Carbon nanotube FETs decorated by gold nanoparticles: Electrical properties and mechanism

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Abstract

The electrical transport behavior of carbon nanotube field-effect transistors (CNT-FETs) decorated with gold nanoparticles (NPs) has been investigated. After decoration with Au NPs, the I_{on}/I_{off} ratios of nanotube FETs decrease and some of the p-type devices even change into metallic ones. The Au NPs decrease the contact resistances between the CNTs and metal electrodes, and accordingly increase the on-state electric currents of the CNT-FETs. The possible mechanisms for the effects of NPs on electrical transport properties of the CNTs have been analyzed qualitatively. Our investigations are closely linked with some promising applications of carbon nanotube hybrid materials in nanoelectronics.

1. Introduction

The surface modification of carbon nanotubes (CNTs), especially decoration by metal nanoparticles (NPs), has recently attracted significant attentions from both the fundamental and technological points of view [1]. Several methods have been developed to decorate carbon nanotubes with metal NPs (e.g. Au, Pt, Pd, Ag and Al) [1-7]. These methods include thermal evaporation[2], self-assembly[3], solution-phase reduction[4] and substrate-enhanced electroless deposition[5]. Among them, the electroless deposition is generally a simple way to implement and thus an attractive route for controllable synthesis of nanotube-NPs hybrid materials. Recently, some important applications of these nanotubes-metal hybrids have been exploited, e.g. the anode catalysts [6], gas sensors [7] and field emitters [8]. However, the possible application of this kind of hybrid materials in nanoelectronic devices has received much less attention. Especially, it remains unclear whether there exist strong effects of metal NPs on the electrical prosperities of CNT and although a few theoretical papers have addressed this issue. Here we demonstrate the fabrication of nanoelectronic devices based on CNT/NPs hybrids using a technique combining the photolithography and in-situ electroless deposition processes. The effects of Au NPs on the electrical transport of the nanotube-based devices have been investigated. We further discuss qualitatively the possible reasons for these effects.

2. Experimental

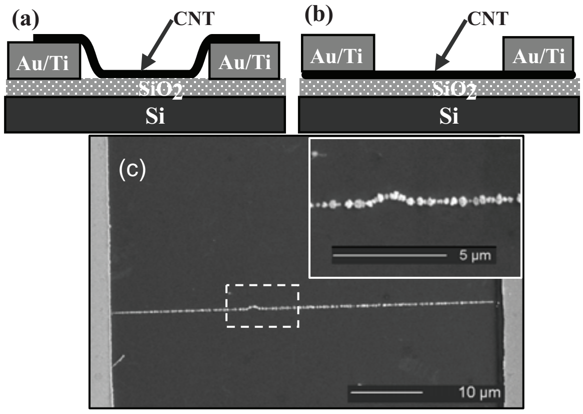

Figure 1 Schematic illustrations of carbon nanotube FETs with bulk-contacted (a) and end-contacted structure (b). FE-SEM micrographs of a carbon nanotube decorated by gold nanoparticles connecting source and drain (c). The inset shows the details of the boxed area.

The structure of FETs based on carbon nanotube/gold NPs hybrids, like conventional silicon-based transistor, consists of a gate, gate insulator, channel, and source/drain (S/D) electrode. The fabrication process of hybrids devices is similar to that described previously [9, 10]. A heavily doped silicon substrate, covered by 300-nm-thick thermally grown SiO_2, was used as a back gate. Ti/Au (10/100 nm) source and drain electrodes were fabricated by optical lithography and lift-off technique. The nanotube hybrids were deposited over predefined S/D electrodes (bulk-contacted, Fig.1 a) or contacted by evaporating electrodes on the top of nanotube (end-contacted, Fig.1b). The CNTs in the former case were synthesized by DC arc-discharge method and then dispersed ultrasonically in N, N-dimethylformamide (DMF), while in the latter case

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they were grown on the Si/SiO_2 substrates by catalyzed chemical vapor deposition (CVD). The Au NPs were deposited on the nanotube channels using an in-situ electroless decoration technique. This procedure is as follows: Aluminum microwires (acted as a reduction agent) were firstly bonded to the gold pads which were predefined on a chip. Then the whole chip including devices and the Al microwires were immersed into an aqueous solution of 1mM $HAuCl_4$. After a few seconds, the chip was dried with a nitrogen stream and Al wires were removed for further measurement. The field-emission scanning electron microscope (FE-SEM) images of CNTs hybrid devices were taken by FEI NanoSEM 430. Electrical measurements were carried out using HP 4156B precision semiconductor parameter analyzer.

