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Citation: J. Appl. Phys. 109, 064304 (2011); doi: 10.1063/1.3552306
View online: http://dx.doi.org/10.1063/1.3552306
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X-ray photoelectron spectroscopy study on Fe and Co catalysts during the first stages of ethanol chemical vapor deposition for single-walled carbon nanotube growth

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(Received 8 September 2010; accepted 24 December 2010; published online 18 March 2011)

Optimized chemical vapor deposition processes for single-walled carbon nanotube (SWCNT) can lead to the growth of dense, vertically aligned, mm-long forests of SWCNTs. Precise control of the growth process is however still difficult, mainly because of poor understanding of the interplay between catalyst, substrate and reaction gas. In this paper we use x-ray photoelectron spectroscopy (XPS) to study the interplay between Fe or Co catalysts, SiO$_2$ and Al$_2$O$_3$ substrates and ethanol during the first stages of SWCNT forest growth. With XPS we observe that ethanol oxidizes Fe catalysts at carbon nanotube (CNT) growth temperatures, which leads to reduced carbon nanotube growth. Ethanol needs to be decomposed by a hot filament or other technique to create a reducing atmosphere and reactive carbon species in order to grow vertically aligned single-walled carbon nanotubes from Fe catalysts. Furthermore, we show that Al$_2$O$_3$, unlike SiO$_2$, plays an active role in CNT growth using ethanol CVD. From our study we conclude that metallic Fe on Al$_2$O$_3$ is the most optimal catalyst/substrate combination for high-yield SWCNT forest growth, using hot filament CVD with ethanol as the carbon containing gas. © 2011 American Institute of Physics. [doi:10.1063/1.3552306]

I. INTRODUCTION

Catalytic chemical vapor deposition (CVD) is currently the most promising and widely used growth technique for the technological integration of carbon nanotubes (CNTs). Optimized CVD recipes can lead to the growth of dense, vertically aligned, mm-long mats or forests of single-walled carbon nanotubes (SWCNTs). Precise control of these processes is however still difficult, mainly because of poor understanding of the interplay between catalyst, substrate and reaction gas.

The interplay between the catalyst and substrate has been studied by several groups. It has been claimed that Fe/Al$_2$O$_3$ interfacial bonding restricts Fe surface mobility and hence allows for high density SWCNT forest growth. In addition, it has been suggested that Al$_2$O$_3$, which is a well known catalyst for hydrocarbon formation, aids in decomposing the carbon precursor and therefore enhances SWCNT forest growth from the catalyst. This suggestion, however, has been rejected by Mattevi et al. In addition, the morphology of the substrate has been proven to play an important role in the behavior of the catalyst, and therefore determines whether or not a SWCNT forest is grown.

Some studies have been done on the oxidation state of the catalyst during CNT growth. In situ x-ray photoelectron spectroscopy (XPS) studies have revealed that the catalyst has to be in its metallic state in order to be active in carbon nanotube growth. However, little is known about the influence of the carbon containing gas on the oxidation state of the catalyst. Mattevi et al. conclude that when C$_2$H$_2$ is used as the carbon containing gas, only metallic Fe/Al$_2$O$_3$ is active in CNT growth. Oxidized Fe/Al$_2$O$_3$ was not active in carbon nanotube growth with C$_2$H$_2$ as the carbon containing gas, since C$_2$H$_2$ did not reduce oxidized Fe/Al$_2$O$_3$.

The purpose of this study is to investigate the effect of ethanol, which is a common carbon containing gas for SWCNT forest growth, on the oxidation state of the catalyst. The most commonly used catalyst-substrate combinations for the growth of SWCNT forest are Co/Al$_2$O$_3$ (Refs. 1 and 2), Fe/SiO$_2$ (Ref. 3), or Fe/Al$_2$O$_3$ (Refs. 2 and 4). Therefore, we have studied the oxidation state of Fe/Al$_2$O$_3$, Fe/SiO$_2$, Co/Al$_2$O$_3$, and Co/SiO$_2$ with in situ XPS before and after exposure to ethanol and have correlated these results with the CNT growth characteristics of these catalyst films. In addition, we have studied the influence of the use of a hot filament during ethanol CVD on the oxidation state of the catalyst film. Hot filaments, plasmas, or hot wall CVD are commonly used to precrack the carbon containing gases. This increases the efficiency of SWCNT forest growth and CNT growth in general. The results presented below provide insight into the interaction between the carbon containing gas and the catalyst/substrate and may serve as a guide for improving the control of SWCNT forest growth.

