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Synthesis of single-walled carbon nanotubes from atomic-layer-deposited Co$_3$O$_4$ and Co$_3$O$_4$/Fe$_2$O$_3$ catalyst films

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**Article info**

**Abstract**

We have investigated the synthesis of single-walled carbon nanotubes (SWCNTs) employing Co$_3$O$_4$ films prepared by atomic layer deposition (ALD). These films dewet into Co catalyst nanoparticles in the furnace before starting CNT growth by chemical vapor deposition (CVD). The facile Co$_3$O$_4$ ALD process allows for excellent film thickness control and very reproducible growth of high quality SWCNTs even from ultrathin, single-digit cycle ALD films. We demonstrate CNT growth on planar and 3-dimensional geometries. A detailed study using a combination of Raman spectroscopy as well as scanning and transmission electron microscopy reveals that the density and diameter distribution of the catalyst particles and resulting CNTs can be controlled by the number of ALD cycles. Moreover, we demonstrate straightforward preparation of Fe/Co bimetallic catalysts by mixing ALD processes of Co$_3$O$_4$ and Fe$_2$O$_3$. Finally, the wide temperature window of Co$_3$O$_4$ ALD allows for patterning of the catalyst via standard electron-beam lithography, as the deposition temperature is low enough to prevent resist reflowing. We conclude that ALD is an ideal technique to deposit Co$_3$O$_4$ catalyst films for SWCNT synthesis in a well-controlled manner, with several advantages over other materials and deposition techniques.

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**1. Introduction**

Carbon nanotubes (CNTs) have drawn great attention because of their exceptional mechanical, thermal and especially electrical properties [1–6]. CNTs find many potential applications in next-generation electronics, mostly as interconnects in the form of dense vertically aligned “forests”, or as the channel material in field-effect transistors. Particularly single-walled carbon nanotubes (SWCNTs) are hailed as candidates for the channel material in scaled transistors [7–13]. Due to their naturally ultrathin body (~1 nm cylinders), they exhibit electrostatics superior to scaled Si channel transistors, allowing carbon nanotube field-effect transistors (CNTFETs) to outperform Si devices while operating at lower voltages [12,13].

CNTs can be synthesized in several different ways, most commonly using catalytic chemical vapor deposition (CVD) [14]. In CVD, small metallic catalytic nanoparticles are exposed to a gaseous carbon precursor at elevated temperatures. The catalyst particles decompose the precursor and the hydrocarbon fragments diffuse into the particles with the CNTs subsequently growing from the surface of the particles. Although a large range of different carbon sources can be used, ethanol is a popular choice and is also used in this work. First introduced by Maruyama et al., ethanol is cheap and safe to handle, and it is commonly believed that the OH radical helps to remove amorphous carbon impurities [15,16].

In general the size of the catalyst particle rules the diameter of the carbon nanotube that grows from it [17]. Large catalyst particles typically result in multi-walled CNTs (MWCNTs) consisting of multiple concentric carbon cylinders, which may be relevant for interconnects or for applications that can benefit from their mechanical properties. For electronic applications however the focus is typically on selectively obtaining SWCNTs. The most popular catalysts include Fe, Co and Ni [18], although CNT growth has been demonstrated for many more catalysts [19,20]. Combinations of multiple materials forming bimetallic or alloyed nanoparticles such as Fe/Co [21] and Co/Mo [22] are well known for leading to improved growth, e.g. by improving the yield or selectivity toward
SWCNTs as compared to MWCNTs [20].

For the growth of SWCNTs, commonly two growth modes can be distinguished [23]: (1) a “tangential” growth where the SWCNT walls nucleate along the sides of the catalyst particle, resulting in a SWCNT diameter comparable to the particle diameter, and (2) a "perpendicular" growth where the SWCNT walls nucleate perpendicular to a small section of the surface of the particle, resulting in a SWCNT diameter some factor smaller than the particle diameter. A key requirement for growing SWCNTs therefore is that the catalyst particles are extremely small, typically about one to several nanometers in diameter. These nanoparticles are most commonly formed by sputtering or evaporation of a few monolayers of a metal film which may subsequently be annealed to promote particle formation [24,25]. The thickness of such films has a direct effect on the diameters and densities of the grown CNTs, which was carefully demonstrated by Noda et al. by making use of gradient catalyst layers [26,27]. However, uniform and reproducible deposition of such thin films by sputtering or evaporation requires very careful optimization of the process and deposition systems. More importantly, due to their line-of-sight deposition method, these techniques struggle to uniformly deposit material around 3-dimensional features. An alternative is wet chemical processing which involves dip- or spin coating substrates in solutions of metal salts (nitrates, sulfates, etc) or metal-organic precursors, which are then dried or calcined to form metal particles [28,29]. This method however leaves little control over the particle diameters and may not be compatible with semiconductor processing.

