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Water–Assisted Synthesis of Long, Densely Packed and Patterned Carbon Nanotubes

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A systematic approach has been adopted to synthesize, long, densely packed, and patterned, multi wall carbon nanotubes (MWCNTs) using water assisted-chemical vapor deposition (WA-CVD) technique. Initially, the growth of MWCNTs has been carried out on Fe/Al/Si multi-layer samples, under the standard- and WA-CVD conditions. Under the WA-CVD conditions, the height of MWCNTs gradually increased form 28 ± 5 to 533 ± 30 μm with subsequent increase in the growth temperature from 650 - 900°C. Details of the growth conditioning have been discussed. Furthermore, the growth of MWCNTs has been investigated by varying the growth time from 10 to 60 min at two temperature regime 700°C and 800°C. The growth rates have been estimated which shows gradual decrease in their magnitude with sequential increase in the growth time. The MWCNT patterning has been demonstrated. The results offers insight to use such MWCNTs for future device interconnects applications. The details of the analysis are presented.

Key words: water–assisted chemical vapor deposition, carbon nanotubes, characterizations, long growth, patterns

1. INTRODUCTION

Since after the discovery of super-growth of single walled carbon nanotubes using water[1], a considerable amount of work related to the water assisted-chemical vapor deposition (WA-CVD) synthesis of the carbon nanotubes (CNTs) has been carried out[2]. The introduction of a small and controlled amount of water into the growth ambient of standard CVD enhances and preserves the activity as well as lifetime of the catalyst particles[3-4], which in turn increases the synthesis efficiency of the CNTs resulting densely packed, impurity-free and vertically aligned CNT forests[5-6].

Here in, we describe a systematic approach to synthesize MWCNTs using the water assisted–chemical vapor deposition (WA-CVD) technique. Initially, the Fe/Al/Si substrate has been fabricated using the routine electron beam evaporation technique. These samples were subjected to the standard as well as WA-CVD synthesis to grow MWCNTs[8-9]. The temperature has been varied from 650 to 900°C and the growth time is kept constant ~10 min. Following this, the samples have been subjected to the scanning electron microscopy (SEM). The analysis revealed that the introduction of controlled and small amount of water dramatically affect the growth of height. Furthermore, at two temperature regime, 700°C and 800°C, the growth of carbon nanotubes has been studied at the variable growth time. The growth time was varied from 10 to 60 min. The SEM analysis revealed that, the over all height of nanotube has been increased at high temperature regime[10-14]. The growth rate has been estimated. The WA-CVD facilitates the grown of densely packed, vertically aligned MWCNT forest. In our case, the optimum height of MWCNTs (> 500 μm) has been achieved at 800°C in 30 min, using WA–CVD process. To obtain MWCNT patterns, initially, two p–type silicon wafers have been taken and one of them was used to construct a porous mask. The pattern growth has been achieved using such masks. The details are presented.

2. EXPERIMENTAL

2.1. Deposition of multi-layers

Initially, a p-type Si wafer of thickness ~ 550 μm has been cleaned chemically by immersing in tri chloro acetate solution and sonicated for a period of ~15 min. Following this, the wafer has immersed in acetone for ~10 min for sonication. After acetone cleaning, in similar fashion, the wafer has been cleaned in methanol solution and (deionized) DI water and kept under dry atmosphere for the deposition process. The cleaned wafer has been subjected to the electron beam (e-beam) evaporation process to obtain ~15 nm thick Al layer with a deposition rate of ~ 0.1 - 0.2 Å - s^{-1} for a period of five hours. Following this, the wafer has been subjected to deposit Fe catalyst layer of thickness ~1 nm using e-beam

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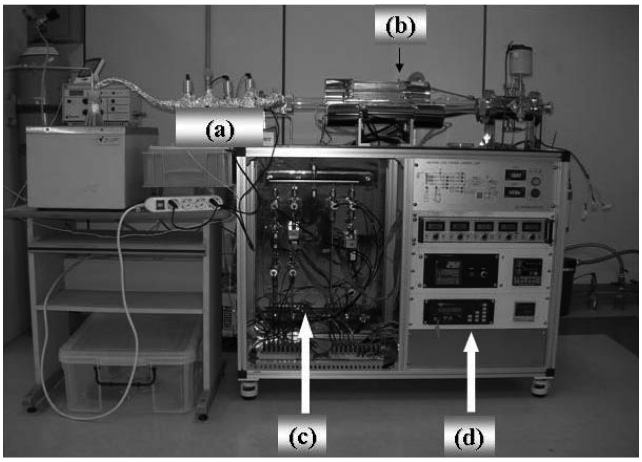
evaporation technique. The Fe deposition process has been carried out in an identical fashion as that described above. To avoid surface oxidation and contamination, the prepared samples were kept under high vacuum conditions maintained at ~10^{-6} Torr.

