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Role of water on the surface-guided growth of horizontally aligned single-walled carbon nanotubes on quartz

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ABSTRACT

The role of water in carbon feed on the surface-guided growth of horizontally aligned single-walled carbon nanotubes (HA-SWCNTs) was investigated. It is shown that the amount of water can be optimized to favor HA-SWCNT growth, which is proposed to be due to selective etching of carbon deposits at carbon-metal interface. Without water, nanotube-nanotube interaction and carbon accumulation at the interface are disproportionately large compared to the rate of nanotube growth, leading to catalyst deactivation. With excess water, suppression of nanotube growth occurs, resulting in reduced carbon yield on the surface. Intermediate carbon/water feed ratios achieve cleaner growth with high efficiency.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) are promising candidates for advanced electronic applications ranging from field effect transistors and interconnects to thin-film electrodes and flexible circuits [1–3] due to their outstanding electronic properties, such as high mobility and high current capacity. In order to realize the potential advantages of SWCNTs, they must be integrated into devices at high densities without losing their intrinsic properties. Efforts to make such high density films from as-synthesized SWCNTs have involved a variety of methods including Langmuir–Blodgett [4], layer-by-layer deposition [5], and spin coating [6]. An alternative method, surface-guided growth of horizontally-aligned SWCNTs (HA-SWCNTs) that utilizes the crystal structure of the substrate to align the nanotubes, may be an effective route towards integrating nanotubes into devices. HA-SWCNTs have been found to grow on a variety of substrates (ST-cut quartz [1], silicon oxide [7], and R-cut sapphire [8]) using chemical vapor deposition (CVD) under a variety of conditions and with different catalysts [9–12]. Films with uniform densities over full wafers have been produced, leading the way for integration into active devices using lift-off transfer techniques [13]. However, in order to achieve large current output from such devices, the tube density must be increased. Efforts have been underway to reach this goal, such as sequential chemical vapor depositions [14].

In many reports using CVD synthesis, HA-SWCNTs were grown using CH_4 or C_2H_4 as the carbon feed source and Fe as a catalyst [15]. However, using ethanol as carbon feed source has been shown to give equal or better results than CH_4 [14,16] and for this reason ethanol was used for this work. It is expected that at the high temperature of the nanotube growth, ethanol decomposes to carbon containing species and water [17]. Therefore, the improved performance of ethanol over pure hydrocarbons might be ascribed to the *in situ* production of water. In fact, some authors have reported improved nanotube growth by directly adding small amounts of water to the ethanol feed. For example, Qian et al. reported the growth of unusually long and well-oriented SWCNT arrays from ethanol mixed with 1-3% water using Fe-Mo nanoparticles as catalyst [18]. Similarly, incorporation of water during the growth of SWCNT forests has shown significant improvement in the tube growth rate [19]. Several mechanisms accounting for the water enhancement have been proposed, including: water-induced oxidation of the catalyst surface [20], inhibition of the Ostwald ripening of the catalyst [21], and etching of carbon coatings around the catalyst particles [22].

While the addition of water has resulted in well-documented enhancement in the growth of vertical SWCNT arrays [19–22], a similar comparison has not been made for the surface-directed growth of HA-SWCNTs. In this work, we have grown HA-SWCNT arrays using as carbon feed pure ethanol and ethanol mixed with 1%, 3%, and 5% water by volume. These results show that the addition of water improves the CNT growth efficiency, but only for the lower concentrations. At the higher concentrations, a decrease in





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tube density is observed. The role of water in the growth of HA-SWCNTs is analyzed and attributed primarily to carbon etching.

2. Experimental

The HA-SWCNTs were grown on 8 mm \times 16 mm pieces of STcut single crystal quartz wafers (Hoffmann Materials). To prepare the catalytic substrates, the wafers were first annealed in air at 800 °C for 8 h and then arrays of Fe lines 0.3 nm thick were fabricated on the substrates using standard photolithography lift-off processes as described by Kim et al. [2], (except in this work the Fe was deposited thermally from a Fe-wrapped W filament instead of an electron-beam evaporator). Finally, the Fe-containing substrates were annealed at 900 °C in air to form iron oxide nanoparticles. Growth of HA-SWCNTs was carried out in a CVD system previously described [23-25]. The substrates were placed in a quartz reactor inside a Lindberg/Blue furnace and heated to 925 °C in hydrogen to reduce iron oxide metallic iron. Upon reaching 925 °C, a carrier gas mixture of Ar and H₂ (3:1) was passed over the sample at a total flow rate of 35 sccm. Subsequently, ethanol (pure or premixed with a pre-established amount of water) was injected from a syringe pump at rate of 0.27 ml/h for 20 min through a heated port into the carrier gas entering the reactor.

