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High density of multiwalled carbon nanotubes observed on nickel electroplated copper substrates by microwave plasma chemical vapor deposition

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Abstract

High density and long multiwalled carbon nanotubes are deposited using nickel clusters formed from an electrodeposited nickel coating treated by ammonia. Tubes of length 40–50 μm having bamboo shaped structure are aligned nearly parallel to the copper substrate. The inner diameter of the tubes is in the range 20–50 nm. The selected area and nano area diffraction spots clearly show the crystalline nature of nickel clusters. At some locations of the samples in the vicinity of graphite layers, Ni_3C phase is also detected. The formation of the Ni_3C phase that is unstable at high temperature supports the idea of a vapor–liquid–solid (VLS) mechanism for the growth of the tubes. © 2002 Published by Elsevier Science B.V.

1. Introduction

Since the first report of the observation of the carbon nanotubes [1], huge interest has been generated in the research of this novel material, promising vast potential for applications [2,3], pyrolitic [4], chemical vapor deposition (CVD) [5,6], laser ablation [7], and arc discharge [8,9] techniques have been used successfully to synthesize the carbon nanotubes. It is established that the presence of suitable clusters [10] of metals such as Ni, Co, Fe, etc. is essential for the deposition of the tubes. Several techniques [11,12] have been used and proposed for the formation of nanometer sized clusters on the substrates. It is observed [13–15] that the diameter of the tubes is related to the size of the clusters present on the substrates and therefore the generation of the nanoclusters on the growing surface has become very important for the tube synthesis. A combination of parameters such as the size of the clusters, the smoothness of the substrate, and the temperature of deposition play an important role in the synthesis of the single-wall nanotubes [16]. Several groups have also carried out a number of very careful measurements to understand the nature and the properties of the tubes. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), scanning tunneling microscopy (STM), Raman spectroscopy have proved very successful in the characterization of the tubes.

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However, despite huge research a large number of the technological and basic issues still remain to be resolved. These are mainly the origin and mechanism of the tubular growth, the deposition of oriented tubes on the substrates, the yield of various processes of carbon deposition.

In the present Letter we report the use of an innovative electroplating technique to deposit the nickel coatings and to subsequently produce clusters which catalyze the synthesis of multiwalled carbon nanotubes. The structure of the tubes is cross-sectional (bamboo shaped) because the cluster size is large. The density of the tubes is high and the diameter to length ratio (aspect ratio) is very small. We have carried out careful HRTEM measurements to study the structure of the tubes. The selected area and nano area electron diffraction patterns (SAD and NAD, respectively) have shown the presence of Ni and Ni_3C phases in the vicinity of the graphite layers.

2. Experimental

Thin copper foils are used in our case as the substrate for the nanotube deposition. The foils have polycrystalline nature and have commercial grade purity (98%) without any special pre-treatment to improve their smoothness. The electroplating of the Ni coatings on copper foils is performed in an electroplating bath whose details are described elsewhere [17]. The copper foils are used as cathode and a thin platinum wire is used as anode. Commercial grade nickel sulfate ($NiSO_4, 7H_2O$), nickel chloride ($NiCl_2, 6H_2O$) and boric acid (H_3BO_3) are used as electrolytes in a dc electroplating process. The bath temperature is maintained at 60 °C and its pH is 3.5. The Ni layers having a thickness 15 μm are treated in plasma of ammonia (NH_3) gas for 2 min prior to the deposition of carbon nanotubes in MPCVD apparatus. The temperature of the NH_3 treatment is 800 ± 20 °C and its flow rate is 180 sccm at a pressure of 20 mbar. Methane (CH_4) and hydrogen (H_2) are used as the precursor gases and their flow rates are 6 and 20 sccm, respectively. The details of the MPCVD apparatus are described elsewhere [18]. The substrate temperature (T_s) during the nanotubes growth is 840 ± 20 °C. The nanotubes are examined using SEM and HRTEM techniques. The samples for HRTEM are prepared using replica technique on a copper grid and no special treatment is required for the observation in TEM. The selected area diffraction and nanodiffraction are performed using HRTEM.