2.2. Growth of carbon nanotubes using water-assisted-chemical vapor deposition technique

The existing water assisted chemical vapor deposition (WA-CVD) set up at SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, is shown in Photograph 1. Portion (a) shows the water bath coupled to the CVD furnace. The water bath is maintained at 60°C coupled to argon gas injection. Portion (b) shows the rapid thermal heating system and horizontally mounted quartz tube (diameter ~5 cm and length ~70 cm), coupled to the rapid thermal heating system. Part (c) shows the mass flow controller and gas lines systems. The mass flow of the feed stocks and dilatants and Ar is controlled electronically and part (d) shows the corresponding control panel for the WA-CVD system.

A few Fe/Al/Si samples were subjected to the standard- and water-assisted chemical vapor deposition (WA-CVD) technique to grow CNTs. A few samples have been loaded in the thermal reactor and the reactor was evacuated to a base pressure of ~20 mTorr. The reactor temperature was raised with a ramp rate of ~200°C/min. Acetylene (C_2H_2) feed stock was used along with argon (Ar) as a carrier gas and the flow rate of Ar/C_2H_2 was maintained at 500 sccm / 180 sccm. The water vapor concentration in the CVD chamber was controlled by bubbling a small amount Ar gas (250 sccm) through water. The water bath was maintained at a constant temperature ~60°C. In all the experiments, the water concentration in the furnace tube was maintained constant until the CVD process was terminated. The growth of the CNTs was carried out at a temperature of 650 - 900°C, for a period of ~10 min. In the standard-CVD process, the synthesis of CNTs has been carried out in identical fashion as that of WA-CVD process without supplying water, to verify the effect of water on the growth rate of CNTs.



Photograph 1. Existing water assisted chemical vapor deposition set up at SKKU Advanced Institute of Technology (SAINT), Sungkyunkwan University.

The surface morphology of samples has been characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The optimized WA-CVD conditions have been used to synthesize CNTs patterns to demonstrate interconnects via.

3. RESULTS AND DISCUSSION

Two typical SEM micrographs recorded for (a) standard-CVD (scale bar: 10 μm) and (b) WA-CVD (scale bar: 100 μm) grown MWCNTs (growth temperature 800°C) are shown in Fig. 1. From Fig. 1(a)-(b) a considerable amount of difference has been observed in the growth behavior of CNTs. In Fig. 1(a), the CNT films attain a height of 70±2 μm, while in Fig. 1(b) the height of CNT film is 533 ± 5 μm. These results clearly demonstrate that the introduction of the water increases the CNT growth rate by nearly one order of magnitude at a temperature ~800°C. For water-stimulated catalytic activity results in the growth of dense and vertically aligned MWCNT forests with height 533±15 μm in just 10 min. The growth of MWCNTs is continuous with no stacks formation. In contrast, with standard-CVD grown MWCNTs the catalysts are active for about one min. In general, the activity and lifetime of the catalyst are dramatically enhanced by the addition of the controlled amount of water vapor in the growth ambient with the assumption that: a) the catalyst shows identical activity, (b) the increase in yield (and thus the height of forests) is directly proportional to the number of active catalysts and (c) the number of catalyst that decay is proportional the number of active sites. Furthermore, balancing of the relative levels of acetylene and water, as well as those of acetylene and argon, is also crucial for achieving long-time activity of the catalyst. A close examination at the ledge of the MWCNT forest (SEM not shown) illustrates that the nanotubes are densely packed and vertically aliened from the substrate. High-resolution transmission electron microscopy (TEM) studies of the standard- and WA-CVD grown MWCNTs (Fig. 1(c)-(d), respectively) reveals the presence of only thin nanotubes and the absence of metallic particles and supporting materials that usually comprises a major constituent of standard-CVD grown MWCNTs. Furthermore, high-resolution TEM analysis reveal that, the diameter of nanotube grown by standard-CVD process varies from 10 to 25 nm, where as for the WA-CVD grown nanotubes have diameter in the range 5 to 10 nm. Moreover, WA-CVD grown nanotubes are clean MWCNTs free from amorphous carbon and metal particles. We have recorded more than fifty high-resolution TEM micrographs, and dou-

