Effect of Titanium on the Growth and Field Emission Properties of MPECVD Grown Multiwalled Carbon Nanotubes

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ABSTRACT

The growth behavior and enhanced field emission properties of multiwalled carbon nanotubes were investigated using Ti as an underlayer and over layer. Ti of 10 nm thickness was deposited underneath Fe catalyst and their interaction behavior was observed for growth of carbon nanotubes. It was observed that underlayer deposition of Ti improves the growth of CNTs by acting as a barrier. In the other set of studies, Ti film of extremely small thickness (15 Å) was post deposited over CNTs to investigate their field emission behavior. The turn on and threshold field values of Ti modified CNTs were found to be low $\sim$ 0.8 V/μm and 2.65 V/μm, respectively, as compared to pure CNTs. HRTEM studies confirmed that Ti nanoclusters on post deposition adsorbs on the edges and walls of CNTs. This improved adhesion and bonding with CNTs is due to the unfilled d-shell of Ti, resulting in the modification of CNTs structure.

Keywords: *Carbon nanotubes (CNTs);; Micro Raman spectroscopy; High Resolution Transmission electron microscopy (HRTEM); Field Emission.*

1 INTRODUCTION

Carbon nanotubes (CNTs) are of special interest due to their promising applications in field emission displays [1-2], nanoelectronics [3-4], hydrogen sensing [5] and fuel cells [6]. Both the electrical properties and geometrical aspects (alignment, diameter, length, etc) are critical factors in device fabrication. The electronic properties of the CNTs differ considerably and depend upon the defect structure, aspect ratio, configuration etc. To grow CNTs of desired characteristics is a real challenge. Thus, to grow CNT of desired characteristics, various metal underlayers have been used.

It is widely accepted that Fe, Ni and Co and their alloys or compounds show the highest catalytic activity for the growth of CNTs [7]. In addition to this, underlayer deposition is also employed for the growth of CNTs. Various metals (Pt, Mo, Ti, Al, and Au) have been used as underlayers for the growth of CNTs. The underlayer metal must not react with the catalyst to form alloys at CNT growth temperatures, which may poison the catalyst in the reaction [8].

On the other hand top coating on CNTs also leads to modification in their properties. Composite materials made of metals or metal oxides and CNT have gained much importance, as it results in the modification in the electrical, structural and mechanical properties of carbon nanotubes through orbital hybridization and thus results in the passivation of defect sites. Recently, various studies have been carried out to modify the electrical and structural properties of CNTs, by coating of various metals, oxides and fluorides such as Ru, Pd, ZnO, RbF, CrO_3 [9,10,11,12].

In this paper we report the results of experiments concerning the MPECVD growth of Fe and Ti-Fe catalyzed multiwalled carbon nanotubes. Ti was used as under layer to study the growth of CNTs. In other set of studies, Ti was used as top layer to investigate the field emission behavior of CNTs.

2 EXPERIMENTAL DETAILS

In the first set of studies, Ti was used an underlayer. MWCNT samples were synthesized using tubular microwave plasma enhanced chemical vapor deposition (MPECVD) [13]. Ti of 10nm thickness was pre deposited on p-type Si wafer that acted as an underlayer. Fe of 10 nm thickness was deposited on Ti coated Si wafer by thermal evaporation at the base pressure of 3×10^{-6} torr. The samples were pretreated in the presence of hydrogen and argon plasma at 720^0C for 15 minutes at 2.5 torr. The microwave power of 550 W was applied to generate the plasma at 1 torr. CNTs were grown on passing acetylene over Ti-Fe catalysts. The reactant gases were a mixture of hydrogen and acetylene with a ratio of 1:5 at a pressure of 5 torr.

In the second set of studies, Ti was used as a top layer. Pristine MWCNTs were grown by the above mentioned method using 10 nm thick Fe as a catalyst. As deposited CNTs were named as A. In the second set, CNTs were modified by Ti coating 15 Å thicknesses. The Ti decorated CNTs were named as B.