II. EXPERIMENTAL DETAILS

Our experimental apparatus consists of four chambers: an evaporation chamber (base pressure ~5.10$^{-9}$ Torr), an XPS analysis chamber (base pressure ~5.10$^{-10}$ Torr), a CVD chamber (base pressure ~1.10$^{-8}$ Torr), and a load lock chamber (base pressure ~1.10$^{-7}$ Torr). Samples can be translated from one chamber into the other without breaking vacuum.
0.3 nm thick and 0.02 nm thick Co and Fe films were evaporated onto 100 nm thick SiO₂ or 30 nm thick Al₂O₃ films on Si substrates. A quartz crystal sensor (Inficon TM-400) was used to monitor the thickness of the catalyst film. Sometimes the catalyst films were oxidized before CNT growth by exposing them to 2.10⁻⁵ Torr O₂ for 250 s in the load lock chamber at room temperature. After the catalyst films were prepared, XPS spectra were obtained from the sample surfaces using a monochromatic Al Kα source (hv = 1486.6 eV). The binding energy calibration was done using the C 1s peak of a carbon containing sample. The catalysts were then annealed in the CVD chamber at 700 °C in a 10⁻⁸ Torr vacuum. Carbon nanotubes were grown at 700 °C in 2 Torr C₂H₅OH with and without the assistance of a hot filament. A graphite rod (diam 0.5 mm) was used as the hot filament and its temperature was kept constant at 1500 °C. The distance between the sample and the hot filament was approximately 8 mm. The temperature of the sample and hot filament were measured with a pyrometer. Scanning Electron Microscopy (SEM) pictures were taken on a LEO 1560 FE-SEM at 5 kV.

III. RESULTS AND DISCUSSION

A. Oxidation state of Fe and Co catalysts on SiO₂ and Al₂O₃ before growth

We first studied the XPS spectra of the as-deposited catalyst films on both SiO₂ and Al₂O₃. Since in the majority of cases in current practice catalyst films are not deposited in the same system in which the CNT growth takes place and are exposed to air before being placed in the CNT growth system, we also studied the oxidation behavior of the catalyst films by exposing them to oxygen at room temperature. We annealed the catalyst films in vacuum at the carbon nanotube growth temperature (700 °C) to determine the extent, if any, of catalyst-support interactions that change the oxidation state of the catalyst films. Unless otherwise noted the catalyst film thickness was 0.3 nm.

1. Fe catalyst

XPS spectra of as-deposited, oxidized, and annealed 0.3 nm Fe films on SiO₂ are shown in Fig. 1(a). The as-deposited 0.3 nm Fe on SiO₂ is in its metallic phase with peaks in the XPS spectrum that correspond to metallic Fe, 2p₃/₂ [706.7 eV (Ref. 15)] and 2p₁/₂ [719.8 eV (Ref. 14)]. When this film was annealed in vacuum at the carbon nanotube growth temperature (700 °C) for 20 s in the CVD chamber, the Fe remained metallic. There is no sign of oxidation of the iron resulting from of Fe-SiO₂ interactions. When only 0.02 nm of Fe was deposited on SiO₂ and subsequently annealed in vacuum [Fig. 1(b), top curve] there was still no sign of Fe-SiO₂ interactions and the Fe also remained purely metallic. This is in agreement with the observations of Mattevi et al.⁶

When the as-deposited 0.3 nm Fe on SiO₂ was exposed to oxygen at room temperature [Fig. 1(a)] the Fe⁰ peaks in the XPS spectrum disappear completely, and the spectrum is indicative of Fe in its fully oxidized state [Fe³⁺ 2p₃/₂ at 711.2 eV (Ref. 15)]. When the oxidized Fe on SiO₂ is annealed in vacuum at 700 °C for 20 s, the Fe³⁺ is partly

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**FIG. 1.** Fe 2p₃/₂ XPS spectra of (a) 0.3 nm Fe on SiO₂, (b) 0.02 nm Fe on SiO₂, (c) 0.3 nm Fe on Al₂O₃, and (d) 0.02 nm Fe on Al₂O₃. These spectra were taken on as-deposited and oxidized catalyst films which were subsequently annealed in vacuum at 700 °C for 20 s.
reduced to Fe$^{2+}$ [Fe$^{2+}$ 2p$_{3/2}$ at 709.6 eV (Ref. 15)], but there is no sign of Fe$^{0}$ in the XPS spectrum.