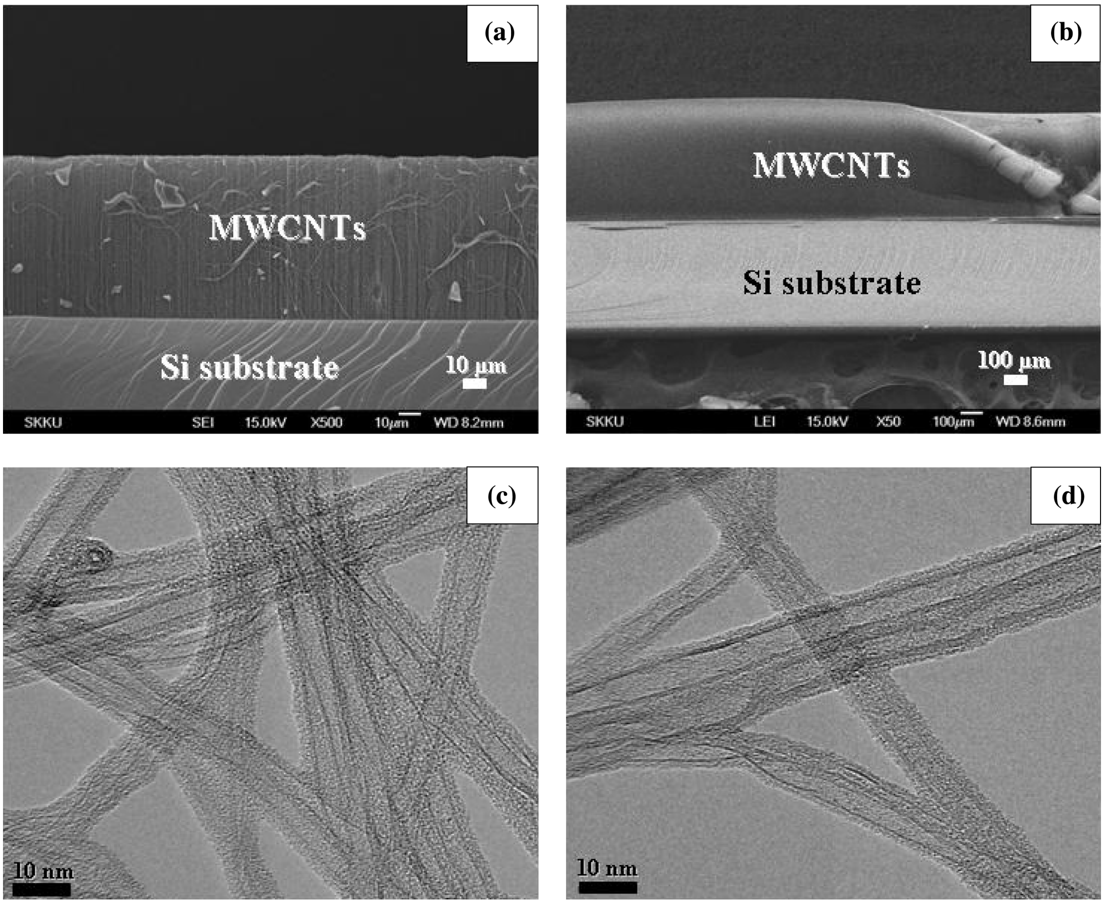


Fig. 1. Recorded SEM micrographs for (a) standard- and (b) WA-CVD grown MWCNTs (Scale bar for: (a) 10 μm and (b) 100 μm). Recorded TEM micrographs for (c) standard- and (d) WA-CVD grown MWCNTs (growth temperature: 800°C).

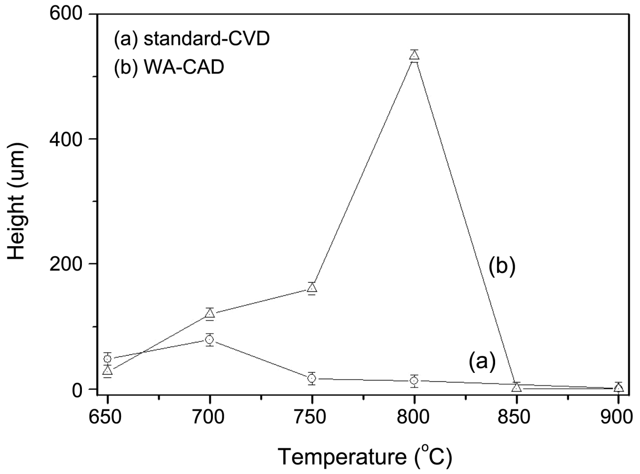


Fig. 2. Variation in height of MWCNTs as a function of temperature for (a) standard- and (b) WA-CVD grown MWCNTs.

ble- or single walled-CNTs have rarely been observed. The growth conditions optimized at 800°C have been used for constructing the MWCNT patterns.