3. Results and Discussion

The morphologies of the carbon nanotubes decorated by gold NPs are shown in Fig.1(c). Gold NPs are nearly uniformly assembled on the sidewalls of carbon nanotubes, with small gaps (~10–100nm) existing between gold particles along the nanotube. From the distribution of NPs, we can infer that these particles may initially nucleate homogeneously on the CNT surface, followed by growth of these nuclei into Au NPs. The NPs are 50−400nm in diameter, as measured in the FE-SEM images. Size control of Au NPs on CNTs can be realized by changing concentration of $[AuCl_4]^-$ ions and the redox reaction time.

We have fabricated air-stable p-type carbon nanotube FETs. Fig. 2(a) shows the electric characteristics of the carbon nanotube devices before and after Au NPs decoration. Upon NPs decoration, the I_{on}/I_{off} ratio of nanotube FET decreases from 10 to 1.2 at V_{ds}=1V. Some p-type nanotubes even change into metallic ones, i.e., the gate effect almost completely disappeared after NPs decoration (not shown). One doubt is that has the metal-like behavior of decorated CNT occurred due to short circuit path created by gold deposited on the CNT, or due to adjacent NPs touching each other throughout along the length of the CNT? This possibility can be excluded since adjacent NPs are separated with nanoscale gaps (~10–100nm) (as shown in Fig.1c).Then what are the possible reasons for the changes in electrical properties of the nanotube devices after decoration by Au NPs? At least two reasons seem possible. Firstly, the radial deformation of nanotube induced by deposited NPs can alter the electronic properties of carbon nanotube. Cha et al. recently reported direct three-dimensional observations of the buried interface between nanotubes and gold NPs. They showed that nanotubes undergo significant radial deformation to accommodate faceting of Au NPs (~10 nm)[11]. Application of radial strain to a nanotube changes its cross section from circular to elliptical one. The radial deformation have a significant impact on the electronic structure of SWNTs. O. Gülseren et al. predicted that the band-gap is reduced and eventually closed to produce an insulator-metal transition under the elastic radial deformation [12]. In the present study, the deposited NPs with larger diameters can induce substantial radial deformation, and hence reduce the band-gap of nanotubes (even to zero). We therefore can understand why some p-type nanotubes change into metallic ones after Au decorations. Another reason may be that the gold NPs distributed along the nanotube channel will partially shield the electric field from back gate and to some extent will decrease the I_{on}/I_{off} ratio of nanotube FETs.

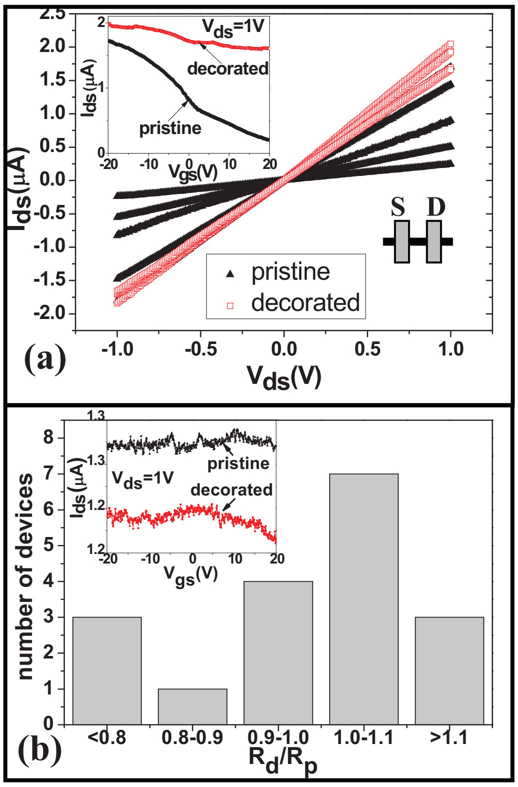

Figure 2 The electric characteristics of the carbon nanotube devices before and after Au nanoparticles decoration (a) The I_{ds}-V_{ds} characteristics of the p-type FETs. Upper inset: the I_{ds}-V_{gs} characteristics of the same FETs ; Lower inset: schematic sketch of the devices configuration. (b)The ratio histograms of the two-terminal resistances of metallic nanotube devices after (R_d) and before (R_p) the Au nanoparticle decorations for 18 devices. Inset: I_{ds}-V_{gs} characteristics of a typical devices

From Fig.2a, we noted that in both pristine and decorated p-type CNT devices, the I_{DS} increase linearly with V_{ds} for a given V_{gs}, which indicates that the electric contacts between CNTs and electrode are ohmic type. This phenomenon also exists in the metallic CNT devices. Fig.2b shows the ratio histograms of two-terminal resistances (R_{2t}) for 18 metallic nanotube devices after and before the Au nanoparticles decoration. To our surprise, the R_{2t} of these metallic devices does not change much after decoration by Au NPs. The ratios of R_d/R_p vary only from 0.51 to 1.23 (Fig.2b). The values of R_{2t} of all metallic devices are in the range from 0.2 to 4.0MΩ(average~2.1MΩ) whether they are decorated by Au nanoparticles or not. What is the reason for this behavior? It may result from the weak interaction between the nanotube and NPs. Zhong et al. has found that gold interacts weakly with the sidewall of carbon nanotubes, and the nature of the interaction is presumably Van der Waals[13]. The strength of the interaction between the nanotube and NPs can be reflected from the shape of deposited NPs. They predicted that metals with weaker interactions (e.g. Au) will form asymmetric NPs, elongating along the transverse direction of the nanotube[14]. This predicted morphology is quite consistent with our observation (Fig.1c).