The resulting HA-SWCNT arrays were characterized by a Zeiss 960 scanning electron microscope (SEM) and by atomic force microscopy (AFM) using a Digital Instruments Nanoscope III or Topometrix Explorer, operating in tapping mode. It should be noted that, although the nanotubes were easily observed by this conventional SEM, we could not measure tube diameters or differentiate two tubes lying close together due to the relatively large diameter of the electron beam compared to the diameter of the nanotubes (sub nm to 5 nm as measured by AFM). Thus, all linear densities derived from SEMs constitute a minimum value. A concern with the AFM measurements in contact and tapping modes is whether the measurement may partially collapse the sample and distort the value. However, the forces provided by normal tapping mode AFM (\sim 1 nN) are less than those required to collapse the nanotubes (\sim 40 nN) [26].

3. Results and discussion

Figure 1 shows SEM images of the HA-SWCNT arrays grown from: (A) a pure ethanol feed, and (B) from an ethanol feed with 1% water content. The pure ethanol feed, Figure 1A, shows a significant number of short SWCNTs, having their growth stopped before bridging the gap between two consecutive catalyst lines. In addition, a considerable portion of substrate surface was depleted of SWCNTs. The average tube density on this sample was approximately $0.6 \ \mu m^{-1}$, as measured by SEM. Moreover, a peculiar feature is clearly apparent. Many of the nanotubes took a sharp bend during growth, producing a 'hockey stick'-like structure. The density of these defects was about $0.2 \ \mu m^{-1}$.

A significantly different growth is observed in the presence of the feed containing 1% water, see Figure 1B. In this case, the substrate surface is covered by a dense array of SWCNTs that are long enough to bridge the gaps between catalysts lines (50–500 μ m). An average density (SEM) of around 1.25 μ m⁻¹ was found on these substrates. Another notable feature of the 1% water feed sample is that the density of hockey-stick structures is substantially reduced, averaging less than 0.03 μ m⁻¹.

While addition of 1% water had a positive effect, higher concentrations resulted in deterioration of the quality of the arrays. Figure 2A and B show the HA-SWCNT arrays obtained with addition of 3% and 5% water in the feed, respectively. While both samples showed aligned tubes, the density and homogeneity of the arrays was significantly reduced. The tube density was below 0.4 μm^{-1} for 3% water and even lower for 5%.

The diameter distributions of SWCNT arrays, obtained by AFM measurements, on samples grown with and without water addition are compared in the histograms of Figure 3. While the distribution of diameters seems to become narrow with the addition of water, no obvious trend in diameter is observed. That is, the presence of water does not result in a clear increase or decrease in nanotube diameter.

To further elucidate the effect of water on the production of SWCNTs and to isolate the water's effect to the growth or postgrowth stage and to the catalyst or SWCNTs, we conducted consecutive reactions on the same Fe/quartz substrate. First, the substrate was exposed to a mixture of ethanol with 3% water at 925 °C to initiate nanotube growth. Then the substrate was re-calcined at 900 °C in air to burn off the newly formed SWCNTs. HA-SWCNTs were then grown on the substrate using ethanol and 1% water feed. If the high water content affects the structure of the catalyst, the subsequent growth with 1% water feed should be significantly different from that of a freshly patterned substrate. However, as shown by the SEM images in Figure 4, the result of re-growth with 1% water on the pretreated substrate is similar to that of the 1% water feed shown in Figure 1. That is, the pretreatment in ethanol with 3% water does not cause an irreversible change on the catalyst that could explain the significant differences observed with 1% and 3% water feeds.

It is also interesting to evaluate the effect of treating with excess water an array that was previously grown under optimal (1% water feed) conditions. If the deleterious effect of water was on the tubes that have already been grown, then the effect of excess water in the feed source should be clear, as the existing nanotubes would be destroyed. However, as shown in Figure 5, the array that was produced with the ethanol/1% water feed was barely affected by a post-treatment in a pure water feed. A useful result of this post-treatment is that, while the HA-SWCNTs lying on the gap remained unaffected, those on the surface of the Fe catalyst lines were gasified and removed. That is, water is only active where Fe is present to catalyze the water–gasification reaction and is not active on fully-grown nanotubes.

From these results obtained with our HA-SWCNTs, we can examine some of the mechanisms suggested for water-assisted growth of SWCNTs recently proposed in the literature. One mechanism frequently considered is that water is an inhibitor of Ostwald ripening of catalyst particles. It has been claimed that the oxygen and hydroxyl species can lower the migration rates of metal atoms along the substrate [21]. Thus, the presence of water would prevent sintering of metal particles and consequently deactivate the catalyst. This effect should then result in a reduction of SWCNT diameter with an increasing amount of water because Ostwald ripening leads to larger catalyst particles and thus nanotubes of larger diameters [27]. However, as illustrated in Figure 3, no clear trend in nanotube diameter was observed with increasing water concentration in the feed.

Another mechanism considered is the water-induced oxidation of the Fe catalysts [20]. Sato et al. [28] have reported that pre-oxidized Fe catalysts can improve growth efficiency of CNT forests. However, their proposed explanation is probably only applicable to Si substrates, where the improved growth efficiency was ascribed to the prevention of the iron silicification by water oxidation of the iron catalyst into iron oxide. This phenomenon should not take place on quartz substrates.