For 0.3 nm Fe on Al$_2$O$_3$, we obtained very similar results (Fig. 1(c)). We do not observe Fe$^{3+}$ or Fe$^{2+}$ contributions in the XPS spectra of the as-deposited and annealed 0.3-nm Fe on Al$_2$O$_3$ samples as was reported earlier. However, when we deposit 0.02 nm Fe on Al$_2$O$_3$ (see Fig. 1(d)) we do find Fe$^{2+}$ and Fe$^{3+}$ oxidation states, which become more pronounced when the sample is annealed. This suggests a strong interaction between Fe and the surface oxygen atoms of the alumina support, consistent with prior reports. It is believed that this interaction restricts Fe surface mobility, resulting in the nucleation of vertically aligned CNT forests.

2. Co catalyst

Identical experiments were performed with 0.3 nm Co as the catalyst film. As for Fe, the as-deposited Co films on both SiO$_2$ (Fig. 2(a) bottom curve) and Al$_2$O$_3$ (Fig. 2(c), bottom curve) are in the metallic phase [Co$^{0}$ 2p$_{3/2}$ at 778.0 eV (Ref. 15) and Co$^{0}$ 2p$_{1/2}$ at 793.0 eV (Ref. 15)] and remain metallic when annealed in vacuum (Fig. 2(a) and 2(c)). Similar to Fe, Co fully oxidizes when exposed to oxygen at room temperature [Co$^{2+}$ 2p$_{3/2}$ at 780.5 eV (Ref. 15) and Co$^{2+}$ 2p$_{1/2}$ at 793.0 eV (Ref. 15), Fig. 2(a) and 2(c)]. However, when the oxidized Co is annealed in vacuum the Co almost fully reduces to metallic Co on both SiO$_2$ and Al$_2$O$_3$ (top curves Fig. 2(a) and 2(c)). This is in sharp contrast with oxidized Fe which only slightly reduced from Fe$^{3+}$ to Fe$^{2+}$ upon annealing. This indicates that the activation energy for reduction of thin films of CoO on SiO$_2$ and Al$_2$O$_3$ is much lower than for Fe$_2$O$_3$. As for Fe, we find catalyst-substrate interactions when 0.02 nm Co is deposited on Al$_2$O$_3$, yielding Co$^{2+}$ in the XPS spectrum (Fig. 2(d), bottom curve). No catalyst-substrate interactions were found when 0.02 nm Co was deposited on SiO$_2$ (Fig. 2(b), bottom curve). 0.02 nm Co/Al$_2$O$_3$ however does not oxidize further when annealed in vacuum (Fig. 2(d), top curve), contrary to 0.02 nm Fe/Al$_2$O$_3$, which oxidized further upon annealing at 700 °C in vacuum (Fig. 1(d) top curve). This is another indication for the more noble metallic behavior of Co.

B. Oxidation state of Fe catalysts on SiO$_2$ and Al$_2$O$_3$ during growth

1. Fe catalyst on SiO$_2$ during growth

Next we investigated the oxidation state of the catalysts on SiO$_2$ during the initial stages of CNT growth. We measured XPS spectra after 20 s of exposure to 2 Torr ethanol at 700 °C with and without the use of the hot filament. Longer exposure times resulted into too much CNT growth, obscuring the XPS signals from the catalyst. We exposed both the as-deposited catalysts and oxidized catalysts to ethanol at growth temperature (700 °C). The resulting XPS spectra for 0.3 nm Fe on SiO$_2$ are shown in Fig. 3(a).

