Effect of buffer layer deposition on diameter and alignment of carbon nanotubes in water-assisted chemical vapor deposition

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ABSTRACT

Vertically aligned carbon nanotubes (CNTs) grown by water-assisted chemical vapor deposition have revealed differences in structure and morphology depending on the deposition rate of the Al buffer layer. Rearrangement of the Fe catalyst during CNT growth is mainly influenced by the buffer layer topography, which in turn depends on the buffer layer deposition rate. A higher deposition rate makes the substrate rougher and causes the growth of more aligned, low diameter CNTs with greater height. In contrast, slow deposition results in a smooth surface, which grows misaligned, large diameter CNTs with less height. Based on the results, a CNT growth model has been proposed.

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1. Introduction

The recent advance in the growth of vertically aligned carbon nanotubes (CNTs) by chemical vapor deposition (CVD) promises various novel applications such as high strength yarns, multi-functional scrolls, torsional artificial muscles, electron emitters, viscoelastic materials, etc. [1–5]. In such applications, the key nanoscale characteristics of CNTs, such as diameter, packing, and alignment, as well as their collective order and arrangement at higher length scales, must be controlled. Despite the interest in the controlled growth of carbon nanotubes, several long-standing questions remain about how ensembles of catalyst nanoparticles respond to processing variables such as choice of substrates, choice of buffer layers, choice of catalyst, growth temperature, gas flux, choice of hydrocarbon gas, and partial pressure. Factors controlling the nucleation efficiency, diameter, wall number, alignment and

chirality of nanotubes remain critical not only for vertically aligned nanotube forests, where macroscopic parameters are developed, such as inter connected nanotubes for spin-capable CNTs, but also in nanoscale electronics, where individual nanotubes are desired.

A variety of parameters can affect nanotube diameter and quality, including the substrate, buffer layer, catalyst composition, type of feedstock gas, partial pressure of feedstock gas, annealing, effects of oxidant or inert background gas, etc. [6–18]. The annealing and gas environment deeply influence the catalyst size distribution, which determines the morphologies of the corresponding CNT arrays [13]. The partial pressure of the carbon feedstock has also been shown to play a major role [14–18]. Cheung et al. showed not only that catalyst particle size governs the diameter of resultant nanotubes but also noted the important role that reactant partial pressure plays in determining the distribution of nanotube diameters that grow from polydisperse particles [14]. Larger diameter nanoparticles were shown to require higher partial pressure to nucleate and grow correspondingly larger diameter nanotubes. Lu et al. showed that by lowering not only the carbon feedstock rate but also the temperature, small diameter single wall CNTs could selectively be grown from a wide distribution of catalyst nanoparticle diameters and proposed an optimal carbon feeding rate to grow single wall CNTs from different diameter nanoparticles, with overfed nanoparticles shutting down growth due to over coating with carbon and underfed particles never nucleating [15]. In water

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assisted-CVD (WA-CVD) the addition of H_2O is observed to inhibit Ostwald ripening due to the ability of oxygen and hydroxyl species to reduce diffusion rates of catalyst atoms together with the selective removal of amorphous carbon around the catalyst, resulting in an enhanced catalyst lifetime with a narrow diameter distribution of grown CNTs [19,20].

The supporting layer beneath the catalyst is known as the buffer layer and it plays an equally important role in controlling the growth characteristics of CNTs. Various materials, such as Al, Al_2O_3, Ti, TiO_2, TiN, Cr, SiO_2 and MgO can be used as buffer layers [21–28]. These layers can prevent the diffusion of catalyst atoms into the substrates, improve the adhesion of CNTs to the substrate and influence the characteristics of the resulting CNTs. A considerable amount of work related to the buffer-layer-mediated growth of CNTs has been carried out. Cao et al. [21] examined the substrate-selective growth of CNTs. de los Arcos et al. [22,23] observed the influence of the buffer layer on the characteristics of CNTs by carrying out in situ X-ray photoelectron spectroscopy (XPS) measurements. Amama et al. studied the lifetime, activity, and evolution of Fe catalyst supports on different types of alumina films, such as sputter deposited alumina films, electron-beam deposited alumina films, annealed electron-beam deposited alumina films, and atomic layer deposited alumina films [28]. They found that low Ostwald ripening, mild substrate diffusion rates and high porosity are the key parameters for sustained growth of CNTs, which can be achieved using sputtered and electron-beam deposited alumina films. However, the critical parameters, such as the deposition rate of the buffer layer, which can influence the substrate morphology, catalyst distribution and characteristics of grown CNTs, are missing in the literature.

In the previous studies, it was found that the number of walls and the alignment of the CNTs in the CNT forest could be controlled by the Fe thickness. Correlation between the surface roughness, catalyst agglomeration, number of walls in the CNT and the alignment of the CNTs in the CNT forest was observed [29]. In another study, the substrate surface morphology, catalytic diffusion and buffer layer oxidation were found to be dependent on the annealing temperature of the buffer layer, which ultimately affects CNT growth [30]. Importantly in this study, we found that different deposition rates of the Al buffer layer give different substrate morphologies, which affects the Fe catalyst particles' distribution and agglomeration during the CNT growth in WA-CVD. The grown CNTs showed changes in the diameter, height and alignment with variation of the deposition rate of the buffer layer. It is believed that this study presents a new insight into how to grow CNTs more efficiently using WA-CVD.