3. Results and discussion

A typical SEM micrograph of the nanotubes grown in our system is shown in Fig. 1. The tubes are long and show typical multiwalled structure. Also it is interesting to note that the density of the tubes is quite high and they appear to be aligned parallel to the substrate plane. Typically the diameters of the tubes grown using our technique (Fig. 2a) range from 60 to 110 nm. The thickness of the core region is approx. 20–30 nm while the walls are 20 nm thick. The structure of the tubes matches with that of the 'bamboo' shaped tubes [19–21] indicating that a further optimization of the cluster size may be necessary to obtain the 'smooth walled' tubes with relatively smaller diameter. An expanded high resolution picture of the graphite walls of the multiwalled tubes is shown in Fig. 2b. The spacing between the graphite planes is estimated to be 0.32 nm (Fig. 2b)

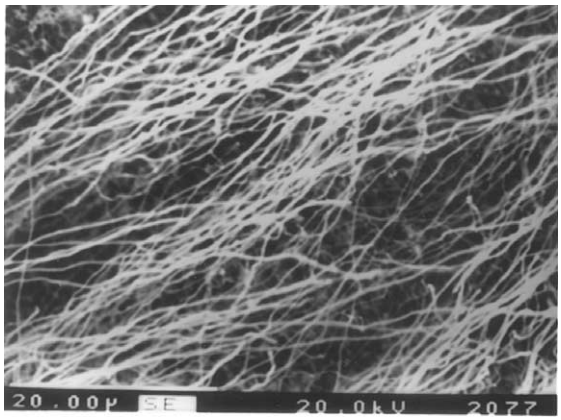


Fig. 1. SEM micrograph showing the morphology of the tubes on copper substrate. The exceptionally long carbon nano tubes nearly parallel to the substrate are noteworthy.

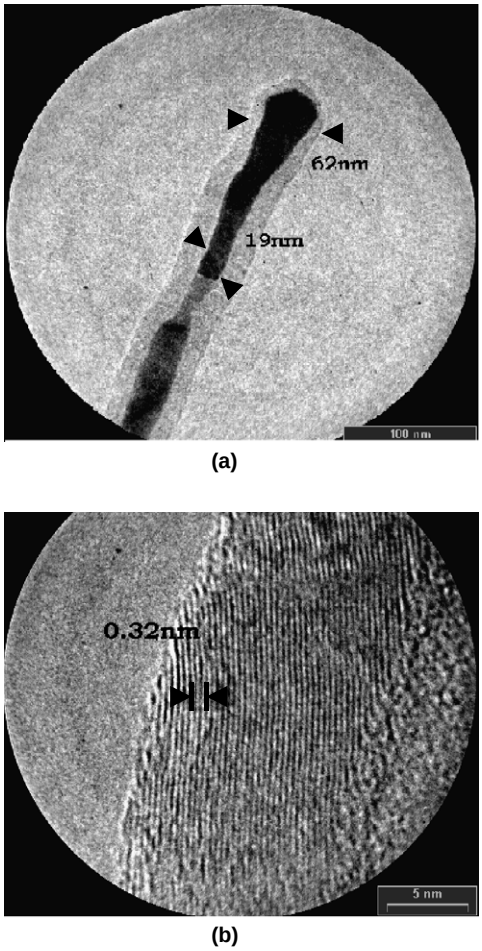


Fig. 2. (a) A magnified image of a typical bamboo shaped tube. The diameter of the core area and the walls are 18 and 22 nm, respectively. The Ni filling at the tube end can be noted. (b) HRTEM image of the graphite planes of the tube.

instead of 0.34 nm as expected from turbostratic graphite [22].

We also observe several clusters of nickel particles ranging from 8–10 nm to 100 nm) embedded in our samples. The clusters are mostly coated with graphite layers that can be observed in HRTEM. Some of the clusters are so tiny that they move under the influence of the high voltage applied in TEM. Fig. 3a,b show the positioning and distribution of the clusters observed in TEM. Graphite layers around the clusters may also be seen. At many locations amorphous or diamond like carbon (DLC) impurities are seen in or on the surface