Figure 2 shows the variations in the height of CNTs as a function of growth temperature for (a) standard- and (b) WA-CVD grown CNTs (growth time ~10 min). One can see that, at lower temperature (650°C), the variations in the height of CNTs is marginal for the CNTs grown by both the techniques. Further, it has been observed that height of the CNTs gradually increases from 28±5 μm to 533±15 μm with sequential increase in temperature from 650°C to 800 °C, for WA-CVD grown CNTs. However, standard-CVD grown CNTs does not show any peculiar trend in the height variations over this temperature range. In case of conventional growth process, initially, the elongation of Fe catalyst particle takes place along with the formation of graphene sheets at the graphene-Fe interface, their basal planes oriented parallel to the Fe surface. The formation of over–layer graphene on the Fe-catalyst during CVD reduces the activity and lifetime of the catalyst, which in turn affect the growth rate and height of the CNTs[15]. However, for WA-CVD process, water acts as a weak oxidizer that selectively removes amorphous carbon from Fe catalyst clusters without damaging the CNTs at the growth temperature. As a result, the growth rate of CNTs has observed to be increased from ~2.8 μm-min^{-1} to ~53.3 μm-min^{-1} with subsequent increase in the temperature. However, an abrupt decrease in the growth rate, ~0.1 μm-min^{-1}, has been observed at temperature regime 850-900°C. It seems that, at this temperature regime the effect of water is insignificant, since no variation in CNTs grown is observed. This indicate that, beyond the optimum temperature, the growth rate characteristics decreases abruptly, which could be attributed to the poisoning of growth process from excess water that might be caused by oxidation of the catalyst or the carbon nanotubes. The growth rate of CNTs is observed to be identical, ~0.1 μm-min^{-1}, at higher temperature range for the samples subjected to the water and without water CNT growth. It can be seen that, the height of CNTs is observed to be 405 ± 10 μm with maximum growth rate ~53.3 μm-min^{-1}, for water assisted CVD process, where as, without water the growth rate is limited up to ~1.3 μm-min^{-1} with average height 13 ± 5 μm.

Figure 3 shows the variations in the height of MWCNTs as a function of growth time at (a) 700°C and (b) 800°C growth temperature. The growth has been carried out using the WA–CVD technique. It can be seen that, for the plot (a), the height of MWCNTs increases gradually from 120 ± 15 to 161 ± 20 μm with sequential increase in growth time from 10 to 60 min. Furthermore, an overall increase in the height of MWCNTs is observed for the nanotubes grown at relatively high temperature (800°C) and is shown in the plot (b). Plot (b) shows, the height of nanotubes increases from 405±10 to 533 ± 15 μm with subsequent increase in growth time from 10 to 30 min. Thereafter the trend of increase in the height of MWCNTs does not hold well and decrease in the nanotube height is observed 481 ± 30 μm. More comments can be made on this issue by computing the growth rates of the MWCNTs. The growth rates have been computed. Figure 4 shows the variations in the growth rates (measured in μm-min^{-1}) as a function of growth time for the MWCNTs grown at (a) 700°C and (b) 800°C. Plot (a) indicate that, the initial growth rate for the MWCNTs is 12 μm-min^{-1} for growth time 10 min and gradually decreased down to 5.07 μm–min^{-1} and finally to 2.69 μm-min^{-1} with subsequent increase in growth time from 30 min to 60 min. However, plot (b) indicates that, at the high temperature the overall growth rate is increased. Plot (b) shows, for 10 min of growth time, the nanotubes grows with a rate 40.5 μm-min^{-1} and observed to be decreased down to 17.76 μm-min^{-1} for 30 min and finally achieve the value 8.017 μm-min^{-1} for 60 min of growth time. Thus, in both the cases the growth rate gradually decreases, however, at higher temperature the tendency to decrease growth rate is drastic. This indicates that, the catalyst poisoning process at high temperature is dominant mode to reduce the catalyst activity which in turn affects the growth rate markedly. We have surmised in a first approximation that the optimum growth condition to obtain long MWCNTs is 800°C with 30 min of growth time. This condition has been used further for obtaining the patterns of the nanotubes on Si substrate.

