Effects of catalyst film thickness on plasma-enhanced carbon nanotube growth

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A systematic study is presented of the influence of catalyst film thickness on carbon nanostructures grown by plasma-enhanced chemical-vapor deposition from acetylene and ammonia mixtures. We show that reducing the Fe/Co catalyst film thickness below 3 nm causes a transition from smaller diameter (>40 nm), bamboolike carbon nanofibers to small diameter (~5 nm) multiwalled nanotubes with two to five walls. This is accompanied by a more than 50 times faster growth rate and a faster catalyst poisoning. Thin Ni catalyst films only trigger such a growth transition when pretreated with an ammonia plasma. We observe a limited correlation between this growth transition and the coarsening of the catalyst film before deposition. For a growth temperature of $\leq 550$ °C, all catalysts showed mainly a tip growth regime and a similar activity on untreated silicon, oxidized silicon, and silicon nitride support. © 2005 American Institute of Physics.

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INTRODUCTION

The controlled synthesis and assembly of nanoscale building blocks, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs), are fundamental requirements for bottom-up device fabrication. Among the various growth methods for CNFs and CNTs, chemical-vapor deposition (CVD) not only allows a scalable process design, but it also enables controlled surface-bound growth, which is more compatible with integration into future devices. Selective growth of aligned CNFs/CNTs can be achieved directly on a substrate by prepatterning a suitable catalyst and applying an electrical field or plasma during growth, which circumvents time- and cost-intensive postgrowth manipulations.

Despite substantial progress reported in the literature, it is still difficult to control the CNF/CNT diameter, structure, and crystallinity, due to an incomplete understanding of the growth process and the role of the catalyst. Evaporated or sputtered thin catalyst films allow an accurate patterning by standard lithography techniques compared to wet catalyst deposition. The catalyst film is roughened or converted into islands by plasma treatment or thermal annealing, forming seed particles for the subsequent CNF/CNT growth. The nature of the nucleating carbon nanostructure, however, depends critically on the process conditions and catalyst-substrate interactions. For thermal CVD, single-walled CNTs or dense arrays of multiwalled CNTs are found when using metal catalyst films of sub-1 nm or 5-nm thickness, respectively, on silicon-based substrates. For dc plasma-enhanced CVD, the diameter of the typically resulting bamboolike CNFs is found to vary with the thickness of the initial catalyst layer.

Here we present a systematic study of nucleation and growth kinetics for dc plasma-enhanced (PE) CVD of carbon nanostructures, focusing on the effect of varying the catalyst metal and the initial film thickness. We show that a reduction of the initial Fe/Co thin-film thickness below 3 nm generally results in the growth of small diameter (~5 nm) multiwalled carbon nanotubes, compared to the larger diameter (>40 nm), bamboolike carbon nanofibers which grow for thicker catalyst films. In our standard conditions, these CNTs grew over 50 times faster than the nanofibers, but with a much faster saturation of the growth rate. Interestingly, thin Ni catalyst films only triggered such a growth transition when pretreated with an ammonia plasma. A plasma pretreatment was also found to enhance the nucleation of small diameter CNTs from Co catalyst films. For a deposition temperature of $\leq 550$ °C, the catalyst films showed similar behavior on untreated silicon, oxidized silicon, and silicon nitride substrates. The small diameter CNTs are observed to bundle, in contrast with the CNFs, indicating that van der Waals interactions dominate over the plasma alignment effects.

