Al_2O_3 Coating and Filling of Carbon Nanotubes

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Aluminum oxide (Al_2O_3) nanotubes and nanorods were fabricated by coating and filling of multiwalled carbon nanotubes (MWNTs) with atomic-layer deposition (ALD). Al_2O_3 material was deposited on the MWNTs at a substrate temperature of 300°C using trimethylaluminum and distilled water. Transmission electron microscopy, high resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy, and selected area electron diffraction of the deposited MWNTs revealed that amorphous Al_2O_3 material coats the MWNTs conformally and that this material fills the inside of the MWNTs. These illustrate that ALD has an excellent capability to coat and fill any three-dimensional shapes of MWNTs conformally without producing any crystallites.

Keywords : Multiwalled carbon nanotubes, Al_2O_3 nanotubes, Filling, Coating, Atomic layer deposition.

1. INTRODUCTION

Since Iijima has been discovered the carbon nanotubes (CNTs) [1], CNTs have been the subject of intense research because the unique electronic properties of CNTs offer the possibilities of using them in a variety of applications ranging from nanoelectronics to chemical sensors. Currently, there has been widespread interest in the fabrication of one-dimensional nanoscale materials by filling or coating of CNTs [2-5]. CNTs have been used as templates for preparing metal oxide nanotubes and nanorods that possess distinctive chemical, mechanical and physical properties, and may be proven to be key components in the next generation of nano-optical and electronic devices.

Aluminum oxide (Al_2O_3) nanotubes and nanorods have especially attracted much attention because of their high dielectric constant, very low permeability, and high thermal conductivity. Several methods for preparing these Al_2O_3 nanomaterials have been proposed, including coating of CNTs with aluminum isopropoxide by sol-gel method [4], electrochemical anodizing of Al films [6], heating of partially hydrolyzed $AlCl_3$ powders [7], and coating of CNTs with Al and Al_2O_3 powder mixtures by chemical vapor deposition [5]. Despite those efforts put on the preparation of the Al_2O_3 nanomaterials, the novel route to Al_2O_3 nanotubes and nanorods with uniform thickness has been not found. Conformally controlled thickness of the nanomaterials is of crucial importance in the fabrication of future nanodevices. Atomic layer deposition (ALD) is one of the adequate methods of producing nano-scaled layers with excellent conformality and precisely controlled thickness [8]. Nevertheless, ALD has not yet been applied to coating and filling of CNTs as templates for the fabrication of Al_2O_3 nanotubes and nanorods.

In this study, Al_2O_3 material was deposited on multiwalled carbon nanotubes (MWNTs) by ALD. The MWNTs coated and filled with Al_2O_3 material were investigated by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and selected area electron diffraction (SEAD) and high resolution transmission electron microscopy (HRTEM). In this paper, the fabrication of Al_2O_3 nanotubes and nanorods by coating and filling of MWNTs is first described and then the bonding mechanism of Al_2O_3 on the MWNTs is briefly discussed.

2. EXPERIMENTAL

MWNTs were synthesized on a Si(100) substrate at 800 °C by thermal chemical vapor deposion [9]. The Si (100) substrate was coated with a drop of 0.01 M ethanol solution of metal salts ($FeCl_2 \bullet 4H_2O$). The substrate was pretreated by NH_3 gas with a flow rate 20 sccm for 10 min at a temperature of 800 °C, forming nanometer-size Fe particles. The MWNTs were then grown using C_2H_2 with a flow rate of 10 sccm for 5 min. Since the tips of the grown MWNTs were closed, the MWNTs grown on the Si substrate were sonicated to separate them from the Si substrate. The opened bases of the MWNTs were exposed after the sonication. Al_2O_3 material was deposited on the MWNTs at a temperature of 300℃ by ALD technique. Trimethylaluminum (TMA) and distilled water (H_2O) were utilized as the precursors for the Al_2O_3 deposition. The process pressure was 250 and 230 mTorr for the dosing of chemical precursors and the Ar purging, respectively. 25, 50, and 100 cycles for the deposition of Al_2O_3 were performed on the MWNTs; one cycle for the deposition of Al_2O_3 is composed of TMA dosing, Ar purging, H_2O dosing and Ar purging. TEM (Philips, CM30), EDX, SAED, and HRTEM (JEOL, JEM 3011) were carried out for the Al_2O_3 layers deposited on the MWNTs.

