Atomic-Level Observations of Carbon Nanotube Growth using a Designer Catalyst

Renu Sharma[1]*, Edward Moore, [2] Peter Rez, [2,3] and M.M.J. Treacy[3]
[1]*LeRoy Center Solid State Science, Arizona State University, Tempe, AZ 85287-9506 USA*
[2]*School of Materials, Arizona State University, Tempe, AZ 8287 USA*
[3]*Department of Physics, Arizona State University, Tempe AZ 85287USA*
*renu.sharma@asu.edu

Introduction

Catalytic chemical vapor deposition (C-CVD) using transition metal catalysts, such as Ni, Co and Fe, is one of the most frequently used methods for the large scale synthesis of carbon nanotubes (CNTs). However, their controlled synthesis and placement, required for their numerous applications, is still an unresolved issue. Atomic level understanding of their growth mechanism can assist us in controlling their synthesis. Such knowledge is also relevant to understand the deactivation process of transition metal catalysts during cracking of petroleum or reforming reactions. In recent years, several in-situ high-resolution transmission electron microscopy observations have revealed that nucleation and growth mechanisms of CNTs are different for Ni and Fe [1-3]. We have designed and fabricated Fe-containing particles, with precise control on their placement and size, on a silica support. These catalyst particles were used to observe atomic-level structural transformations occurring during nucleation and growth of CNTs. Based on high-resolution imaging and electron energy-loss spectroscopy in an environmental TEM, we present an atomic model for the complete reaction sequence; from fabrication of arrays of equidistant and same-diameter Fe-containing nanoparticles, to the synthesis of multi-walled carbon nanotubes.

Materials and Methods

We use the column of an environmental scanning transmission electron microscope (E(S)TEM) as a flow reactor for both Fe particle and CNT synthesis. First, we fabricate arrays of equidistant Fe particles on a perforated SiO_2 thin film on a Si wafer (SPI Supplies) by electron beam induced decomposition (EBID) of nonacarbonyldiiron vapors ($Fe_2(CO)_9$; Alfa Aesar) at room temperature in the column of the E(S)TEM. Next, these particles were heated to reaction temperature in hydrogen which was replaced by acetylene to form carbon nanotubes.

Results and Discussion

Selectively fabricated nano-particles on silica substrates, using EBID (Figure 1a) were found to contain both Fe and C, but the amount of C was below the detection limit after the samples were heated to 650 °C in 90 mTorr of H_2 (Figure 1b). Time-resolved high-resolution images, extracted from a video sequence recorded at 650 °C, after replacing H_2 by C_2H_2, revealed Fe-containing particles to be magnetite (Fe_3O_4) (Figure 2a-c) nano-crystals. The face centered cubic (fcc) magnetite structure transformed to a body centered cubic (bcc) oxide structure before being reducing to ferrite (bcc α–Fe) (Figure 2d-f). In the next stage, the particles are carburized to iron carbide (cementite, Fe_3C) (Figure 2g-i) before creating carbon nanotubes (Figure 2j). The crystal structure of the catalyst remained as Fe_3C after nucleation and growth of CNTs (Figure 2k-l).

Significance

Controlled placement of catalyst particles allows us to obtain atomic level information of the catalytic processes.

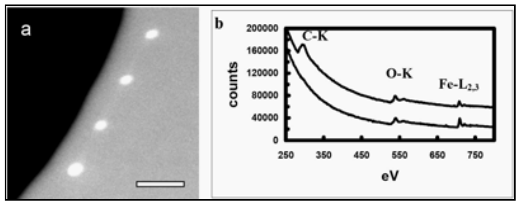

Figure 1. (a) Annular dark field image of 20-nm particles separated by 100 nm deposited by EBID. The bar is 100 nm. (b) Electron energy-loss spectra collected from the particle (top spectra) after deposition, and (bottom spectrum) after heating at 650 °C in 90 mTorr of H_2.

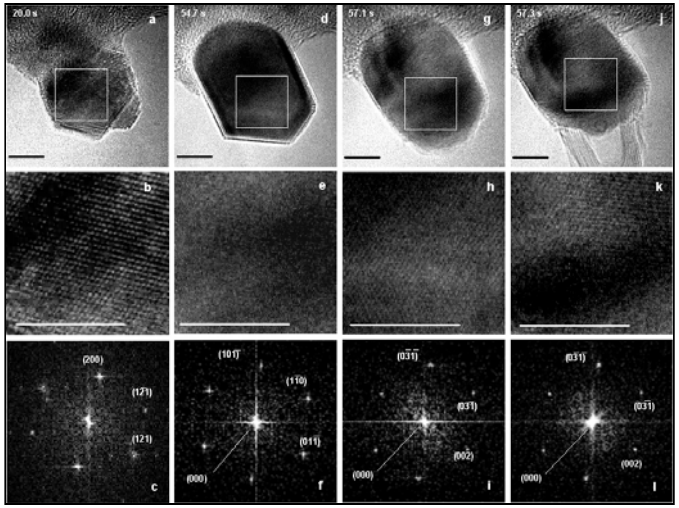

Figure 2. HREM images extracted from a video sequence recorded at 650 °C in 10 mTorr of C_2H_2 showing the structural transformations occurring prior to CNT growth.

References

1. Helveg, S., Lopez-Cartes, C., Sehested, J., Hansen, P.L.,Clausen, B.S., Rostrup-Nielsen, J.R., Abild-Pedersen, F., and Norskov J., *Nature*, 427, 426 (2004).
2. Sharma, R.; Rez, P.; Brown, M.; Du, G. H.; Treacy, M. M. J., *Nanotechnology* 18, 125602 (2007).
3. Yoshida, H., Takeda, S., Uchiyama,T., Kohno, H.,Homma, Y., Nano Letters (2008)
4. Sharma, R., *Journal of Materials Research* 20, 1695 (2005)