EXPERIMENTAL DETAILS

Iron, cobalt, and nickel films were either thermally evaporated, electron-beam evaporated, or rf sputtered. For comparison to previous work, we also used magnetron-sputtered nickel. The base pressure was $\sim 10^{-6}$ mbar for the thermal evaporation and magnetron sputtering and between $10^{-7}$ and $10^{-8}$ mbar for the rf sputtering and electron-beam evaporation. No substrate heating was used during the thin film deposition. The film thickness was monitored in situ by a quartz-cystal-based thickness monitor, as well as measured ex situ by atomic force microscopy (AFM, Nanoscope...
and spectroscopic ellipsometry (J. A. Woollam Co., M-2000 V). We used polished, cleaned, n-type Si(100) wafers either untreated, i.e., with a native oxide layer, or with a thermally grown thicker (20–40 nm) oxide as substrates. Alternatively we used silicon nitride membranes supported on Si(100 nm, Agar Scientific). To allow a more accurate analysis of the growth rates, we patterned the catalyst films either by using transmission electron microscopy (TEM) grids as stencil masks or by photo- and e-beam lithography using AZ5214 or poly(methylmethacrylate) (PMMA) as resist.

The CNFs and CNTs were grown in a dc PECVD system in a stainless-steel diffusion-pumped vacuum chamber with a base pressure below 10⁻⁶ mbar. The samples were transferred in air and loaded onto a resistively heated graphite stage. In contrast with the previous work, the process gases were typically introduced through the side of the chamber, approximately 30 cm away from the heater stage, to avoid a directed gas flow and nozzle effects. Samples were heated in 0.5-mbar NH₃ electronic grade for 15 min until a temperature of typically 550 °C continuously monitored on silicon substrate was reached. For plasma preetching and deposition, a dc discharge between the heater stage and a stainless-steel anode, approximately 2–3 cm above the heater stage, was ignited by applying a fixed voltage of 600 V. C₂H₂ (grade 1.5) was introduced via a separate mass flow controller at a typical ratio of 50:200 SCCM (standard cubic centimeter per minute) C₂H₂:NH₃ at a total pressure of 0.7 mbar. The discharge current was around 30 mA, corresponding to <20 W plasma power, which is much lower than typically found in the literature.

The carbon nanostructures were analyzed by scanning electron microscopy (SEM, Jel 6340 and LEO 1530VP FEGSEM) and by high-resolution transmission electron microscopy (HRTEM, Jel JEM 4000EX, 400 kV). The CNFs/CNTs were removed from the substrates and dispersed onto Cu TEM grids for HRTEM analysis.

RESULTS AND DISCUSSION

Figures 1 and 2 compare the catalyst film behavior for two very different thickness regimes upon predeposition annealing and exposure to an NH₃ plasma. The AFM measurements were performed in tapping mode at ambient conditions. Root-mean-square (rms) roughness was measured over the whole area. Figure 1(a) shows the surface of an as-deposited, nominally 17-nm-thick Fe film thermally evaporated onto silicon with a ~2-nm-thick native oxide layer. The film is continuous and has a rms roughness of 0.6 nm. For comparison, the rms roughness of the silicon substrate is 3 nm. The section analysis shows the topography profile along the lines marked in the respective amplitude image.
~0.2 nm. When this 17-nm-thick catalyst layer is thermally annealed in NH₃ gas at ~550 °C, its surface topography changes to become dominated by islands of ~250 nm in diameter and 100 nm in height [Fig. 1(b)]. This agglomeration is driven by a surface and elastic energy minimization, enabled by a greater surface mobility. The average metal island size generally increases with initial film thickness and with the annealing temperature. Here, the splitting is inhomogeneous, giving a broad size distribution, including very large clusters. It can be assumed that the larger metal islands are polycrystalline.

Figure 1(c) shows a 17-nm-thick Fe film after thermal annealing in NH₃ gas at 550 °C for 15 min and subsequent exposure to an NH₃ plasma for 10 min (600 V and 10 mA) at the elevated temperature. The surface now has a rms roughness of 3 nm and is smoother and more homogeneous than the film in Fig. 1(b), indicating the effect of the pretreatment conditions. Plasma etching has been often reported to result in a higher nucleation density for the growth of CNTs/CNFs especially at low temperatures. Catalyst clusters can form from polycrystalline metal by a preferential etching at grain boundaries.