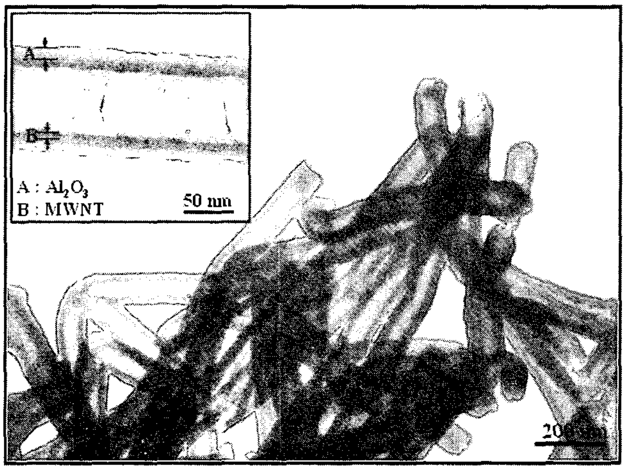

Fig. 1. TEM image of MWNTs coated with Al_2O_3 material by ALD. The magnified TEM image in the insert illustrates discretely a cylindrical Al_2O_3 layer (marked by two arrows) coating a selected MWNT and the multiwalls of this MWNT. This cylindrical Al_2O_3 layer corresponds to a 10 nm-thick Al_2O_3 nanotube with an inner diameter of 75 nm.

3. RESULTS AND DISCUSSION

Figure 1 shows a TEM image of MWNTs deposited with Al_2O_3 material by ALD. The magnified TEM image in the insert of Fig. 1 illustrates discretely a cylindrical Al_2O_3 layer (marked by two arrows) and multiwalls of a selected MWNT. The thickness of the Al_2O_3 layer and the outer and inner diameters of the MWNTs determined from this magnified TEM image are 10, 75, and 60 nm, respectively. These TEM images reveal that Al_2O_3 material coats the outer multiwalls of the MWNTs conformally; the thickness of the coating material is uniform. These show that 10 nm-thick Al_2O_3 nanotubes with an inner diameter of 75 nm are fabricated by the coating of the MWNTs.

A TEM image in Fig. 2 shows a cylindrical Al_2O_3 layer coating the inner multi-walls as well as the outer multi-walls in the opened base of a selected MWNT; the Al_2O_3 layer coating the inner multiwalls is indicated by six arrows, for emphasis. Namely, this TEM image shows that the 5-nm thick Al_2O_3 layer wraps the whole multiwalls of the MWNT having an inner diameter of 40 nm. Any Al_2O_3 crystallites on the MWNT are not seen in this TEM image. ALD does not produce any Al_2O_3 crystallites, since H_2O and TMA molecules are alternately dosed to the MWNTs; in contrast, Al_2O_3 crystallites are present on the Al_2O_3 nanotubes prepared by other methods [4, 5], for example, the Al_2O_3

nanotubes obtained after oxidizing the carbon nanotube template at 1023K [4]. These illustrate that ALD has an excellent capability to coat any three-dimentional shapes of MWNTs conformally without producing any crystallites.

