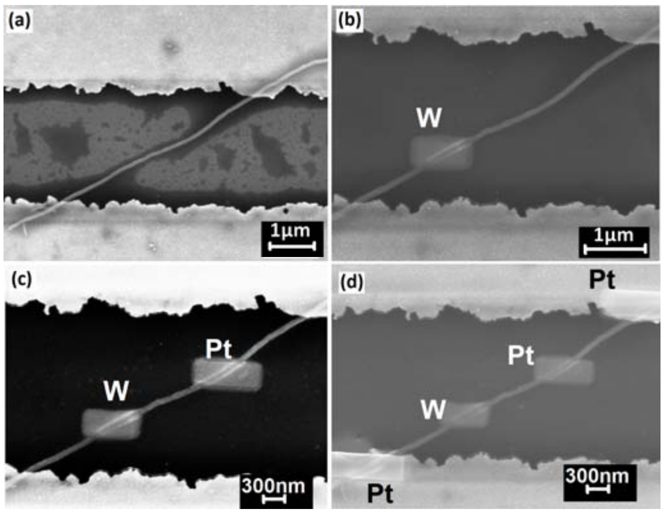

Figure 4. (a) MWNT without metal deposition,(b) MWNT with thin W metal deposition at middle (c) MWNT with thin Pt metal deposition at middle, (d) MWNT with Pt metal deposition at bottom contact.

The trend of the improvement in zero bias conductance for 10 such tubes with W and Pt metal depositions in middle was studied and results indicated that the major contribution in conductance improvement is observed after first metal deposition. It is important to mention here that the electrical properties like current capacity of the tube, breakdown voltage etc. are different for different tubes and depend on the tube diameter, nature of shells carrying current and defects present on the tubes, however the difference in the conductance before and after each step of metal deposition shows the same trend i.e. for all tubes, maximum change in conductance occurs after first metal deposition and is irrespective of metal (Pt or W). However, these results are typical for the thick metal deposition. For thin metal deposition (thickness compared about the half of the thick metal case), the maximum improvement in zero bias conductane has been observed to come after random step i.e it is not necessory to observed it after first metal deposition. We conclude that thick metal deposition introduce more radial stress on the tube and therefore in the previous experiment with thick metal deposition, a significant contribution could be achieved by the first metal deposition and less improvement has been observed after any subsequent depositions while in case of thin metal deposition the maximum change in conductance improvement does not come after first metal deposition, it is observed in the subsequent steps and this time contribution of metal deposition on contacts is significant.

We propose that the metal deposition on the tubes leads to the change in the density of states available for conduction, not only by the charge transfer to align the metal fermi-level with the nanotubes molecular energy orbitals due to the work function difference of the these two (WF of Pt ~ 5.3 eV and WF of MWNT ~ 4.95 eV) [6] but it is also affected by the radial stress created by the metal deposition on the tube. The therоretical studies like density functional calculatations presented by Kim *et. Al* [7] for the single wall nanotubes, support the increased density of states of the tubes after Pt metal decoration on the tubes via charge transfer. In reference 7, the attachment of Pt metal clusters has been demonstrated to lead to the semiconducting tubes to become of more metallic nature by closing their band gaps. As MWNTs can be considered to be formed by many concentric single walled nanotubes, similar phenomena of change in the density of states is expected to happen because of charge transfer. However, the metal deposition is also supposed to create radial stress on the tubes which may also lead to the change in DOS of the tubes. The density funtional calculations based on the change in the band gap of semiconducting single wall carbon nanotubes created by the stress on the tubes in radial direction conclude a band gap closing for the zigzag type (n,0) semiconducting SWNTs. Closing of the band gap for (8,0), (10,0) (11,0) and (16,0) tubes under radial compression has been indicated by Shan *et al*. using first principle density functional theory (DFT) within local density approximation and tight binding calculations however for (9,0) and (12,0) which are zigzag metallic CNTs, having hybridization induced band gaps, the band gaps first increses but finally closes for higher degree of deformation.[8] Similar semiconductor to metal transition for (8,0), (12,0) and (14,0), zigzag tubes under radial compression has been also suggested by Yoshitaka Umeno et al. [9]

Again, as multiwalled carbon nanotubes (MWNTs) comprise of many concentric single walled nanotube and out of these shells, each one can have any of the three geometrical arrangement of carbon atoms, well known as armchair, zigzag and chiral structures proposed for SWNTs. The elctronic properties of the tubes depend on the chirality of the shells and the DOS of the tubes depend on the semiconducting or metallic nature of the tubes. [10] Hence both the charge transfer and the radial stress induced band gap changes after metal deposition on the tubes are expected to lead to the overall DOS change.

In order to investigate the effect of metal deposition on the structural properties of the tubes, the high resolution transmission electron microscopy (HRTEM) has been performed on the metal deposited tubes. The metal has been deposited after locating the tubes in the mesh with respect to the circular center of the conventional Cu TEM grid, using the same EBID technique reported in this paper. HRTEM investigation of the metal deposited tubes indicates that the metal atoms diffuse within the deep shells of the tube causing increased intershell interactions and hence improved electrical conductance of the tubes.

In figure 5 a, the HRTEM image of a Pt metal deposited tube is shown. Two sites of the tubes covered in the squares in the inset of figure 5a, are magnified in the main figures 5a and 5b. Figure 5 a, corresponds to the site near the end of the metal deposition window so both the tube walls and the intercalated Pt metal clusters can be seen in the image, while in figure 5 b, only the dark metal clusters are visible. These situations also provide an intimation of the cases of consequences of thin metal deposition and thick metal deposition respectively.

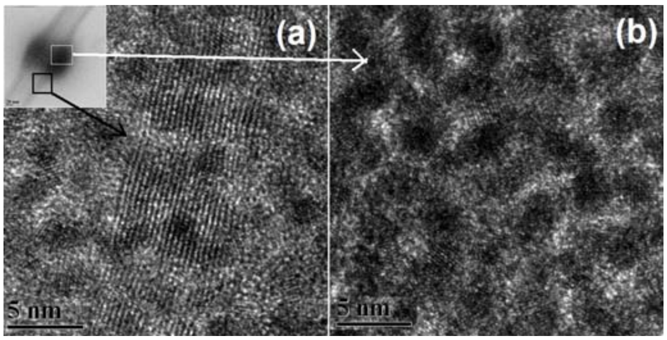

Fig.5, (a) HRTEM image of the metal deposited tube (shown in the inset). Arrows are shown corresponding to the areas covered in the squares. Pt metal clusters intercalated in the graphitic walls of the tube are visible in figure5 (a). In figure5 (b) only the dark clusters and no graphitic walls are visible.

5 CONCLUSION

We have demonstrated the improvement in electrical conductance of multiwalled carbon nanotubes by W and Pt metal depositions. Our experimental results indicate that the deposition of metal by typical nanofabrication techniques like electron beam induced deposition, which are generally used to contact the nanotube electrically, modify the electrical conduction through the tube. We have demonstrated that the change in the inherent properties of the tubes is responsible for the major improvement in electrical conduction rather than just the contact improvement. HRTEM investigation indicates that the metal clusters interact with the graphitic walls of the nanotubes and hence modify the electrical properties of the tubes; the amount of improvement is susceptible to the thickness of the deposited metal. The change in conductance is explained in terms of the change in the density of states at Fermi level, due to charge transfer between metal atoms and nanotube as well as by radial stress created on the tube. An improvement of 540% observed in zero bias conductance of the tubes suggests that this type of modified intershell interaction is different from the high bias assisted tunneling type carrier transport These experimental results are important for electronic device fabrication incorporating the nanotubes.

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