Figure 2 shows an AFM analysis for rf-sputtered Fe films with a nominal thickness of 2 nm, estimated by the Fe deposition rate. The AFM section analysis, however, gives a thickness of 3–4 nm for the as-deposited film. This could be due to an immediate oxidation of Fe upon air exposure. At ambient conditions the self-limited native oxide layer measures typically 1–2 nm in thickness. This indicates that the Fe film might be fully oxidized, occupying roughly twice the volume per Fe atom. For convention, all thickness measurements in this paper refer to the preoxidized, in situ value. The as-deposited film shown in Fig. 2(a) is continuous and very smooth with a rms surface roughness of 0.5 nm. Typically, as-deposited metal films nucleate in a Volmer–Weber mode, i.e., can be discontinuous for very low thicknesses depending on material and deposition conditions.

In order to simulate our normal conditions just prior to CNF/CNT growth, the Fe film was annealed for 15 min in NH₃ (200 SCCM and 0.5 mbar) at 550 °C and subsequently a dc plasma (600 V, 10 mA) was ignited for 2 s in this atmosphere. Figure 2(b) shows the film after this treatment. A regular pattern of islands emerges with an average diameter of ~60 nm, embedded in an increased film thickness of ~28 nm. The rms roughness is 4 nm. It must be emphasized that, despite the likely reduction in the ammonia atmosphere, the pretreated Fe film has reoxidized on air exposure for the AFM scanning. For comparison, Wei et al. calculate a smaller average island size of under 10 nm upon vacuum annealing of a 5-nm-thick Fe film at 600 °C. Nerush et al. report an average island diameter of 26 nm for ~1–2 nm-thick Fe films and ~100-nm island diameter for 5-nm Fe after treatment at 750 °C in a H₂/Ar mixture. Wang et al. report structures of ~10–15 nm and a surface roughness of 0.4–0.5 nm for 0.3- and 0.5-nm Fe films. Without the use of a barrier, silicide formation is likely forming a similar island pattern.

Figures 3–5 show SEM images of carbon nanostructures grown from the various catalyst films. Figure 6 shows HR-TEM images of the as-grown products. Figure 7 summarizes the observed variation of CNF/CNT growth rate and outer diameter with the initial catalyst film thickness. No nanofiber or nanotube growth was seen in the absence of a catalyst. For films above 4-nm initial thickness, sputtered and evaporated Fe, Co, and Ni each behaved in a similar manner, catalyzing the growth of vertically aligned, bamboo-structured CNFs with diameters exceeding 40 nm [Figs. 3(a), 4(a), 5(a), 5(b), 6(a), and 6(c)]. As in previous reports, the Co-catalyzed CNFs appear to be more branched, while Fe gave on average a lower growth rate. Rutherford backscattering spectroscopy (RBS) SEM images [Figs. 3(b), 4(b), and 5(c)] and HRTEM analysis [Fig. 6(a)] show that all CNFs have a conical inclusion of the catalyst in their tip. This is characteristic of a tip growth regime. A tip growth regime is generally indicative of...
a weak metal-support interaction, but does not imply that there is no catalyst material left at the support interface. Most groups find that metal-catalyzed CNFs grow by tip growth rather than base growth. A change in the growth regime was observed to also depend on growth conditions. Figure 7 shows that for a catalyst film thickness variation from 5–15 nm there is a steady increase in the average CNF diameter, whereby the diameter distribution widens.

We observe far greater changes for very thin (<3 nm) metal catalyst films. Under standard conditions, nominally 2-nm-thick evaporated and sputtered Fe [Fig. 3(c)] and Co [Figs. 4(c) and 4(d)] films result in the growth of very dense arrays of small diameter (~5 nm) CNTs, with almost a factor of 100 faster growth rate (Fig. 7). HRTEM shows that the