The surface morphology of MWCNTs were characterized by scanning electron microscopy (SEM: ZEISS EVO 50) operating at 20 kV accelerating voltage by secondary electron imaging. Carbon films were scratched from the substrate and ultrasonicated in acetone at least for 15 minutes so that CNTs could disperse properly. Few drops of the suspension were then transferred on to carbon coated copper grid. Their microstructures were analyzed by transmission electron microscope (TEM: Philips CM 12) and high resolution TEM (HRTEM: Technai G^2 20 S-Twin model) operating at 200 kV. Energy dispersive analysis of X-rays (EDAX) was carried out for the elemental analysis. Micro Raman studies (Micro-Raman T64000 Jobin Yvon triple monochromator system) of the samples were carried out at an excitation wavelength of 514.5 nm to analyze the structure of the samples. Field Emission measurements were carried using a diode set up in the vacuum chamber at $2x10^{-6}$ torr. CNTs were used as cathode and stainless steel plate was used as anode. Emission current density was determined by dividing current with the area of the sample.

3 RESULTS AND DISCUSSION

3.1 Ti as an underlayer

The results are discussed when Ti was used as an underlayer.

3.1.1 Surface Morphology and Structure of CNTs

First, we study the effect of catalyst (Fe) film on the growth of CNTs. As seen in Fig 1(a), the size of the particles varied from 20-100 nm. Breaking of pure Fe film into nanoparticles is due to the continuous collisions of active ions in the plasma with the film and due to heating in the plasma; nanoparticles of Fe agglomerate and become isolated bigger nanoclusters on which he growth of CNTs take place. Figure 1(b) shows the SEM image of Ti-Fe nanoparticles, formed after plasma treatment.
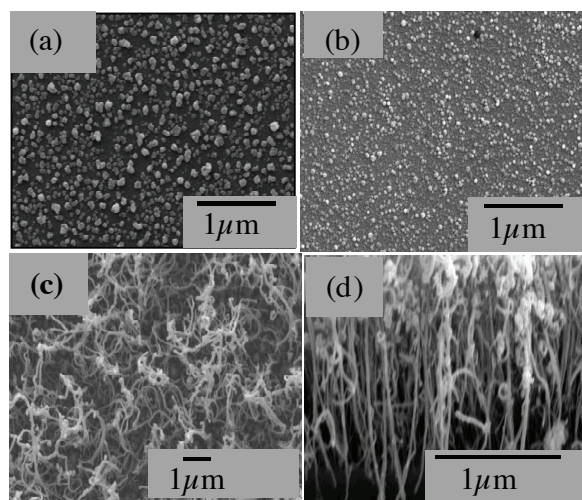

Figure1: SEM images showing (a) Fe nanoparticles (b) Ti-Fe nanoparticles (c) CNTs grown on Fe catalyst (d) CNTs grown on Ti-Fe catalyst.

The thickness of Ti as an underlayer and Fe as catalyst film was kept 10 nm.

Fe deposited on Si forms iron silicide that hinders the growth of CNTs. In order to prevent the iron silicide formation upon heating the samples to 700 °C, a layer of Ti
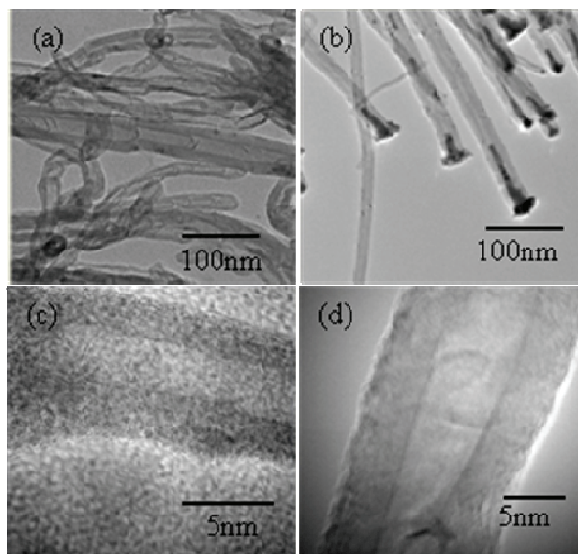