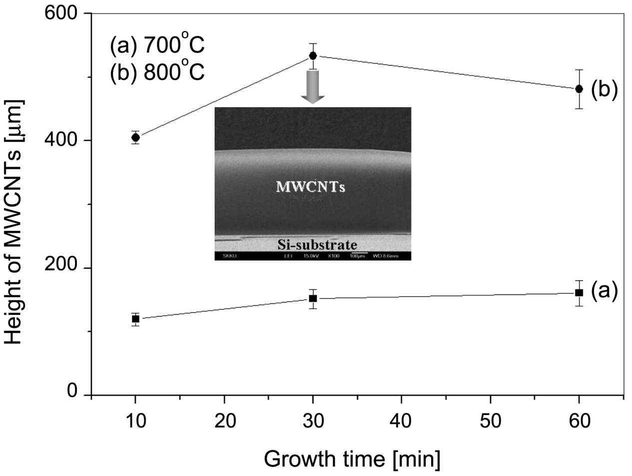


Fig. 3. Variations in height of MWCNTs as a function of growth time at (a) 700°C and (b) 800°C growth temperature. The MWCNTs has been grown by the WA–CVD technique. Inset shows the recorded SEM micrograph for maximum height of the MWCNT-film grown at 800°C.

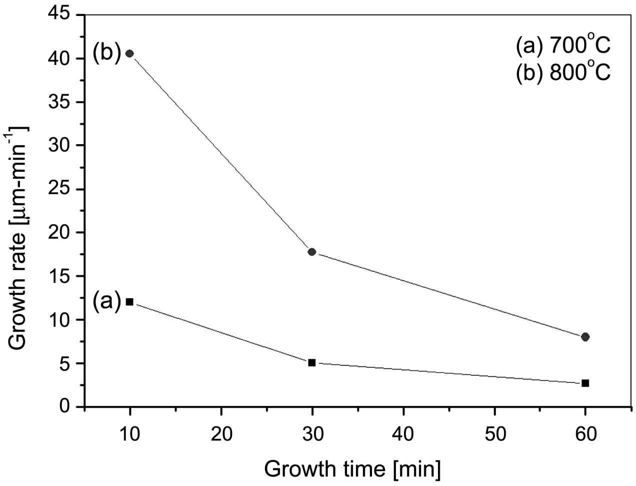


Fig. 4. Estimated growth rate (in μm–min^{-1}) for MWCNTs grown at (a) 700°C and (b) 800°C.

To demonstrate this, we have used two silicon wafers, one as porous patterning mask and other to deposit the MWCNTs. Initially, a p-type silicon wafer of thickness ~ 550 μm has been patterned using the negative photoresist (PR). The deep etching upto ~350 μm, from the surface, has been carried out followed by the removal of the PR. The etched wafer has been subjected to the chemical mechanical polishing that facilitates the separation of the pattern porous structure from the silicon wafer. The polished side has been used as a mask to deposit Fe catalyst on other Si wafer. After assembling the porous mask on the Si substrate the system has been subjected to the e–beam evaporation to obtain Fe layer of thickness ~1 nm. The deposition has been carried