A potential solution to these challenges is the use of atomic layer deposition (ALD) for the catalyst preparation. In ALD, ultrathin metal or metal-oxide films are deposited in a layer-by-layer fashion by cycle-wise and alternating exposure to a precursor and a reactant. A high-temperature H2 anneal step that is part of the CNT synthesis process can subsequently reduce the metal-oxide and dewet the thin films into metallic catalyst particles. ALD relies on self-limiting surface reactions such that the film thickness increase per cycle is very reproducible and independent of precursor flux. A typical ALD process is able to deposit films with sub-monolayer thickness control which are highly uniform over large areas and conformal around 3-dimensional structures. Moreover, ALD allows for unique features such as area-selective deposition [30]. Finally, ALD is already widely used in semiconductor processing, for example for the deposition of thin high-k dielectrics, metal gate materials and dielectric spacer materials [31].

Clearly, ALD seems like the ideal candidate for highly reproducible and uniform deposition of catalyst films for SWCNT synthesis. However, only a few reports in literature demonstrate CNT growth from catalyst films prepared by ALD. The most common catalysts prepared by ALD are Fe/FeOx [32–35] and Ni/NiOx [35], and more recently ALD of Al2O3 has been employed [36]. Curiously, reports on SWCNTs are rare and most authors demonstrate the growth of MWCNTs. Moreover, the influence of the number of ALD cycles on the evolution of the catalyst particle and CNT diameters is not thoroughly investigated. Film thickness control is one of the core strengths of ALD, and this could be an ideal way to control the CNT synthesis as well. Finally, most authors report that many tens or even hundreds of ALD cycles are used to deposit the catalyst film, which is remarkable considering the very low amount of material that should be required to grow CNTs.

In this work, we explore ALD of cobalt oxide (Co3O4) films to create catalysts for CNT synthesis. The Co3O4 films are reduced to Co and form particles by an H2 anneal as part of the CNT synthesis process, as schematically depicted in Fig. 1. Co is very popular as a CNT catalyst and several straightforward Co3O4 ALD processes have been published [37–39]. However, Co3O4 ALD has not been previously employed for CNT growth (although some similarities exist with previously published wet-chemical molecular designed dispersion of Co [40,41]). In contrast to Fe and Ni (oxide) ALD, Co3O4 deposition is possible over a very large temperature window between 100 °C and 400 °C. The low temperature may enable possibilities such as patterning the catalyst film by conventional lithography, which is not possible at higher temperatures due to reflowing of the resist [42]. Furthermore, Co3O4 ALD growth does not exhibit a nucleation delay and growth starts virtually immediately, which greatly improves reproducibility for deposition of ultra-thin films as required for SWCNT growth. As a result, we will show that SWCNTs can be grown from even a single cycle of Co3O4 ALD. We also demonstrate CNT growth around 3-dimensional features. We investigate the influence of the number of ALD cycles on the catalyst particle size and catalyst particle density as well as on the resulting CNT diameter and CNT density. Next, we show how simply combining Co3O4 and Fe2O3 ALD can greatly increase the CNT yield by forming the very popular bimetallic Fe/Co catalyst particles. Finally, we demonstrate that the combination of a low number of cycles and low substrate temperature enables patterning of the catalyst using standard electron beam lithography (EBL).

2. Experimental

2.1. Catalyst film deposition

Co3O4 and Fe2O3 films were deposited using a home-built ALD setup described extensively in previous work from our group [43]. Unless mentioned otherwise, Si with 90 nm thermal SiO2 was used as the substrate. Co3O4 films were deposited using cobaltocene precursor (CoCp2, 98%, Strem Chemicals) and O2 plasma at a substrate temperature of 200 °C (or 100 °C for EBL-patterned substrates). The precursor bubbler was kept at 80 °C to ensure adequate vapor pressure, the gas line was heated to 120 °C to avoid condensation and clogging, and the precursor was carried into the reactor using Ar bubbling. The precursor exposure time was typically 3–5 s to ensure saturated growth. The O2 plasma exposure time was 5 s at an O2 pressure of 0.01 mbar and plasma power of 100 W. Both cycles were separated with a 3 s pumping step to evacuate reaction products. More details about the process and reactor can be found in an earlier publication [39]. Fe2O3 films were
deposited in the same ALD setup using a substrate temperature of 300 °C. The ALD process was adapted from Ramachandran et al. [44] and consists of tert-butyl ferrocene (TBF, 98%, Strem Chemicals) precursor exposure (10 s using Ar bubbling) and O2 plasma (10 s, 0.01 mbar, 100 W) separated by 10 s pump steps. The TBF precursor bubbler was heated to 100 °C, while the delivery line was heated to 120 °C.

