

Controlling the Size and Composition of Iron Nanoparticles for Carbon Nanotube Growth

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Carbon nanotubes (CNT) are promising material for making electron field emission sources [1] but one of the key challenges has been the synthesis of arrays of nanotubes with controlled size and placement. Recently, we reported the site-specific deposition of Fe catalyst particles using electron beam induced deposition (EBID) in an environmental scanning/transmission electron microscope (E(S)TEM) [2]. The column of the E(S)TEM can also be used as a reactor for CNT formation in which the nucleation and growth processes can be directly observed with atomic resolution [3]. For chemical vapor deposition, the catalyst size is one of the factors that determine the size of the CNT. In this study, we examine how the size of the nanoparticles fabricated for CNT growth using EBID can be controlled using different deposition conditions.

A Tecnai F20 E(S)TEM was used for both EBID and CNT growth. The substrates were perforated SiO₂ membranes. Two organometallic precursors were used as Fe sources; diiron nonacarbonyl (Fe₂(CO)₉) and ferrocene (Fe(C₅H₅)₂). For this study, we varied three deposition parameters; temperature, pressure and deposition time. Inlet gas pressures from 0.06 Pa to 0.33 Pa and substrate temperatures up to 450°C were used. Composition of the deposited particles was obtained from electron energy loss spectroscopy (EELS) data. As reported earlier [2], the catalyst nanoparticles are heated in 13 Pa of hydrogen up to 650°C prior to introducing acetylene for CNT growth.

In Figure 1, we show an example of Fe nanoparticles deposited in a patterned array using EBID and the line profiles used to measure the diameter of these particles. As expected, we observe that the diameter increases with deposition times. However, at diameters greater than ~18 nm, the growth morphology goes from lateral growth to vertical growth, leading to dendrite-like structures. For diiron nonacarbonyl, the deposit diameter showed weak dependence on both temperature and pressure. In addition, at substrate temperatures above 100°C, the precursor decomposed thermally, resulting in the deposition of a Fe film. Using ferrocene, we were able to deposit particles up to 450°C. As shown in Figure 2(a) the deposited particle diameter decreased with increasing substrate temperature. At room temperature and 150°C, the particle diameter showed only weak pressure dependence and long deposition times resulted in dendritic growth. On the other hand, at 300°C and 450°C, the deposited particle diameter showed a marked increase with pressure (in Figure 2(b)). Lastly, we observe from the EELS data (given in Figure 3) that the particles deposited using ferrocene has a much higher carbon content compared to particles deposited using diiron nonacarbonyl and the carbon content is not significantly reduced by higher deposition temperatures. The effect that composition of these particles has on their activity for carbon nanotube growth will also be presented.

References:

- [1] N. de Jonge, J.M. Bonard, *Phil. Trans. R. Soc. Lond. A* 362 (2004) 2239
- [2] R. Sharma *et al*, *Nano Lett.* 9 (2009) 689

[3] R. Sharma, *J. Mater. Res.* 20 (2005) 1695

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[5] The full description of the procedures used in this abstract requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or are recommended by NIST or that they are necessarily the best materials, instruments, software or suppliers for the purposes described.

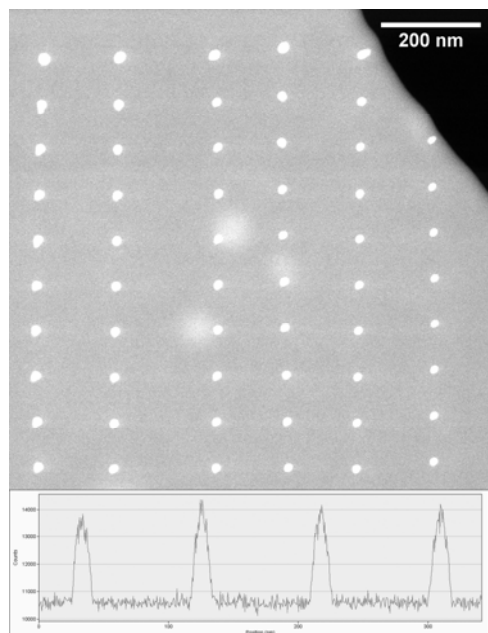


Figure 1. Annular dark field image (top) of an array of Fe particles of ~16 nm diameter deposited using

ferrocene as measured from a line profile (bottom)