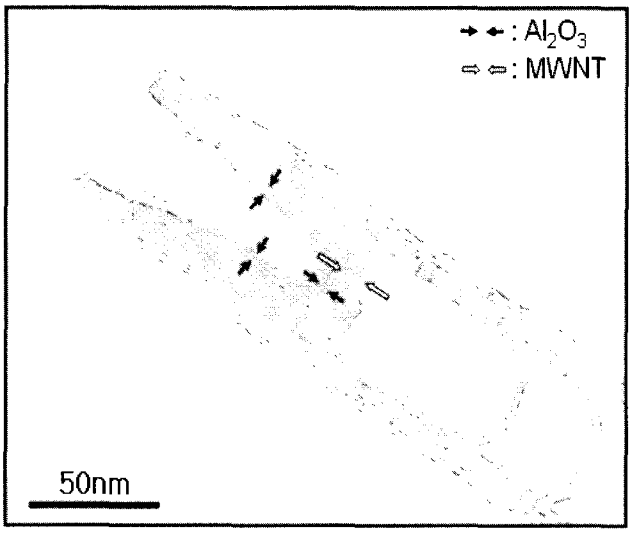

Fig. 2. TEM image of a cylindrical Al_2O_3 layer coating the inner and outer multiwalls in the opened base of a selected MWNT. The 5 nm-thick Al_2O_3 layer coating the inner multi-walls is indicated by six arrows.

TEM images in Fig. 3 show Al_2O_3 filling of the interior part of the inner multi-walls as well as coating of the outer multi-walls in the opened bases of two selected MWNTs having inner diameters of 20 and 45 nm, respectively. The interior parts of the MWNTs filled with Al_2O_3 material are defined by the inner multi-walls, the first comparting walls, and the ending edges. The Al_2O_3-filled parts of the MWNTs are darker than the other parts in Fig. 3. These Al_2O_3-filled parts correspond to Al_2O_3 cylindrical nanorods; one cylindrical nanorod (Fig. 3(a)) has a diameter of 20 nm and a length of 150 nm, and the other cylindrical nanorod (Fig. 3(b)) has a diameter of 45 nm and a length of 45 nm. These indicate that the Al_2O_3 cylindrical nanorods are fabricated by the filling of the MWNTs with ALD and that the physical sizes of the Al_2O_3 nanorods may be controlled by the selection of the inner diameters of the MWNTs and the positions of the inner comparting walls inside the MWNTs.

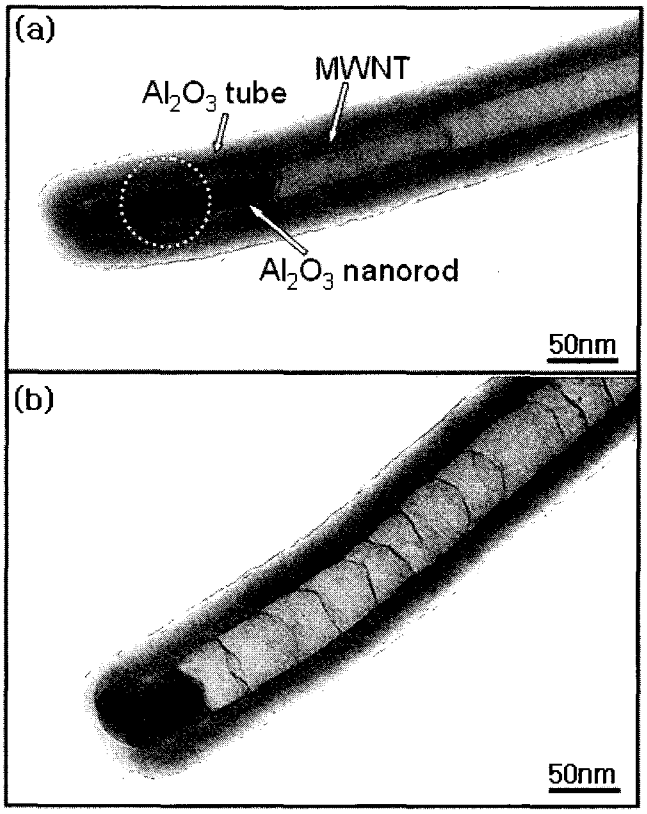

Fig. 3. TEM images of Al_2O_3 filling and coating of two selected MWNTs. The Al_2O_3-filled parts correspond to Al_2O_3 cylindrical nanorods. One cylindrical nanorod (a) has a diameter of 20 nm and a length of 150 nm and the other cylindrical nanorod (b) has a diameter of 45 nm and a length of 45 nm.

