Electron Irradiation Induced Structural Changes in Nickel Nanorods Encapsulated in Carbon Nanotubes

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ABSTRACT

Nickel nanorods encapsulated inside the multiwalled carbon nanotubes were prepared using microwave plasma chemical vapor deposition (MPCVD) technique. The as prepared tubes were investigated by scanning electron microcopy (SEM), x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). HRTEM study of these tubes exhibits long, good crystalline nickel filled CNTs with well-graphitized walls. Different orientations of filled metal with respect to graphitic walls have been observed and the orientations were found to get affected by the electron accelerating voltages of 200 KeV. We report that by deliberate e-irradiation at specific sites the crystalline planes of nickel can change their orientation. With continuous irradiation for 10-15 minutes the nickel starts evolving out of the tube. We propose that metal at the tip of the tube may be exposed by employing e-beam irradiation and it may be useful to study the true electrical properties of both the multiwalled carbon nanotubes and Ni nanorod inside the tube.

Keywords: Ni nanorods, carbon nanotubes, electroplating, electron irradiation.

1 INTRODUCTION

Carbon nanotubes are the most investigated nanostructures in the research area of nanoscience and nanotechnology. These peerless nanostructures are well known for their excellent structural, electrical and mechanical properties and find their proposed applications in almost all fields varying from basic science to advance chip technology [1,2,3] and space exploration [4], however very few realized applications such as in composites, probe tips and field emission displays exist at present [5,6]. On the other hand nanoscale magnetic materials also find significant interest in the wake of their revolutionary applications in magnetic memory devices. While the stability of nanoscale materials is a critical issue, incorporation of these two important nanomaterials is inevitably interesting for both the pedagogical and experimental viewpoint. The nanotube walls protect the magnetic material against oxidation and other damages and the process of filling and interaction of filled magnetic metal with the walls of carbon nanotube itself provide insight for the various phenomena in low dimensional physics.

CVD technique has been recognized as an easy method for the synthesis of ferromagnetic metal (such as Ni, Co or Fe) nanowires or nanorods inside nanotubes as the large amount of same metal which is used as a catalyst for CNT growth can be filled in situ through controlled experimental conditions [7,8].

Besides the important and useful applications of ferromagnetic metal filled carbon nanotubes, as suggested by the experimental studies on magnetic properties of these structures, such as nanomagnets [9] and high density magnetic recording media [10,11], engineering of these nanostructures by electron irradiation is another interesting aspect. Electron beam irradiation has been employed to get atomically sharp tips and soldering through the filled metal [12].The high pressure caused by e-beam irradiation in the core of closed shell carbon structures has been found to induce the phase transition and deformation of filling material, suggesting their use as nanoextruders or high pressure cylinders [13].

In this paper we report that the electrons in HRTEM at accelerating voltage of 200 KeV can be used to study and alter the structure of both the Ni nanorod and the nanotube encapsulating them. We propose that the nanorod can be exposed at any desired site by deliberate e-beam irradiation for their further important applications such as for contact formation for electrical measurement purpose.

2 EXPERIMENTAL

Commercially available copper foils of thickness about 0.2 mm are used as substrates for the growth of nanotubes filled with Ni nanorods. These copper substrates were thoroughly cleaned and coated with nickel layers of approximately 5μm thickness by electroplating technique. The details of nickel electroplating process can be found elsewhere [14]. However no boric acid has been used to balance the pH of the nickel sulphate and nickel chloride solution. For the synthesis of these Ni nanorods encapsulating tubes the ammonia plasma treatment has been carried out at a pressure of 10 torr for 15 seconds with ammonia flow rate of 180 sccm. The plasma treatment temperature has been kept 350 ± 10^0C. The treatment of the nickel layer by ammonia (NH_3) plasma converts the nickel layer into the nanoclusters of 50-60 nm size and facilitates the filling of nickel inside the MWNTs in the subsequent growth. Feedstock gas methane (CH_4) decomposes over Ni clusters in hydrogen plasma created at the pressure of 40 torr and 800^0C temperature. The flow rates of CH_4 and H_2 have been kept 8 sccm and 40 sccm respectively. In the growth time of 4-5 minutes a good black deposition becomes visible thorough the viewport in the MPCVD chamber and the methane flow has been stopped while H_2 flow still continuing up to 400^0C in order to ensure the less amorphous carbon deposition during growth.