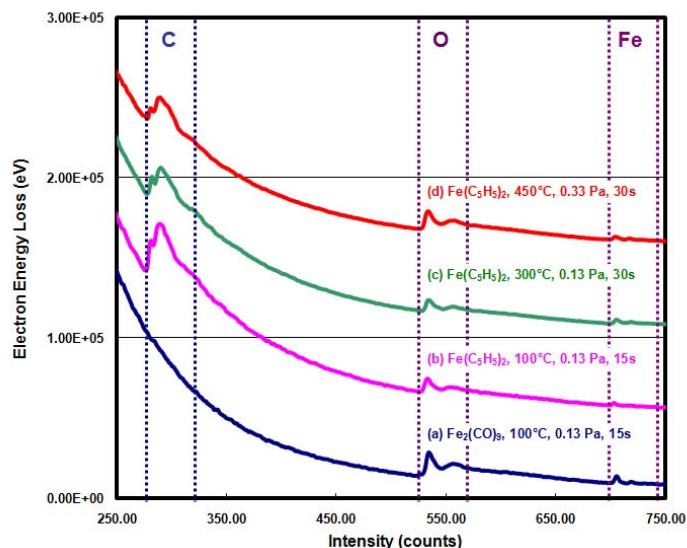


Figure 3. EELS Spectra from nanoparticles deposited using (a) diiron nonacarbonyl at 100°C, 0.13 Pa, 15s and using ferrocene at (b) 100°C, 0.13 Pa, 15s, (c) 300°C, 0.13 Pa, 30s, (d) 450°C, 0.33 Pa, 30s

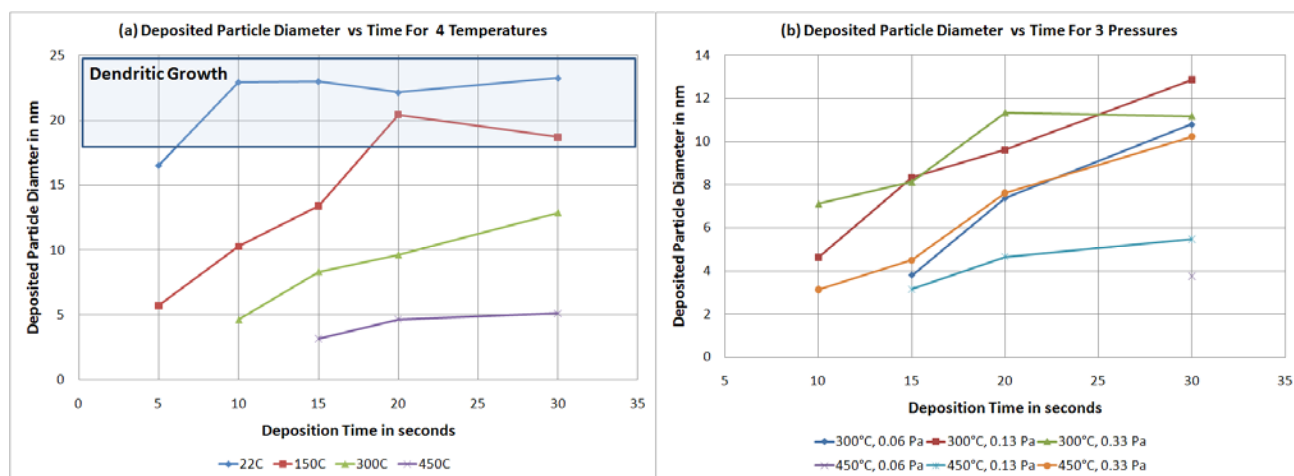


Figure 2. Diameter of particle deposited using ferrocene as a function of deposition time for (a) 4 different temperatures using 0.13 Pa inlet pressure and (b) 3 different pressures at 300°C and 450°C (for dendritic growth, the diameter is measured from the base of the deposit)