Figure 4(a) shows the EDX spectrum taken for the Al_2O_3-filled part of the MWNT marked by A in Fig. 3(a). Only the C-, O-, Al-related peaks are present in the EDX spectrum, revealing that the filled part is indeed Al_2O_3; the Cu-related peaks in the spectrum come from the Cu grids. It has been demonstrated in Refs. 10 and 11 that metal catalysts such as iron and nickel often form as fillings when the MWNTs are produced, but the absence of the metal-catalyst-related peaks in the EDX spectrum indicates that the filled part is not metal catalysts. Any other metal-related peaks except the C-, O-, Al-related peaks were not observed in EDX spectra taken for many other parts of the Al_2O_3-deposited MWNT, so the cylindrical layer coating the outer multi-walls is also indeed Al_2O_3. Figure 4(b) shows the SAED pattern of the

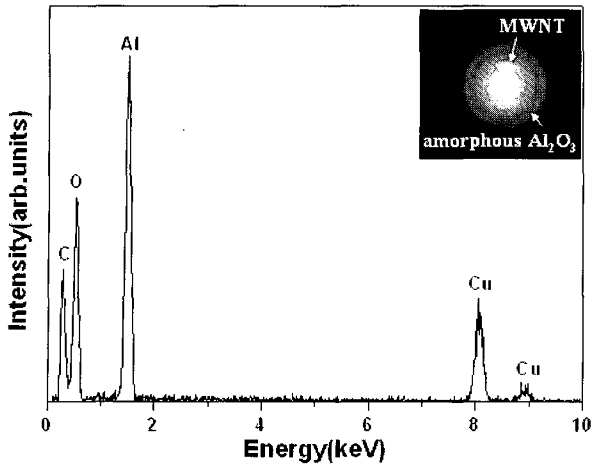

Fig. 4. EDX spectrum (a) taken for the Al_2O_3-filled space of the MWNT marked by A in Fig. 3(a) and SAED pattern (b) of the Al_2O_3-deposited MWNTs.

Al_2O_3-deposited MWNT in Fig. 3(a). The SAED pattern shows the halo, but it does not show any set of single-crystal electron diffraction spots. The absence of the spots indicates that the coating and filling Al_2O_3 material is amorphous.

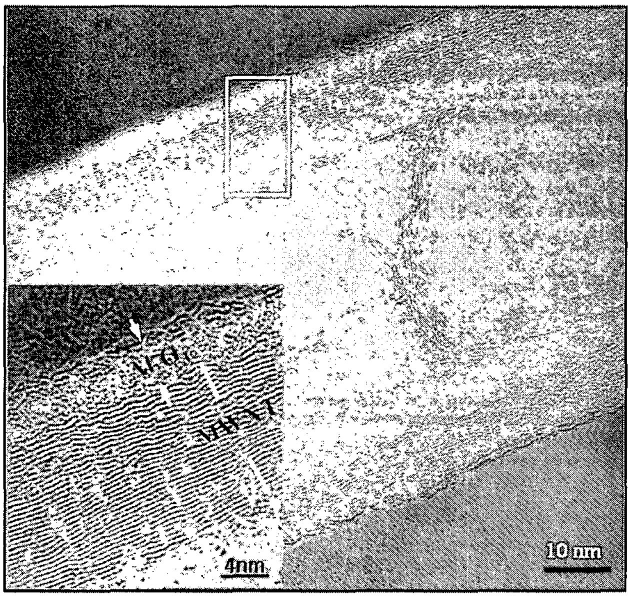

Fig. 5. HRTEM image of an Al_2O_3-coated MWNT. An enlarged image (in the inset) of the box drawn by white line illustrates clearly the periodic multiwalls of the MWNT and the amorphous Al_2O_3 coating layer (indicated by two arrows).