Figure2: TEM micrographs showing (a) Fe catalyzed CNTs. (b) Ti-Fe catalyzed CNTs. HRTEM images showing planes of (c) Fe catalyzed and (d) Ti-Fe catalyzed CNTs.

was pre deposited onto the Si wafer prior to the deposition of Fe film. Ti underlayer acts as a buffer layer and prevents the formation of iron silicide and thus optimize the growth of CNTs. Two intermetallics are formed between Fe and Ti depending on the concentration of particular metal. In our studies, CNTs grow on the nanoparticles of Fe rich phase. Further no growth of CNTs could be seen on Ti covered substrates without Fe. According to Sun et.al, there is not much strong interaction occurs between Fe and Ti underlayer [8]. This leads to the growth of CNTs on Ti-Fe catalyst.

The surface morphology of Fe based CNTs and Ti-Fe based carbon films can be seen in fig 1(b) and 1(c). It can be inferred that CNTs grown on Ti-Fe catalyst are much denser than Fe catalyzed films. Also, CNTs are vertically aligned through this combination of catalysts.

TEM images, in Fig. 2 shows the Fe and Ti-Fe catalyzed CNTs. Fe catalyzed CNTs have bamboo shaped, having diameter in the range of 20-30 nm, as seen in Fig. 2(a and c). From Fig. 2(b and d), Ti-Fe catalyzed CNTs are stacked up nanostructures having diameter 30-40 nm.

3.2 Ti as top layer

The results are discussed when Ti was used as a top layer.

3.2.1 Microstructure of pristine and Ti coated MWCNTs

Fig. 3 (a and b) shows the HRTEM images of pristine and Ti coated CNTs. HRTEM studies of Ti coated MWCNTs were carried out to observe the effect of defect passivation. In the present study, it is observed that due to very thin coating of Ti (15Å), Ti nanoparticles gets adsorbed on the CNT walls, because of the presence of certain defects. The defects reduce the cohesive energy of Ti to a negative value which improves its adhesion of Ti to the CNT walls [14]. Incorporation of Ti overcomes the defects and thus enhances the emission and crystallinity of CNTs.
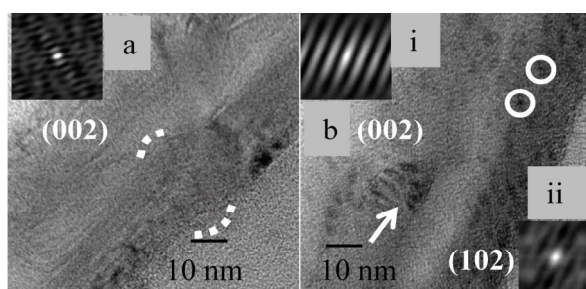

Figure3 HRTEM images showing (a) defect planes in bare MWCNTs and (b) Ti decorated MWCNTs, where Ti nanoparticles have been encircled. Inset: (a) MWCNT planes (b) (i) MWCNT planes; (ii) Ti planes.

3.2.2 Micro Raman spectroscopy of pristine and Ti coated MWCNTs

Fig. 4(a) shows the first-order Raman spectra of pristine and Ti coated CNT samples (A and B). Two major peaks observed at 1355 cm^{-1} and 1584 cm^{-1} are referred to as D and G-band [15, 16]. In addition, a shoulder peak, referred to as D^*, is evident towards the higher wave number side of the G-band peak, located at 1625 cm^{-1}.
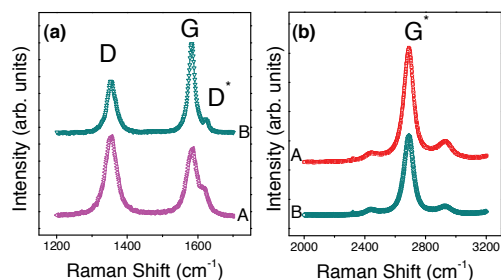

Figure4 (a) First-order Raman spectra showing the increasing order of crystallinity of samples A and B where (A) pristine CNTs (B) Ti coated CNTs of thickness 15Å. (b) Second- order Raman spectra showing decreasing D^* mode of samples A and B.