When as-deposited metallic Fe on SiO$_2$ is exposed to 2 Torr ethanol at 700 °C without the filament on [Fig. 3(a), second curve from top], the iron oxidizes, leaving only a very small fraction of the Fe in the metallic state (small shoulder at 706 eV). Oxidized Fe on SiO$_2$ remains oxidized until annealed in vacuum at 700 °C for 20 s.
after exposure to ethanol at growth temperatures (700 °C) [Fig. 3(a), top curve] and does not partly reduce to Fe2+, which was the case upon annealing at 700 °C [Fig. 1(a), top curve]. These results indicate that ethanol atmosphere at CNT growth temperatures oxidizes Fe on SiO2.

This experiment was repeated with the hot filament on. The as-deposited metallic Fe on SiO2 still partly oxidized, but the fraction of metallic Fe on the substrate is much larger than when the hot filament was off [compare second and bottom curve in Fig. 3(a)]. The oxidized Fe on SiO2 partly reduced to metallic Fe when exposed to ethanol with the hot filament on [Fig. 3(a), third curve from top]. A small peak at 706.7 eV, corresponding to metallic Fe, became visible. This indicates that the hot filament decomposes the ethanol in such a way that the original oxidizing atmosphere becomes partly reducing, such that even fully oxidized Fe becomes partly metallic after exposure.

We tried to investigate the decomposition of the ethanol by a hot filament with mass spectroscopy. We used one of the view ports of the CVD chamber to connect a mass spectrometer (Ametek, Dymaxion) to the CVD chamber (distance between hot filament and mass spectrometer head ~50 cm). However, we found that the influence of the hot filament is so localized, that we could not measure any difference in the mass spectrum of ethanol when the filament was turned off and on. When ethanol was transported through a separate furnace tube (hot wall CVD reactor) we were able to measure the ethanol decomposition by a hot surface with mass spectroscopy (see Fig. 4). In the hot wall CVD reactor, at 800 °C ethanol typically decomposes forming H2 and carbon species such as ethylene, acetylene, and methane and its radicals. It is likely that something similar happens at the hot filament (1500 °C): the ethanol decomposes into reactive carbon species, while forming hydrogen, contributing to the reduction of the Fe catalyst. Most likely, the temperature of the hot filament will effect the ratio of the formed carbon species, but in this paper we choose to keep the temperature of the hot filament constant at 1500 °C.

2. Fe catalyst on Al2O3 during growth

As-deposited and oxidized 0.3 nm Fe on Al2O3 films were also exposed to ethanol at 700 °C with the hot filament off and on. Since CNT growth turned out to be more efficient on Al2O3 than on SiO2 we had to reduce the ethanol exposure time to 5 s in order to still observe XPS signals from the catalyst. The results of the XPS measurements are shown in Fig. 5(a).

After exposure to 2 Torr ethanol for 5 s at 700 °C, the as-deposited metallic Fe on Al2O3 oxidizes partly [Fig. 5(a), second curve], but not as strongly as on SiO2 [Fig. 3(a) second curve]. The fully oxidized Fe on Al2O3 partly reduced upon 5 s exposure to ethanol at 700 °C, yielding a small Fe0 peak in the XPS spectrum at 706.7 eV [Fig. 5(a), top curve], while in the case of SiO2 the Fe remained fully oxidized [Fig. 3(a), top curve]. When these experiments were repeated with the hot filament on, the oxidized Fe on Al2O3 reduced even more [Fig. 5(a), third curve from top], resulting in a strong Fe0 peak at 706.7 eV. The Fe 2p3/2 XPS spectrum of as-deposited metallic Fe on Al2O3 exposed to ethanol at 700 °C for 5 s was not measurable due to the formation of large amounts of carbon [Fig. 5(a), bottom curve]. This obscured the XPS signals from the catalyst film. It was therefore necessary to reduce the exposure time further, to less than 0.5 s, in order to measure an XPS spectrum of the catalyst film (see Fig. 6). In the first 0.5 s the atmosphere typically has not
stabilized yet, but since our system does not have a shutter in between the hot filament and the substrate, this does represent the first stages of growth in our case. In the first 0.5 s the C 1s peak (same peak position as C1s of graphite) increases strongly, indicating that carbon nanotube formation has commenced (Fig. 6, bottom curve), while the Fe remained in its fully metallic state. (Fig. 6, top curve)