Figure 5 shows a representative HRTEM image of an Al_2O_3-coated MWNT. An enlarged image (in the inset of this figure) of the box drawn by white line illustrates clearly the periodic multiwalls of the MWNT and the amorphous Al_2O_3 coating layer (indicated by two arrows). This HRTEM image demonstrates the uniform thickness of the Al_2O_3 coating layer, but it does not show any interfacial alloy layers between the coating layer and the MWNT. The thicknesses of the amorphous Al_2O_3 layers deposited after the ALD of 25, 50, and 100 cycles sdetermined from the TEM images of Figs. 1-3 and 5 are 5, 10, and 20 nm, respectively. The deposition rate for the Al_2O_3 layers is accordingly determined in a straight way to be 0.2 nm/cycle. This value agrees with the deposition rates for the Al_2O_3 layers deposited on semiconductor nanowires including ZnO, SiC, GaN, InP, and GaP nanowires under the same deposition procedure as for the MWNTs, which indicates that the different lattice structure of MWNTs from semiconductor nanowires does not affect the deposition rate of the Al_2O_3 layers. The excellent uniform thickness and inert deposition rate could be due to the amorphous properties of the Al_2O_3 coating material. If the Al_2O_3 coating layer is not amorphous, the thickness of the Al_2O_3 coating layer would not be uniform. For instance, the TiO_2 and ZnO films deposited by ALD are microcrystalline and these deposited layers are not uniform on the nanometer scale [12, 13].

The bonding mechanism of Al_2O_3 on MWNTs during ALD must be different from that for semiconductor nanowires, since carbon atoms comprising MWNTs have sp^2 hybrid orbitals. Although the bonding mechanism is not well understood at present, we suggest here that the hydrogen atoms of H_2O molecules rather than the oxygen atoms may be bonded to the carbon atoms. The reason for this is as follows; MWNTs are not oxidized until they are dealt with boiling acid solution or with oxidant gas at high temperature(above 700°C)[14] and it is well known that water vapor is absorbed on the surface of MWNTs through bonding between the hydrogen atoms of water and the carbon atoms [15]. However, there is still a strong possibility that the Al atoms of TMA molecules may be bonded to the carbon atoms, since Si-C bonds are formed for SiO_2-coated MWNTs [16]. For the formation of either the H-C or Al-C bonds, the orbitals of the carbon atoms may be partially rehybridized from sp^2 to sp^3 [16].

Filling MWNT with metal oxides has been accomplished via wet chemical method [2, 17]. The filling of nanotubes is directly related to the surface energies of interaction between the liquid and the solid surface of the nanotube. In the cases of metal oxides with unusually low surface tensions such as lead oxide (132 mN/m) and bismuth oxide (200 mN/m), it was allowed that the inside of the MWNT is filled by capillary forces [14,18]. Considering high surface tension of Al_2O_3 (350 mN/m) [19], we may expect that the inside of the MWNT would not be filled with Al_2O_3 through wet chemical method. Hence, it is noteworthy that the inside of the MWNT is filled with Al_2O_3 by ALD, one type of chemical vapor depositions.

4. CONCLUSIONS

Al_2O_3 nanotubes and nanorods were fabricated by coating and filling of MWNTs with ALD. TEM, HRTEM, EDX, and SAED of the deposited MWNTs revealed that amorphous Al_2O_3 material coats the MWNTs and that this material fills the inside of the MWNTs. These illustrate that ALD has an excellent capability to coat and fill any three-dimentional shapes of MWNTs conformally without producing any crystallites. The physical sizes of the Al_2O_3 nanotubes and nanorods may be controlled by the selection of the inner diameters of the MWNTs, the positions of the inner comparting walls inside the MWNTs, and the number of the ALD cycles.

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