The D-band corresponds to the defects and structural disorders in polycrystalline graphite. The G-band corresponds to the tangential vibrations of carbon atoms. The intensity ratio of the D band to G band (I_D/I_G) is used as one of the parameter to ascertain the degree of crystallanity of CNT samples. The I_D/I_G ratios are 1.24, and 0.57 for the samples of A and B respectively. It is clear that Raman spectra exhibit a decreasing trend in the I_D/I_G ratio of Ti coated CNTs. This trend with increasing Ti thickness corresponds to the increased crystallanity of CNTs and decreased sp^3 bonded carbon. It was found that Ti coated CNTs were more crystalline than the pristine CNT samples. This was possibly due to passivation of defect sites and resulting changes in local order. The peaks at 2689 and 2691 cm^{-1} are referred to as G^* mode of the pristine and Ti coated CNTs, respectively, that corresponds to the second-order overtone of D mode, seen in Fig. 4(b).

3.2.4 Field Emission Studies

The field emission behaviour of pristine and Ti coated CNTs was investigated using diode setup. The emission characteristics were studied at a distance of 200 μm between the cathode and anode.
Field emission behaviour was analyzed using Fowler-Nordheim (F-N) equation [17]:

$$J = (A\beta^2 E^2 / \varphi) \exp (-B\varphi^{3/2} / \beta E) \quad (1)$$

where, J is the emission current density; φ the work function, E is the electric field and β the enhancement factor.
The F-N plot is obtained by plotting between ln (J/E^2) and 1/E. The enhancement factor was calculated from the slope of F-N plot by considering the work function of CNTs as 5 eV [18, 19]. Fig. 5 (a and b) shows the emission current density versus electric field (J vs. E) and Fowler- Nordheim plots (F-N) plots for the samples A and B respectively. A significant change in field emission behaviour of pristine and Ti coated CNTs were observed, as seen from Fig. 5 and table 3. The turn on field at 10 μA/cm^2, as seen in Fig.5(a) is found to be 1.8, and 1.4 V/μm for samples A and B. The threshold field at 1mA/cm^2 for the same samples was found to be 4.0, 2.1 V/μm (Fig. 5(b)). The field emission properties of Ti coated CNTs were enhanced as compared to pristine CNTs. This is due to the lower work function of Ti (4.29 eV) as compared to CNTs (5.0 eV). As very thin layer (15 Å) of Ti is coated on CNTs, Ti nanolusters adhere on the tip and edges of MWCNTs, thus shifting the Fermi level towards the higher energy side. The presence of Ti nanoparticles is expected to reduce the local surface work function of CNT film leading to the enhancement in the electron emission. This leads to the increase in the field enhancement factor. Consequently, the density of states increases near the Fermi level resulting in the enhancement of tunnelling current.
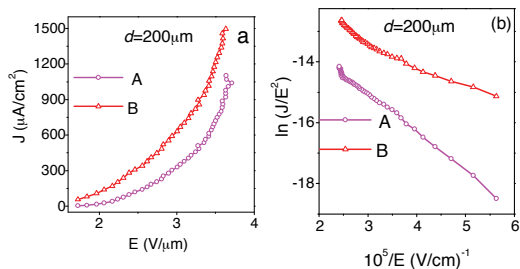
Figure5 (a) J vs. E plot for samples A and B at the distance of 200 μm (b) corresponding F-N plot. *d* is the distance between the cathode and anode. The turn on and threshold field values are taken at 10 μA/cm^2 and 1mA/cm^2.

4 CONCLUSIONS

In conclusion, we have reported the role of Ti on the growth and enhanced field emission properties of multiwalled CNTs. Ti, as an under layer improves the growth of CNTs without poisoning the catalysis, and as top layer improves the emission characteristics and crystallanity of CNTs as compared to pristine CNTs. It was observed that Ti coated CNTs have low function and higher field enhancement factor as compared to pristine CNTs. The enhancement in the field emission properties of Ti coated CNTs was due to the shifting of the Fermi level towards the higher energy side that lead to the increase in the density of states near the Fermi level resulting in the enhancement of tunnelling current.

ACKKNOWLEDGEMENTS

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