These results demonstrate that in the presence of Al2O3, ethanol partly reduces Fe. Fully oxidized Fe on Al2O3 becomes partly metallic when exposed to ethanol at 700 °C. This is not the case when fully oxidized Fe on Al2O3 is annealed at 700 °C in vacuum (partial reduction from Fe3+ to Fe2+ is observed, but no measurable metallic Fe is produced [Fig. 1(c), top curve], or when the fully oxidized Fe on SiO2 is exposed to ethanol (it remains fully oxidized, Fig. 3(a), top curve). In addition, metallic Fe on Al2O3 does not oxidize as much as on SiO2 when exposed to ethanol without the filament on [compare Fig. 3(a) and 5(a), second curves], while, with the filament on, the metallic Fe/Al2O3 seems to remain fully metallic during carbon nanotube growth, which is not the case on SiO2 [the iron partly oxidizes, compare Fig. 3(a) and 5(a), third curves]. Alumina is a well known catalyst in hydrocarbon reforming. Our experiments indicate that ethanol decomposes on Al2O3, creating a local reducing atmosphere which reduces oxidized Fe. This has been suggested before, but here we provide strong evidence that the carbon containing gas (in this case ethanol) is catalytically cracked on Al2O3.

3. Correlation between x-ray photoelectron spectra and CNT growth characteristics of Fe catalyst on SiO2 and Al2O3

With these XPS results, we can determine the effects of the metal catalyst oxidation state on the CNT growth characteristics. As-deposited and oxidized 0.3 nm Fe films on SiO2 and Al2O3 were exposed to ethanol at 700 °C for 5 mins with the hot filament off and on. After growth SEM pictures were taken of the CNT films. The results are depicted in Figs. 3(b) (SiO2) and 5(b) (Al2O3).

We found a strong correlation between the intensity of the Fe0 peak in the XPS spectrum after ethanol exposure and the growth characteristics. When the Fe0 peak is absent, no growth was observed (oxidized Fe/SiO2, filament off). A small amount of Fe0 gives rise to a mat of CNTs, while catalysts exhibiting a strong Fe0 peak (metallic Fe on SiO2 and Al2O3, filament on) grow to a SWCNT forest. This strongly suggests that Fe is only active in CNT growth in its metallic phase. This is consistent with previous results, however, the metal oxidation state is not the only variable influencing CNT growth. Surprisingly, the oxidized Fe on
Al2O3 exposed to ethanol with filament on did not give a SWCNT forest, while the Fe0 peak is relatively strong, while metallic Fe on SiO2 exposed to ethanol with the filament on has a smaller Fe0 signal, but does grow a small forest. These observations demonstrate that factors other than Fe oxidation state also play important roles in the CNT growth kinetics. One possibility is that the oxidation of Fe/Al2O3 might have changed the morphology of the catalyst, and that the additional effects also influence carbon nanotube growth. One possibility is that the oxidation process does more than merely change the oxidation state of the catalyst, and that the additional effects also influence the growth characteristics.9,10

4. Oxidation state of Co catalysts on SiO2 and Al2O3 during growth

Next, we turn to the oxidation state of Co during the first stages of CNT growth. In the case of 0.3 nm as-deposited and oxidized Co on SiO2 the catalyst film was exposed to ethanol at 700 °C for 20 s with and without the hot filament on. In case of Al2O3 the exposure time was reduced to 5 s. The measured XPS spectra can be found in Figs. 7 and 8. As was noted earlier, oxidized Co on both Al2O3 and SiO2 is almost completely reduced to the metallic state when annealed in vacuum at the carbon nanotube growth temperature (700 °C) [see Fig. 2(a) and 2(c), top curves]. As-deposited metallic Co remained in the metallic state upon annealing [see Fig. 2(a) and 2(c), third curves]. When as-deposited metallic Co on both SiO2 and Al2O3 is exposed to ethanol with or without the hot filament on the Co remains in the metallic state in all cases [Fig. 7 (SiO2) and Fig. 8 (Al2O3)]. This is in sharp contrast with Fe, Fe (partly) oxidized in the presence of ethanol both on SiO2 and Al2O3 with and without the filament on. Oxidized Co on both SiO2 and Al2O3 reduced mostly to metallic Co (very small fraction of CO2+ remaining) upon exposure to ethanol at 700 °C with and without the hot filament on [Figs. 7 and 8]. The XPS spectra were very similar to the XPS spectra of the annealed oxidized Co [Figs. 2(a) and 2(c), top curves]. This again demonstrates the relative ease of reduction of Co compared to Fe. Even in the presence of ethanol, which oxidizes Fe, the Co remains in its metallic state.