2-nm-thick evaporated and sputtered Fe [Fig. 3(c)] and Co [Figs. 4(c) and 4(d)] films result in the growth of very dense arrays of small diameter (~5 nm) CNTs, with almost a factor of 100 faster growth rate (Fig. 7). HRTEM shows that the
CNTs consist of two to five graphitic shells parallel to the tube axis with intershell spacings of 0.355±0.015 and 0.371±0.023 nm for Fe and Co catalysts, respectively [Figs. 6(b) and 6(d)]. The deviation from the 0.335-nm (002)graphite layer separation or the 0.344-nm interplanar distance in turbostratic graphite, respectively, can be related to the defective structure of the CNT walls and to the small number of walls. This also inevitably affects the precision of the spacing measurements. The CNTs no longer show the usual, regularly spaced bamboo intersects seen in fibers grown with thicker catalyst films. However, the CNT walls do seem to incorporate lattice defects, which cause some bending, kinking, and small variations in tube diameter.

Unlike to Fe and Co, we found no systematic change in the growth mode from CNF to CNTs when using as-sputtered or as-evaporated Ni catalyst films without pretreatment. Sometimes long CNT bundles could be found at a scratch of a thin Ni film. However, thinner Ni films typically led to the growth of thinner and shorter CNFs (Fig. 7) under standard conditions. Generally, this dependence on the catalyst metal is not fully understood yet, but it is related to the initial catalyst film coarsening and island formation. For sub-2-nm films, the grain-size distribution could also be influenced by a different intermittent oxidation behavior. Ni is the most noble and oxidizes the least among the transition metals studied here.39

In contrast to standard conditions where C2H2 is introduced shortly after plasma ignition, an additional 5-min preetching of thin Ni films (2 nm) in a pure NH3 discharge triggers the growth of CNT bundles [Fig. 5(d)], similar to those found for the other transition metals. This underlines the important effect of plasma conditions on the catalyst film. If thermal annealing does not lead to a catalyst restructuring suitable for CNT growth, plasma etching can activate these changes in catalyst surface topography [Fig. 1(c)]. Although sub-3-nm Co films can catalyze CNT bundles under standard conditions, we find that a plasma pretreatment enhances the nucleation of small diameter nanotubes (Fig. 7). For Fe films, on the other hand, a mild plasma pretreatment has no significant effect except to enable thicker films to nucleate CNTs [Fig. 1(c)]. A more detailed study of the influence of various catalyst pretreatment procedures is currently conducted.

Smaller diameter CNTs tend to form bundles [Figs. 3(c), 4(c), 4(d), 5(d), and 6(b)], unlike the thicker and freestanding, field-aligned CNFs [Figs. 3(a), 4(a), 5(a), and 5(b)]. This bundling is often found in CNTs grown by arc discharge, laser ablation, or by thermal CVD.16 It is believed to arise from the van der Waals attractions between tubes. Clearly, this horizontal attraction is now stronger for narrow tubes than the vertical forces due to electric fields in the plasma sheath.

RBS [Figs. 3(d) and 4(e)] can resolve (the larger) Fe and Co catalyst clusters at the top of some CNT bundles, indicating a tip growth regime. HRTEM [Fig. 6(b)] shows Fe inclusions at the tip of individual CNTs. However, Co [Fig. 4(c)] and Ni samples were found where neither RBS [Fig. 5(e)] nor HRTEM (with the preparation used) could give a clear indication of the predominant regime. For comparison, small diameter CNTs are typically reported to follow a base growth mechanism16,31,37,40 with few exceptions.41

A strong correlation between initial island size and the nanotube or nanofiber diameters is reported for many catalyst systems.17,42 Note that a strict 1:1 correlation between initial catalyst dimensions and CNT/CNF diameter is not necessarily expected. Regarding CNF nucleation, for instance, it depends to an extent on the deformation of the catalyst during nucleation43,44 into the typical, long conical grains as well as on whole islands.26

Comparing the ex situ AFM film analysis (Figs. 1 and 2) with the Fe-catalyzed carbon nanostructures (Fig. 3), the growth transition observed from CNFs to CNTs is not directly reflected in the (oxidized) catalyst surface morphology. The significant influence of the plasma atmosphere on the catalyst splitting is, however, pointed out. Interestingly, Delzeit et al.45 previously observed a transition from CNF to CNT growth, attributing it to a change in plasma bias conditions. However, the effect on the catalyst morphology was not clearly described there.