2. Experimental

A chemically cleaned, 500-μm-thick n-type Si (1 0 0) wafer with a 4 nm native oxide layer was used to deposit an 18-nm-thick Al-buffer layer. Four kinds of Al buffer layer were deposited at room temperature (substrate temperature) by varying the Al deposition rate, viz. 0.1, 0.2, 0.3 and 0.4 Å/s, using electron-beam deposition. The deposition rate was monitored using a quartz crystal sensor fixed inside the electron-beam deposition chamber. The electron-beam deposition chamber was evacuated to $\sim 3 \times 10^{-6}$ Torr prior to the deposition. The substrate was removed from the deposition chamber and cut into several identically sized pieces for further studies. Some of the substrates were reloaded into the deposition chamber for the Fe catalyst deposition. The Fe catalyst was deposited at a rate of $\sim$0.1 Å/s to a thickness of 2 nm. The substrate was then removed from the deposition chamber and again cut into several identically sized pieces for CNT growth using WA-CVD.

Details of the existing WA-CVD process are reported elsewhere [18]. Briefly, in typical experiments, after loading the samples, the CVD chamber was evacuated to <0.01 Torr. Then Ar, H_2O vapors and C_2H_2 were injected into the CVD reactor at room temperature. No H_2 was used in this process. A rapid thermal heating system was used to reach a temperature of 700 °C in 6 min and CNT growth was carried out at 2.42 Torr for a further 10 min. After removing the samples from the reactor, they were analyzed by scanning electron microscopy (SEM; JSM6700F, JEOL) to determine the height and morphology of the CNT forest. The height was measured at various places and the average height was taken. For the high resolution-transmission electron microscopy (HR-TEM; JEOL 300 kV) observations, the CNTs were removed from the substrates, dispersed in methanol and drop coated onto a copper grid. In typical HR-TEM observations, each sample was analyzed at 50–60 places and the number of walls and the inner diameter were noted. The statistical distribution of the numbers of walls in the CNTs was calculated (Fig. S1; Supporting Information).

The effect of the CNT growth temperature on the topography of the buffer layer was studied using simulated CNT growth conditions. The substrates (with only a buffer layer) were heated at CNT growth conditions (i.e. at 700 °C for 10 min w/o C_2H_2). The annealed samples and the as-deposited samples were studied for surface topography using atomic force microscopy (AFM; SPA-300HV, SII Nanotechnology Inc.) operating in the tapping mode with a scan rate of 2 Hz using Si_3Ni_4 tip cantilevers with a tip curvature radius of less than 10 nm. The cantilever oscillation frequency was set as $\sim$312 kHz. The height, amplitude, and phase data were acquired simultaneously for a scan size of 5 μm $\times$ 5 μm. The images acquired were flattened to remove any tilt in the image, and statistical roughness analysis was performed on the same scale of 5 μm using the SPMLabAnalysis V7.00 software. In all measurements, grain heights as opposed to widths were measured because heights are unaffected by the variations in the tip radius, and the minimum cutoff particle height used for analysis was 0.1 nm.

3. Results and discussion

It was observed that the structural and morphological properties of CNTs were dependent on the buffer layer deposition rate. It was observed that buffer layer samples with deposition rates of 0.1 and 0.2 Å/s grow CNTs with 5–10 walls, with an abundance of 8-wall CNTs, whereas samples with deposition rates of 0.3 and 0.4 Å/s grow CNTs with 4–9 walls, with an abundance of 6-wall CNTs (Fig. S1; Supporting Information). Typical 8-wall CNTs grown using 0.1 and 0.2 Å/s deposition rate-buffer layer samples are shown in Fig. 1(a) and (b). The inner diameter of the CNT grown using the 0.1 Å/s deposition rate-buffer layer sample is 9.39 nm. The inner diameter of the CNT grown using the 0.2 Å/s deposition rate-buffer layer sample is 7.37 nm. A further increase in the deposition rate decreases the inner diameters of CNTs. Typical 6-wall CNTs grown using 0.3 and 0.4 Å/s deposition rate-buffer layer samples are shown in Fig. 1(c) and (d). For the 0.3 Å/s deposition rate-buffer layer sample, the CNT shows an inner diameter of 7.18 nm, whereas for the 0.4 Å/s deposition rate-buffer layer sample the CNT shows an inner diameter of 3.7 nm. Similarly, CNTs with 4–10 walls showed a trend of decreasing inner diameter with increasing deposition rate of the buffer layer. The dependence of the CNT diameter on the deposition rate of the buffer layer is plotted in Fig. 2.

Generally, in high temperature CVD growth, it is assumed that the catalyst size governs the CNT inner diameter, but in the present study the catalyst thickness was kept constant and the deposition rate of the buffer layer was varied. Our results suggest that the deposition rate of the buffer layer might have played an important role in controlling the catalyst diameter. It will be worthwhile to