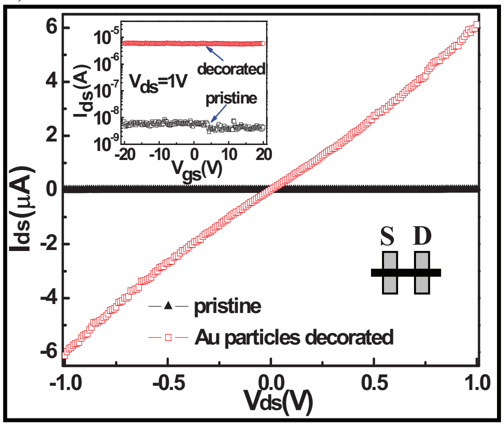

Figure 3 The I_{ds}-V_{ds} characteristics of the carbon nanotube devices before and after Au nanoparticles decoration. Upper inset: the I_{ds}-V_{gs} characteristics of the same devices; Lower inset: schematic sketch of the devices configuration.

As shown from the above analysis, the decorated Au NPs cause a semiconductor-to-metal transition for semiconducting CNTs; while the transport properties of the metallic CNTs seem to be only slightly affected by Au NPs. Here one question may be raised. Can gold NPs reduce the contact resistance? To clarify this we fabricated nanotube devices with bulk-contacted geometry, i.e. the nanotube are bridged over predefined S/D electrodes. Fig.3 shows the I_{ds}-V_{ds} characteristics of the CNT devices before and after Au NPs decoration. For the pristine metallic devices, the R_{2t} is in the order of hundreds of mega-ohm. Decorated with Au NPs, the R_{2t} of CNT devices indeed decrease. It usually drops three orders of magnitude. However, the R_{2t} of decorated metallic devices (bulk-contacted) is still in the order of hundreds of kilo-ohm, which is the same magnitude as that of the decorated metallic CNT devices (with end-contacted structure). Therefore, we conclude that the contact resistance of CNT devices finally depends on the kind of metal used for decoration of CNTs. This suggests that a promising strategy to decrease the contact resistance is to select a suitable metal to decorate the CNT devices.

4. Summary

In this paper, we have presented a simple and reliable method for the fabrication of FETs based on CNT-gold NPs hybrids using a combination technique of the photolithography and in-situ electroless deposition process. The electrical transport properties of hybrid CNT FETs have been investigated in detail. Results show that after decoration with Au NPs, the I_{on}/I_{off} ratios of CNT-FETs decrease and some of the p-type devices even change into metallic ones. The Au NPs decrease the contact resistances between the CNTs and metal electrodes, and consequently increase the on-state electric currents of the CNT-FETs. The possible mechanisms for the effects of NPs on electrical transport properties of the CNTs have been proposed. Our investigations may pave the way for creation of nanodevices based on CNTs-NPs hybrid materials with promising applications in sensor, memory and interconnector.

Acknowledgments

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References

[1] G. G. Wildgoose et al., Small, 2, 182(2006).
[2] H.-S. Kim, et al., Appl.Phys.Lett.,91,P153113 (2007).
[3] B. J. Taft et al., J. Am. Chem. Soc., 126, 12750(2004).
[4] K. Y. Lee. et al., Chem. Phys. Let., 440, 249 (2007).
[5] L. Qu and L. M. Dai, J. Am. Chem. Soc., 127 10806 (2005).
[6] Y. Y. Mu et al., J. Phys. Chem. B, 109, 22212(2005).
[7] A. Star et al., J. Phys. Chem. B, 110, 21014(2006).
[8] K. Kim et al., Adv. Mater. 15, 1618 (2003).
[9] A Guo et al., Nanotech. 18, 125206(2007)
[10] C. Wang et al., J. Nanosci. and Nanotec. 9, 2004(2009)
[11] J. J. Cha. et al., Nano Lett. 7, 3770(2007).
[12] O. Gülseren et al., Phys. Rev. B, 65, 155410(2002).
[13] J. X. Zhong and G. M. Stocks, Appl. Phy. Lett., 87, 133105 (2005).
[14] H. C. Choi. et al., J. Am. Chem. Soc., 124, 9058(2002)