The diameter and length of the nickel filled tubes and hence the nanorods inside them can be controlled by the ammonia plasma treatment time and temperature and their synthesis time in MPCVD. For the ammonia plasma treatment at 350 ^0C and synthesis time about 5 minutes the diameter and length of the tube were obtained to be 20-50 nm and 1 µm-3µm respectively.

3 CHARACTERIZATION

The XRD pattern of the as grown tubes is shown in figure 1, with an SEM image in inset. The high intensity peaks are of different polycrystalline (hkl) planes of Cu and Ni, as indexed by using joint committee on power diffraction Standards (JCPDS) file numbers and 03-1005 (Cu), 04-0850 (Ni) for copper and nickel respectively. One clear peak corresponding to (002) reflection plane of HCP graphite (file no.75-2078, C) is also visible. Other graphite peak corresponding to (010) plane is also present in the pattern but not clearly visible due to the high intensities of the peak corresponding to Cu (111) and Ni (111). The graphite peaks inform the growth of carbon nanotubes on Ni electroplated Cu foil.

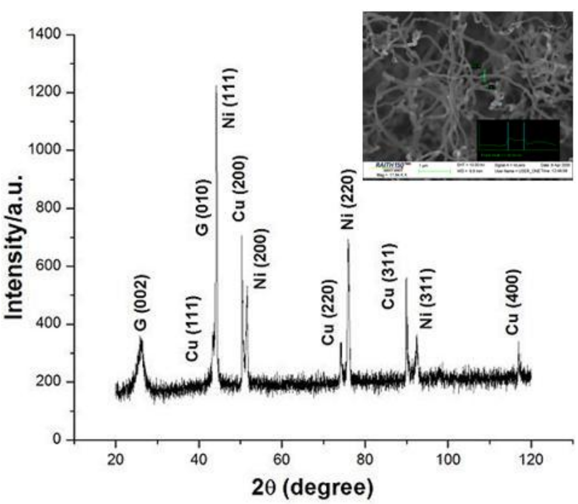

Figure 1: XRD of as grown Ni filled tubes.

The surface morphology of as grown tubes on Ni electroplated copper substrate is shown in figure 2. It has been found that large density of tubes grows in big clusters.

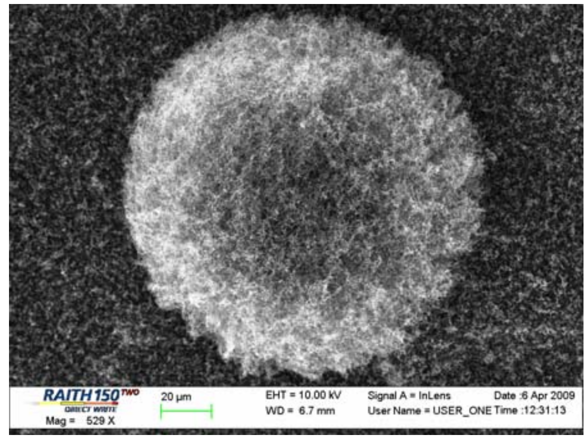

Figure 2: SEM image of Ni filled carbon nanotubes

During the optimization of growth parameters for best filling inside the tube it has been observed that the quality and density of the metal filled carbon nanotubes can be improved if the Cu foils are made rough using some sharp pin hammer before the Ni layer electroplating. And on these rough substrates the tubes deposit in a form of flower like clusters as is shown in the figure 2. We suggest that surface roughness facilitates the well separated Ni nanoclusters during the plasma treatment of Ni layer. The nanotubes grow densely over these nanoclusters rather than the other sites at the substrate.

However SEM images of the as grown Ni encapsulated tubes can show merely the morphology of tubes in bulk on the substrate and transmission electron microscopy (TEM) imaging is needed in order to see the filling inside the tube.

For the TEM investigation the as grown tubes were detached from the substrate and ultrasonicated for 15 minutes in isopropyl alcohol. Few drops from the solution containing carbon soot which includes carbon nanotubes, catalytic nanoparticles and some amorphous carbon have been dispersed on conventional copper grids used for TEM analysis. The same technique has been used to prepare sample for HRTEM analysis. In the TEM image shown in figure 3 the Ni nanorod is clearly visible inside the multiwall carbon nanotube with outer diameter of about 50 nm and the inner diameter which is the diameter of the nanorod also is about 30 nm.