It is difficult to vary the CNF/CNT density independent of the nanofiber/tube diameter for homogeneous thin-film catalysts. In the case of dc plasma-aligned CNF growth, the fiber density was found to steadily decrease with an increasing fiber diameter triggered by an increasing catalyst film thickness.17 For sub-1-nm Ni, however, the growth has been
reported as less well aligned and less homogeneous, giving smaller diameter carbon structures with a lower density.\textsuperscript{13} Extended plasma etching can be used to deliberately lower the CNF density,\textsuperscript{36} which can be attractive for some applications. On the other hand, sub-1-nm catalyst films are used for the thermal growth of lateral networks of single-walled CNTs.\textsuperscript{4,14,47} Recently, very dense and therefore vertically aligned single-walled CNT forests were nucleated from a 1-nm Fe film on Si in an ethylene/argon/water atmosphere.\textsuperscript{15} Here we observe a continuous transition from plasma-aligned CNFs to dense CNT films vertically aligned by van der Waals interactions. The dc conditions used might be, however, too aggressive for the nucleation of defect-free, single-walled CNTs.

The use of ammonia or nitrogen is also often linked to the C–N defect creation and impurity incorporation.\textsuperscript{46} Electron energy-loss spectroscopy (EELS) of our plasma-aligned CNFs shows a very weak nitrogen signature indicative of a few at. % N. We are currently comparing plasma grown CNTs with nanotubes growth thermally under similar conditions to further elaborate on the role of the plasma. It must be emphasized that at \( \sim 550 \, ^{\circ}\text{C} \) dense CNT carpets similar to Fig. 3(c) can be nucleated by, e.g., a 2-nm Fe film under purely thermal conditions without plasma assistance. This paper focuses purely on the influence of the catalyst layer thickness under otherwise identical deposition conditions. As in our previous work on thicker catalyst films,\textsuperscript{19} a systematic study of the growth temperature dependence for sub-2-nm catalyst films is currently being conducted, comparing the thermal- and plasma-assisted CNT depictions.

Previous literature reports on a critical catalyst thickness beyond which no thermal CNT growth was observed.\textsuperscript{24} On the other hand it was reported that CNTs grew over the entire catalyst thickness range under dc plasma conditions.\textsuperscript{24} We observe similar effects, however, would like to emphasize that for our experiments this refers to isobaric conditions. Thermal growth of thick CNFs can be observed from thicker catalyst layers by increasing the pressure at otherwise similar deposition conditions. It is interesting to note that Fe films nominally \( \leq 0.1 \, \text{nm} \) in thickness do not lead to any growth under plasma conditions, whereas for the thermal CVD we observe sparse CNT growth with a too low nucleation density to vertically align the CNTs by van der Waals interactions. This difference is due to plasma etching of the catalyst metal prior to the introduction of the hydrocarbon feed gas [Fig. 1(c)].

It is generally well known that the chemical state of the catalyst metal and its support can significantly influence its catalytic properties.\textsuperscript{48} The deposition of a buffer layer/diffusion barrier is a common practice for catalytic CVD of CNT/CNF on Si substrates to prevent the metal-forming silicides with the underlying Si.\textsuperscript{13} On the other hand, in one case, a deliberate formation of silicide was found to enhance the CNT growth rate.\textsuperscript{49} At the conditions used here, all metal films showed similar catalytic behavior on Si with a native oxide layer, thermally oxidized Si, and on a commercial silicon nitride membrane support. This might be due to our relatively low process temperatures of only up to \( \sim 550 \, ^{\circ}\text{C} \). A higher surface roughness of the initial substrate material was not found to be essential, unlike previously reported for thermal growth.\textsuperscript{16} For Ni under standard conditions, however, CNT bundles were typically found at scratched substrate positions. A more detailed study including various other buffer layers and multilayer catalyst systems is currently being conducted.