5. Correlation between x-ray photoelectron spectra and CNT growth characteristics of Co catalyst on SiO2 and Al2O3

For the case of Co catalysts we also correlated the XPS spectra with the CNT growth characteristics. As-deposited and oxidized 0.3 nm Co films on SiO2 and Al2O3 were exposed to ethanol at 700 °C for 5 mins with the hot filament off and on. After growth SEM pictures were taken of the CNT films. The results are depicted in Fig. 7(b) (SiO2) and 8(b) (Al2O3).

Since Co is mostly metallic under all growth conditions on both SiO2 and Al2O3 we observed CNT growth in all cases. On Al2O3 the yield of CNTs was larger than on SiO2, both with the filament on and off. This is probably caused by the catalytic cracking of the ethanol on the Al2O3, which most likely creates more active carbon species. However, the stronger catalyst-substrate interaction on Al2O3 also could promote CNT growth on Al2O3 (Ref. 6). Also, when the hot filament was turned on, we observed higher yields of carbon nanotubes [Figs. 7(b) and 8(b), third and fourth pictures]. Since Co remains completely in its metallic state when exposed ethanol, this increased yield when the hot filament is on can only be explained by the creation of more active carbon species and not by the more reducing atmosphere, since the Co does not require any further reduction. This shows that the hot filament has two effects: (1) it creates a reducing atmosphere, which is beneficial for CNT growth in the case of Fe, and (2) it creates active carbon species, which are requisite for forest growth on both Fe and Co.

In addition, when the CNT growth on oxidized Co was compared with the CNT growth on metallic Co, the metallic Co samples were in all cases (SiO2, Al2O3, filament off and on) more active in CNT growth, while the XPS spectra during growth were the same. This again suggests that the oxidation process does more than merely change the oxidation state of the catalyst, and that the additional effects also influence the carbon nanotube growth. One possibility is that the oxidation process changes the morphology of the catalyst, which could change the growth characteristics.9,10
When the growth characteristics of as-deposited Fe on Al₂O₃ and as-deposited Co on Al₂O₃ were compared [respectively, Fig. 5(b) and 8(b), fourth picture], we observed that Fe gives higher yields than Co [forests are a factor 2 taller for the Fe than for the Co, while keeping the growth time (5 min) the same]. Therefore we concluded that, although harder to reduce, Fe is more active in carbon nanotube growth than metallic Co.

IV. CONCLUSION

In conclusion, we studied the oxidation state of Fe and Co catalyst films on SiO₂ and Al₂O₃ before and during (hot filament) ethanol CVD for CNT growth with XPS spectroscopy. Ethanol oxidizes iron catalyst films at CNT growth temperatures. This reduces the yield of CNT growth, since only metallic Fe is active in CNT growth. Ethanol has to be decomposed (yielding a partly reducing atmosphere close to the catalyst) in order to be a active carbon species. This results in a higher CNT yield for both Fe and Co when CNT growth takes place on Al₂O₃ substrates.

We have also shown that the activation energy of reduction for Co is much lower than for Fe, which would, by itself, make Co a better catalyst for CNT growth. However, if conditions are employed in which the Fe is reduced to the metallic state during the growth process, the Fe is much more active in CNT growth than metallic Co, making Fe a better choice for SWCNT forest growth.

Therefore, we conclude that metallic Fe on Al₂O₃ is the most active catalyst/substrate combination for SWCNT forest growth. When ethanol is used as the carbon containing gas for SWCNT forest growth it needs to be activated with either a hot filament, plasma or hot wall CVD both to provide reducing conditions and to create active carbon species, such as ethylene. Although ethanol is not the most reactive carbon species for carbon nanotubes synthesis due to its oxidizing nature, it will in some instances still be the best choice for carbon nanotube growth, since it prevents soot formation and therefore give a cleaner CNT product. These results bring us one step closer to the understanding and precise control of SWCNT forest growth.