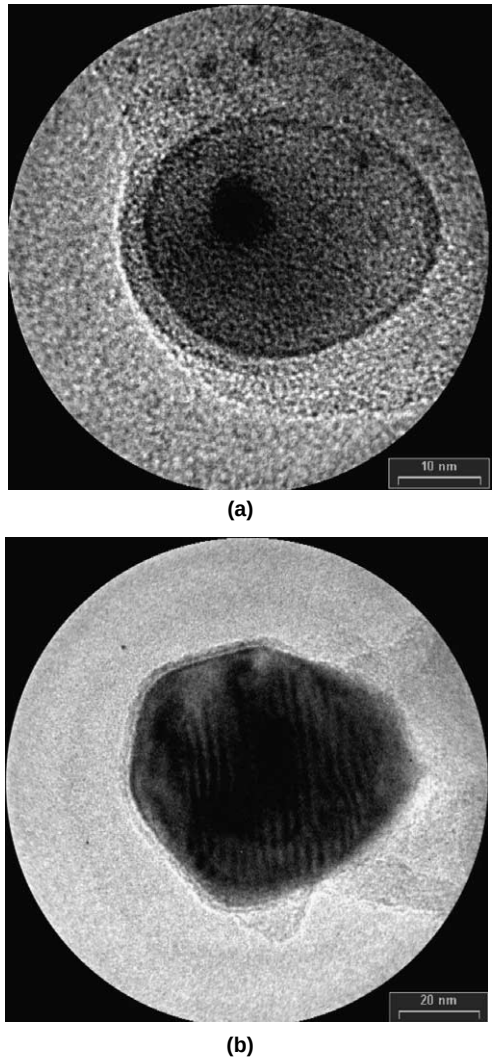


Fig. 3. (a) The location of nickel clusters (darker particles) in the HRTEM image. The dark large particle is carbon. (b) A large faceted nickel cluster showing the graphite layers around it.

of the tubes. The energy dispersive X-ray analyses (EDS) reveal the composition of the clusters to be only Ni. No other metallic impurities can be observed within the limitations of the EDS. Several areas of the metallic clusters were selected to perform SAD and NAD. The area selected for SAD was a few microns while for NAD it was in the nanometer range. Fig. 4a–c show the SAD and NAD patterns obtained with different zone axes

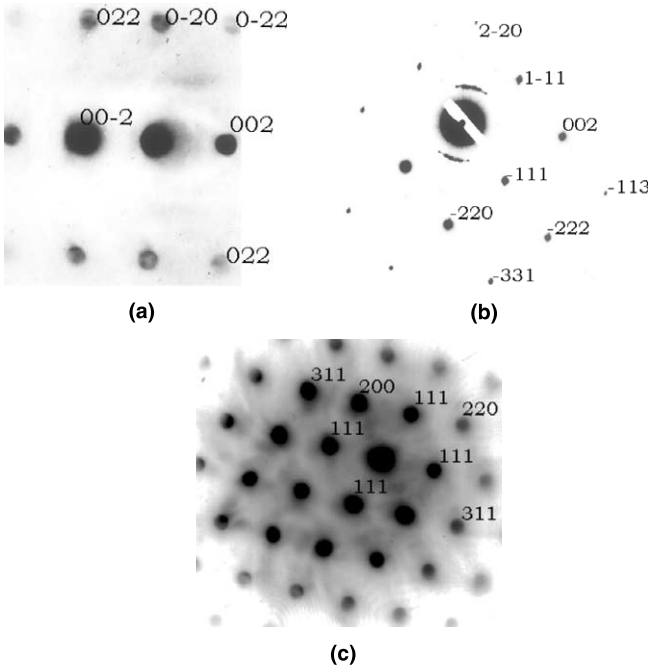
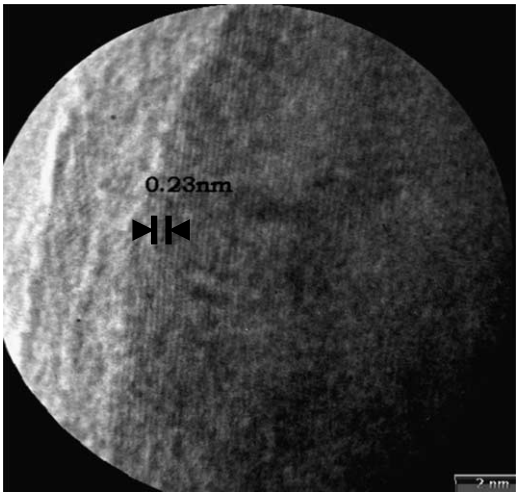


Fig. 4. (a) and (b) show the selected area electron diffraction spots on a nickel cluster with electron beam along the (100) and (110) zone axes and (c) shows nano area electron diffraction spots for nickel cluster with electron beam along the (110) zone axis.