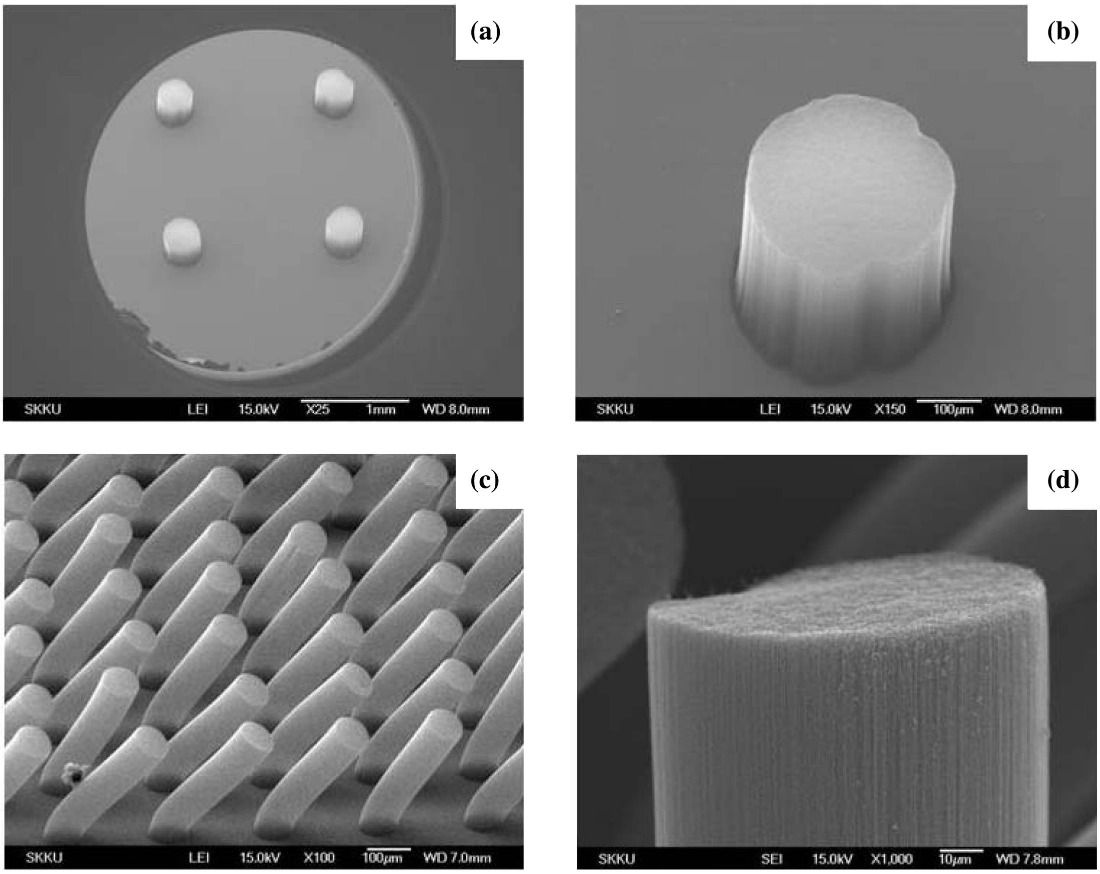


Fig. 5. Typical SEM micrographs for MWCNTs patterned on Si substrate. Photograph (a) 300 μm pillar diameter, and (b) 100 μm pillar diameter.

out for 10 in with deposition speed of ~ 0.2 Å-s^{-1}. After Fe deposition, the mask has been removed and Si wafer was subjected to WA-CVD technique, to synthesize MWCNTs, at the optimized conditions mentioned above. Al barrier layer has been used due to its better adhesion and favorable conduction properties beneath the Fe catalyst layers. Figure 5 shows four typical SEM micrographs recorded for shadow mask growth of MWCNTs. Figure 5(a) shows the growth of MWCNTs via a mask of pore diameter ~ 300 μm and (b) shows corresponding details of the nanotube pillar, where as photograph (c) shows the pore diameter of mask ~100 μm. It can be seen that, tower–like MWCNTs has been grown. The result offers insight to use such technique for interconnects application.

4. CONCLUSIONS

In summary, water–assisted synthesis of long, densely packed and patterned MWCNTs has been carried out. Initially, a few Fe/Al/Si samples were subjected to the standard- and water-assisted chemical vapor deposition (WA-CVD) technique to grow the MWCNTs. The synthesis of nanotubes has been carried out under standard as well as WA-CVD conditions over the temperature range 650-900°C. The SEM results revealed that, the height of nanotubes increases with increasing temperature and at a temperature of 800°C, the maximum height of ~533 μm has been achieved by the MWCNT film. Furthermore, the growth time has been varied from 10-60 min and the growth of nanotubes has been carried out at two temperature regime 700°C and 800°C. The SEM analysis of showed that, the over all height of nanotubes is increased. At this temperature regime, the growth rate has been estimated. For the regime of 700°C the growth rate decreases monotonically from 12 to 2.69 μm-min^{-1}, where as the over all growth rate is observed to be increased at high temperature regime of 800°C. The growth rate for this regime also decreases monotonically from 40.5 to 8.017 μm-min^{-1}, however, the decrease in the growth rate is drastic as compared to the lower temperature regime. The patterned growth of MWCNTs has been achieved on the Si wafer by using shadow mask catalyst deposition technique. The result offers insight to use such long, densely packed, patterned nanotubes as the vias in layer-by-layer electronic interconnects.

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