4 STRUCTURAL STUDY IN HRTEM

High resolution images of Ni filled tubes were obtained using JEOL- JEM 2100 field emission electron microscope. HRTEM study of these tubes exhibits long, good crystalline nickel filled CNTs with well-graphitized walls as shown in figure 4. It has been observed that the nickel filling inside might be single or poly crystalline as shown in figure 5 and 6 respectively. We have also observed that the Ni planes can have different orientations with respect to graphitic walls. In some extreme cases they may be parallel to the tube walls (figure 5) and in some they were perfectly perpendicular with respect to the graphitic walls (not shown here). It is new observation as in the earlier reported works different planes of Ni or Ni alloys were always found to be inclined at some angle with respect to nanotubes walls [15, 16]. However in reference 17 the fcc Ni (111) planes were reported parallel to tube axis which is contrary to reference 15 where the fcc Ni (111) planes were said to always have an angle of 39.6^0 with respect to the tube axis. For The particular tube shown in the figure 5, the lattice fringes of the Ni nanorod encapsulated inside 9 graphitic walls is visible. The spacing between observed Ni lattice planes is 0.20 nm. This d-spacing corresponds to the Ni (111) planes with fcc structure. These (111) Ni planes are parallel to the tube walls and hence the nanotube axis, maintaining the same orientation and spacing throughout the tube. This indicates the single crystalline nature of filling. While in figure 6, the randomly oriented different planes of filling indicate the polycrystalline nature of Ni.

We observed that electron beam irradiation affects the orientation of Ni planes. The graphitic walls of CNT, which are more sensitive to e-beam irradiation get distorted and sometime disappear. For 10-15 minute time of e-beam irradiation, a prominent change in the Ni planes becomes visible as shown in figure 7. With continuous irradiation on particular sites the metal of that site starts evolving out of the tube.

In another interesting observation we found that, owing to the combined effect of temperature and pressure conditions at the time of growth and e-beam irradiation during TEM imaging, nickel rod may come out from the tube by breaking the walls of the tube as shown in figure 9. This type of structures are useful for making the contacts for electrical measurement in both the side wall geometry and top contact geometry as the better electrical coupling between shells of nanotubes and contacting metal can be achieved.

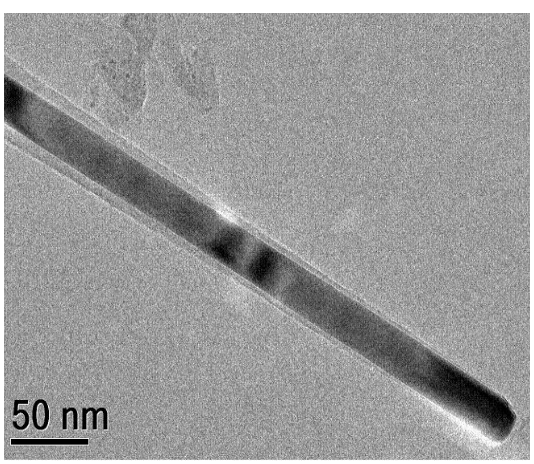

Figure 3: TEM image of Ni nanorod inside MWCNT.

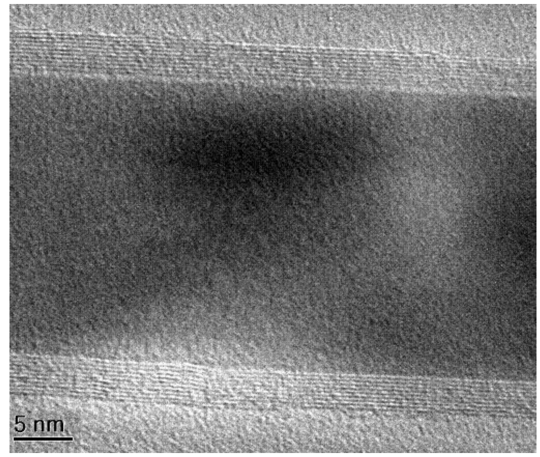

Figure 4: HRTEM image showing graphitic walls of the tube.

