## Electron microscopy characterization of Al<sub>2</sub>O<sub>3</sub> and ZnO coated carbon nanotubes

Joshua M. Green\*, Timothy Gutu\*, Lifeng Dong\*, Jun Jiao\* John F. Conley, Jr.\*\* and Yoshi Ono\*\*

\* Department of Physics, Portland State University, Portland, OR 97207-0751

\*\* Integrated Circuit Process Technology Group, Sharp Labs of America, Camas, WA
98607

Because of their many unique structural and electronic properties, carbon nanotubes (CNTs) have been investigated for use in devices ranging from flat-panel displays to electron microscopes. ZnO has also demonstrated its usefulness in applications ranging from UV photonics to nanowire-based electronics. Al<sub>2</sub>O<sub>3</sub> is often used in conjunction with ZnO films to increase their conductivity. In this study, we combined the properties of these disparate materials in an effort to creat a new form of materials with enhance properties. This approach resulted in exotic morphologies of coated carbon nanotubes.

Multi-walled carbon nanotubes (as shown in Fig. 1) were grown using a chemical vapor deposition (CVD) process, with Fe as a catalyst. They were then coated, using atomic layer deposition (ALD), with a thin layer of  $Al_2O_3$  followed by a layer of ZnO. The samples were characterized both at as-made stage and also following a post-deposition anneal.

Using a scanning electron microscope (SEM), the morphologies of the coated CNTs were studied. After the ALD process but before annealing, the deposited films appeared as a thick uniform layer around the carbon nanotubes, increasing the diameters of the structures. Small particles were also present on the surface of the coated nanotubes as shown in Fig. 2. After annealing, small dendritic protrusions appeared on the surface of the coated nanotubes, as demonstrated in Fig. 3. These dendrite-shaped growths appear to have diameters approximately similar to those of the original uncoated CNTs.

A transmission electron microscope (TEM) equipped with an energy-dispersive x-ray (EDX) spectrometer was used to determine the internal structure and chemical composition of the coated nanotubes. Fig. 4 is a low magnification TEM image revealing the dendrite-shaped ZnO/Al<sub>2</sub>O<sub>3</sub>/CNT morphologies. These structures were found to be single-crystalline, indicated by the HRTEM image in the inset To further characterize the chemical composition distribution, an EDX line scan was performed. The line scan, Fig. 5 (b), revealed the Zn and O to be concentrated in the dendritic protrusions while Al and C were evenly distributed throughout the structure.

All of this evidence suggests that ZnO forms the dendrite-shaped growths during the annealing process. The initial nucleation of ZnO is affected by the surface conditions of the substrate. The coating layer of  $Al_2O_3$  on the CNTs creates a unique surface morphology; thus, the deposited ZnO forms novel structures under these conditions. Further tests are needed to discover the exact growth mechanism of these structures.

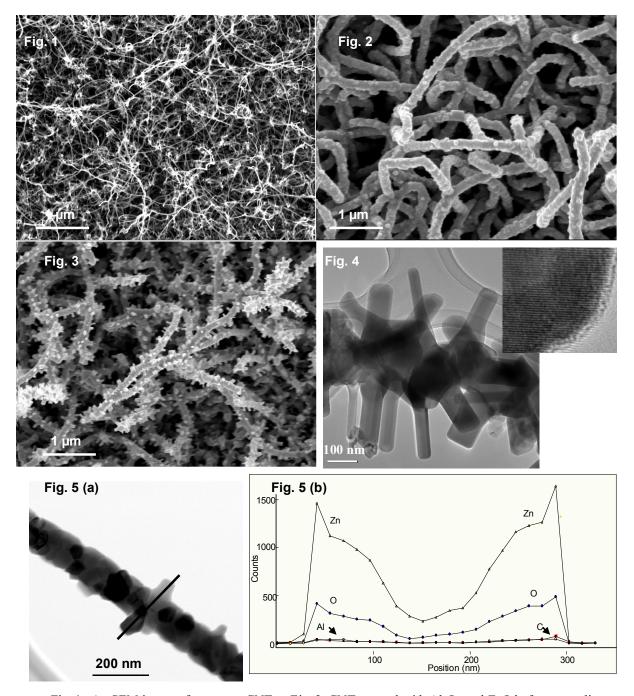


Fig. 1. An SEM image of as-grown CNTs. Fig. 2. CNTs coated with  $Al_2O_3$  and ZnO before annealing. Note the significantly increased diameter. Fig. 3. Coated CNTs after annealing, showing the dendritic protrusions. Fig. 4. A TEM image of a coated CNT showing details of the dendrite-shaped growths. Inset: HRTEM image showing lattice fringes. Fig. 5 (a) A STEM image of a coated CNT showing the line where an EDX line scan was performed and (b) results of the line scan. Note that Zn and O have much higher counts than Al and C. It is possible that the C and Al signals have been buried beneath the ZnO coating layer.