Transferring transition-metal catalyst films in air from the evaporation/sputter system to the growth system leads to the formation of a metal oxide layer. Without a pretreatment in a reducing atmosphere, the oxide and not the pure metal is often assumed to catalyze CNT growth.\textsuperscript{50} However, x-ray diffraction (XRD) and Mössbauer spectroscopy for Fe indicate that the catalyst film is reduced during the growth process.\textsuperscript{51,52} In situ XRD measurements further suggest that the Fe catalyst remains as a solid during thermal CNT growth at \( 700 \, ^{\circ}\text{C} \).\textsuperscript{51} Lattice-resolved in situ HRTEM at 500–550 \( ^{\circ}\text{C} \) also showed that Ni particles in the range of 5–20 nm are crystalline during CNF growth, but very deformable.\textsuperscript{44} It is therefore reasonable to assume that, under our conditions, the CNFs/CNTs are catalyzed by solid metal clusters.

The carbon atoms from the catalytic dissociation of adsorbed gas precursors are transported by surface or bulk diffusion to feed the growing nanofiber. A plasma can deliver a more effective carbon supply as well as keep surface transport paths open.\textsuperscript{19} Comparing the approximate number of carbon atoms per unit CNF/CNT length to the catalyst surface that nucleated the respective nanostructure, we find that the catalyst activity per unit surface area is roughly the same for the thick CNFs [Fig. 6(a)] and the small-diameter CNTs [Fig. 6(b)]. The growth is diffusion limited in PECVD for all temperature regimes. For thicker Ni catalyst films, we argued that surface diffusion is predominant at low temperatures.\textsuperscript{19} Whichever is dominant, bulk or surface diffusion, the diffusion distance is roughly equal to the diameter, so the growth rate should scale inversely with catalyst diameter. Although incomplete at present point, Fig. 8 shows that the available
data roughly follows that proportionality, which explains the observed rapid increase in the growth rate of the narrow CNTs in Fig. 7.

The different catalyst size also leads to a different saturation behavior. The thin metal films [Figs. 3(c), 4(c), 4(d), and 5(d)] are found to poison quickly after typically a few minutes, whereas CNFs nucleated from thicker catalyst films [Figs. 3(a), 4(a), 5(a), and 5(b)] continued to grow in length for at least 1 h. Generally, catalyst poisoning is attributed to a progressive blocking of the active surface by excess amorphous carbon. This was supported by the observation of a thin layer of carbon on the front face of inactive particles during in situ experiments, and by experiments that showed that the catalyst could be reactivated by removing this layer. The plasma plays a role in etching away this blocking carbon. However, small catalyst clusters with a smaller active surface are likely to poison more quickly. It is interesting to note that, unlike the recent results on thermal growth in an ethylene/argon/water atmosphere, with the gas ratios used here, plasma etching could not prevent this deactivation. Although the different saturation behavior of the films was considered in the calculated growth rates shown in Fig. 7, the sometimes unpredictably fast growth rate and saturation for CNTs can lead to an underestimation of the cited values.

In conclusion, the effect of catalyst thickness on plasma-enhanced carbon nanostructure growth has been discussed in detail. A reduction to sub-3-nm thickness for Fe and Co triggered a transition from bamboolicke, larger diameter (>40 nm) CNTs to small diameter (~5 nm) CNTs with two to five graphitic shells. This is accompanied by a much faster growth rate and a faster catalyst poisoning. Only a limited correlation could be observed between this growth transition and the predescription film coarsening. A plasma etching can trigger a similar growth transition for thin Ni films, but could not prevent an early catalyst poisoning during growth. All catalysts mainly showed a tip growth regime and similar activity on silicon support with a native oxide, a thicker thermal oxide, and silicon nitride. The results bridge previous reports on thermal and plasma-enhanced CNF and multi- and single-walled CNT growth and show that they can be embedded in the same growth model.

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