A mechanism more consistent with the results of this contribution is the role of water as a carbon-etching agent catalyzed by the metal [20]. It should be noted that this mechanism may also involve surface oxidation of the catalyst, but only as a transient



Figure 1. SEM images of HA-SWCNT array grown with: (A) a feed of pure ethanol and (B) an ethanol feed containing 1% of water. The lower images (C and D) of (A and B) are enlarged sections of the upper images as shown.



Figure 2. SEM images of HA-SWCNTs grown from: (A) ethanol feed with 3% water and (B) ethanol feed with 5% water.

species. The Fe-group metals are well-known catalysts for the water-vapor gasification of carbon (so called catalytic hydrogasification [29–31]). One of the most generally accepted mechanisms for this reaction is the oxygen-transfer mechanism, which is supported by a 'volcano correlation' that exhibits a maximum in catalyst activity as a function of free energy of formation of the corresponding oxides. That is, the most active catalysts are those with intermediate oxide stability. These catalysts form oxides relatively easily, but the oxides are not stable enough to avoid decom-

position. As a result, the proposed steps in the water-assisted carbon etching process are as follows:

$$Fe + H_2 O \rightarrow Fe(O) + H_2 \tag{1}$$

$$Fe(0) + C \rightarrow C(0) + Fe \tag{2}$$

$$C(0) \rightarrow CO$$
 (3)

$$C+H_2 O \rightarrow C O+H_2 \tag{4}$$



Figure 3. Histogram of the diameter distribution (± 0.5 nm) for arrays grown with three different feeds, using tapping mode AFM. (Inset) AFM micrograph of the 0% water growth.

In this mechanism, the oxygen transfer from Fe to C (step 2) has been found to be the rate-limiting step and its activation energy depends on the type of metal catalyst used, which reflects the importance of the metal oxide stability in this reaction [30]. Eq. (4) represents the overall gasification reaction.

Encapsulation of the metal catalyst by carbon is generally considered to be the root cause of SWCNT growth termination [21,32]. Excessive carbon accumulation leads to faster deactivation and shorter HA-SWCNTs. This is most likely to occur using a pure ethanol feed, which upon decomposition produces some water, but also ethylene and acetylene. As a result, the overall carbon/water balance is still high and a rapid deactivation occurs. In the presence of the right amounts of water (around 1% in this case), excess carbon deposits are etched away, leaving catalyst particles active for continuous incorporation of C atoms into the growing nanotube. With excess water (in this case, 3% or 5%) the elimination rate of carbon from the catalyst surface is approaching the accumulation rate so that the growth of nanotubes is prevented. This situation is analogous to the case of water-assisted growth of SWCNT



Figure 4. (A and C) SEM images of HA-SWCNT arrays grown with an ethanol feed containing 3% of water; (B and D) arrays re-grown over the same substrate as (A), but with 1% water in the feed. Red circles in (A and B) denote the areas in (C and D). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Figure 5. SEM images of samples after water injection for 5 min. The inset in (A) illustrates the image before the water injection, which shows a much higher emission from the catalyst stripes, covered with nanotubes. The emission from these areas is greatly reduced after the water treatment, due to the loss of SWNT.

forests, for which it has been shown that the growth efficiency is optimum at intermediate carbon/water ratios [33].

The appearance of the hockey stick structures and their elimination by the addition of water deserves further discussion in light of the proposed operating mechanism. It has been shown that water only plays a role in the presence of the metal catalyst. Thus, the appearance or elimination of these structures with a change in the feed-source water content strongly suggests that these defects are produced at the nanotube/metal interface. The immediate consequence of this conclusion is that tip-growth is operative in this case.

It is generally believed that the nanotube orientation on ST-cut quartz is surface guided, i.e., through the interaction between the substrate surface lattice and the precipitated carbon shell on the outer surface of the metal cluster [11], or between the substrate surface lattice and the carbon nanotubes [34–36]. An irregular accumulation of carbon on the growing tip (catalyst particle) will lead to a local distortion in the carbon shell or tube morphology, disrupting the carbon shell- or nanotube-substrate interaction and breaking the substrate alignment. Thus the creation of this defect would cause the observed bending and the characteristic hockey stick structures. By contrast, when water is introduced at the right carbon/water ratio, the unwanted carbon excess is etched away by the metal-catalyzed hydrogasification reaction, keeping a stable and uniform carbon concentration at the surface. As a result, straighter, longer, and denser HA-SWCNT films are obtained.

4. Conclusions

From the analysis of the morphology of HA-SWCNT arrays grown on ST-cut quartz substrates we propose an explanation for the beneficial effects of adding small amounts of water to the ethanol feed. We propose that the predominant role of water is the hydrogasification of excess carbon deposits on the catalyst particle, keeping the metal surface available for incorporation of carbon into the growing nanotube and preventing carbon encapsulation. This hydrogasification reaction is catalyzed by the metal and is optimized at intermediate carbon/water ratios, leading to enhanced SWCNT length, density, and uniformity.

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