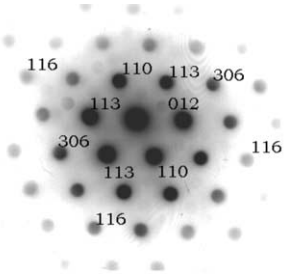
on various locations of Ni clusters. Clearly all the spots correspond to the different planes of the cubic Ni structure. While at most places we observed the Laue spots corresponding to Ni clusters at some locations amongst the clusters we also observe the formation of Ni_3C. The layers corresponding to 100 planes of Ni_3C observed in the samples at some locations are seen in Fig. 5. The separation between the layers is 0.226 nm and they appear to be relatively defects free. The NAD and SAD patterns corresponding to the Ni_3C phase are shown in Fig. 5a,b, respectively. Rings of the (012), (113) and (119) index planes are evident which means that the Ni_3C domains are mainly polycrystalline.

The formation of the carbon nanotubes in our case appears to be mostly bamboo shaped. It is, however, interesting to note that the tubes are mostly aligned parallel to substrates and are very long. The bamboo shaped tubes have mostly cross-sectional structure with the tube comprising of several sections. The large inner diameter of 20 nm (Fig. 2a) of the tubes in our case may be related to the size of the clusters. In some cases Ni cluster encapsulating one termination of the tube is observed. The nanosized clusters of Ni mostly appear to be well faceted in HRTEM pictures (Fig. 3). The faceting of the Ni particles is observed by many workers [23] and plays an important role in the growth of the tubes. The crystal facets are most likely produced during the NH_3 treatment and might be related to the differential etching rates for different crystal directions. The large clusters (of the size 100 nm), as is apparent from our study, normally do not support tubular growth and only a few graphite layers are formed around these (Fig. 3). This may be due to the fact that the weight of the cluster is too high to be supported by the tubes in the catalytic growth mode, within the assumption of a top growth model [23]. The walls of the tubes (Fig. 2b) appear defective in the present case with a high density of planar dislocations.

The SAD as well as NAD spots clearly indicate the structure of the clusters to be cubic nickel. Fig. 5a,b correspond to SAD whereas Fig. 4c correspond to NAD patterns. The Laue spots are ob-



(a)



(b)

Fig. 5. (a) The HRTEM image of the planes of Ni_3C. The spacing of 0.226 nm match closely with (100) planes of Ni_3C. The faint image of graphite planes can also be seen in the vicinity. (b) Shows the nano area diffraction spots of the Ni_3C phase.

tained with different zone axes. The formation of Ni_3C phase is however observed near some of the clusters. This is interesting in view of the fact that the Ni_3C is well known to be difficult to form. The spacing between the layers of Ni_3C is measured to be 0.226 nm and matches well with the 100 interplaner spacing of cubic nickel carbide. The NAD and SAD patterns corresponding to the carbide phase are shown in Fig. 5a,b, respectively. The Laue spots are obtained with zone axis $\langle 110 \rangle$ and $\langle 100 \rangle$, respectively. Strong reflections from (113), (306), (110), and (116) planes of Ni_3C are seen. We should mention here that this phase never appears to be pure Ni_3C but a mixture of Ni and Ni_3C phases as the faint reflections of Ni could also be obtained in the pattern. Also the (111) reflections of the Ni fall at the same position as (113) reflections of Ni_3C. The formation of a Ni_3C phase appears to be interesting as the deposition conditions at the time of CVD are not conducive. It must therefore be formed during the cooling phase at 200–450 °C, as the nickel carbide phase is not thermodynamically stable at high temperature. This will however support the vapor–liquid–solid (VLS) growth model mechanism for the growth of nanotubes implying that the carbon saturation of the nickel particles occurs during the CNT growth [24].

4. Conclusions

The 'bamboo shaped' exceptionally long multiwalled carbon nanotubes are deposited using electroplated nickel coatings as catalyst. The capping of tubes with nickel is observed in few cases. The nano area and selected area electron diffraction spots indicate the cubic structure of nickel particles. At some locations the evidence for the synthesis of Ni_3C phase is also found having interesting consequences for the growth models.

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