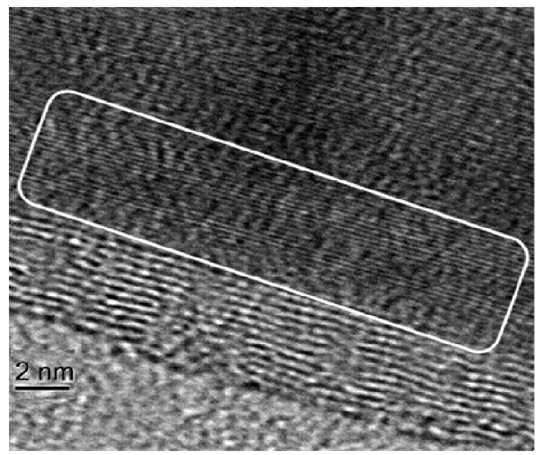

Figure 5: Single crystalline Ni planes parallel to the tube walls.

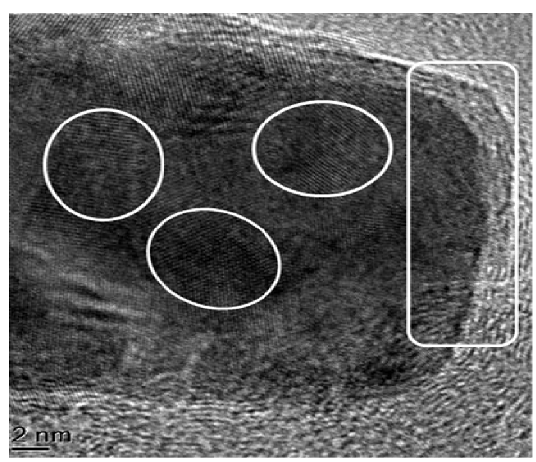

Figure 6: Polycrystalline nature of filled Ni in another tube.

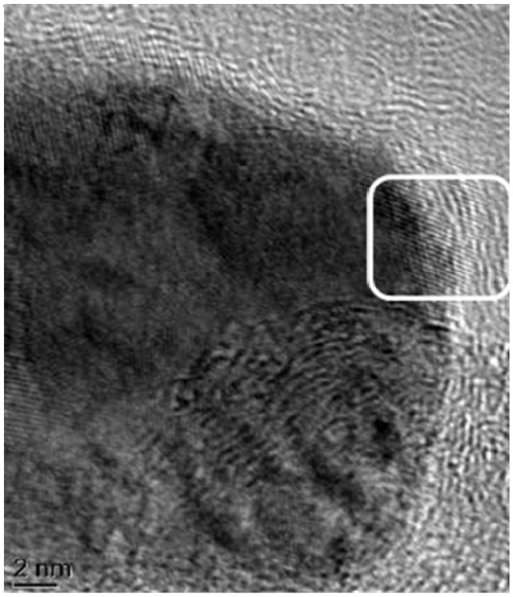

Figure 7: Evolution of Ni planes as a result of electron irradiation.

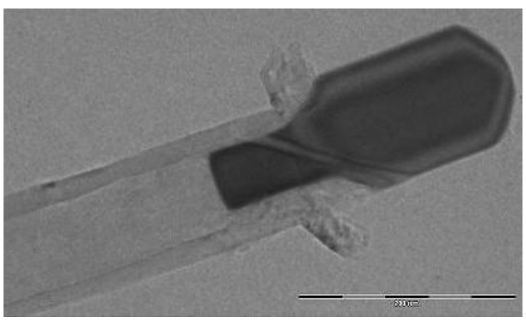

Figure 8: Ni nanorod evolving out from the tube.

5 CONCLUSION

Nickel nanorods encapsulated inside multiwalled carbon nanotubes have been synthesized by MPCVD technique. Good, uniform rod shaped filling has been obtained using the process parameters described in the present work. Different orientations of the filling metal inside the tube have been observed and found to get affected by electron beam irradiation. Electron irradiation studies done in situ in HRTEM reveal the structural changes both in multiwall structure of the carbon nanotube and the Ni nanorod inside the tube.

Our results of filling evolution during e-beam irradiation may provide insight for various phenomena related to the interaction of filling metal and nanotube walls. The so obtained CNTs with exposed metal at the tip of the tube may prove ideal for contact formation to study the electrical properties of these intriguing multiwalled structures.

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