2.2. Synthesis of SWCNTs

Single-walled carbon nanotubes were grown using atmospheric pressure CVD with ethanol as the carbon source (often called ethanol CVD [15]). The setup consists of a quartz tube surrounded by a Mellen tube furnace. The tube was evacuated and filled with N2 several times prior to synthesis to remove any air from the system. A 500 sccm flow of 5% H2 in Ar was introduced at atmospheric pressure while the oven ramps to the synthesis temperature of 875 °C in approximately 15 min. After reaching the desired temperature the samples were annealed for 45 min in the H2/Ar flow to reduce the Co3O4 films (or Co3O4/Fe2O3 films) to metallic Co (or Fe/Co) catalyst particles. To start the growth of CNTs, the H2/Ar flow is diverted through an ethanol bubbler chilled to 0 °C to reduce the vapor pressure. After 10 min of synthesis, the oven is allowed to cool naturally in 500 sccm Ar flow over the course of several hours, and the samples are removed from the furnace once the temperature has dropped below 50 °C.

2.3. Electron-beam lithography patterning

Standard EBL patterning was carried out in an FEI Nova 600i DualBeam system, using an electron beam acceleration of 30 kV. PMMA A4 950k (Micro Chem) resist was spincoated at 2500 rpm for 60 s for an approximately 200 nm film. After ALD of Co3O4, lift-off was carried out in hot acetone (60 °C).

2.4. Characterization

The thickness of the ALD films was measured in situ during the ALD process using spectroscopic ellipsometry (SE) with a J.A. Woollam, Inc. M2000 ellipsometer [45]. Scanning electron microscope (SEM) images were obtained in a FEI Nova 600i DualBeam system. Raman spectra were obtained using a Renishaw inVia confocal Raman microscope at 514 nm laser wavelength. Transmission electron microscope (TEM) studies were performed on electron-transparent Si3N4 membrane substrates using a JEOL JEM-ARM200F system at 200 kV acceleration voltage. The membrane substrates were covered with 5 nm SiO2 by ALD [46] so that they are more comparable to the 90 nm SiO2 on Si substrates used for the other analysis techniques.

2.5. Diameter measurements

The nanoparticle diameter distribution and particle density was measured from TEM images using ImageJ software. The area $A$ of each particle was measured and the diameter $d$ was then calculated as $d = 2\sqrt{A/\pi}$. On images with sufficient contrast between the particles and the background, particle areas were measured automatically using the default thresholding algorithm to distinguish particle from background, followed by the built-in “Analyze Particles” function. This automated method was cross-checked with manual measurements of the diameter on randomly selected particles to verify accuracy. For images with insufficient contrast (or in cases where the cross-check revealed inconsistent results), diameters were measured manually by overlaying elliptical shapes over the particles and calculating their area. The particle density was obtained by dividing the total number of particles by the total image area that was analysed.

SWCNT diameters were measured manually using ImageJ software. For all TEM images, additional intentionally defocussed images were taken in which the SWCNT are much more easily observed. The defocussed images were used to determine the location and extent of the SWCNT such that a single long SWCNT is not counted more than once in multiple image locations on the same sample. Diameters were finally measured on the focused images using the average of 3–5 measurements along the length of the SWCNT. The diameter was defined as the distance between the centers of the SWCNT walls, perpendicular to the length of the SWCNT.

3. Results and discussion

3.1. ALD of Co3O4

First the ALD process of Co3O4 has been investigated in detail. Since we anticipate that a film thickness on the order of a monolayer is required for SWCNT growth, we focus specifically on the first few ALD cycles. During the H2 annealing step immediately prior to the CNT synthesis process, thin films of Co3O4 will reduce to metallic Co, which then forms the catalyst nanoparticles. The latter is caused by dewetting due to the surface energy difference of the Co and the substrate. According to a simple theoretical model proposed by Zhong et al. [47], the diameter $d$ of the particles depends on the thickness $h$ of the initial film as approximately $d = 6h$, assuming no loss of material (e.g. by evaporation) and a contact angle of 90° (half spheres). Furthermore, the reduction of Co3O4 to Co likely results in a volume decrease (approximately a factor 2 using the volume of Co3O4 and Co unit cells). Therefore, to obtain Co particles between 1 and 3 nm, the target initial Co3O4 film thickness should be around 0.3–1.0 nm. With a typical growth of 0.05 nm per cycle [39] this translates to about 6–20 ALD cycles. However, many ALD processes (especially those of metals) struggle with reproducibility during initial growth due to a nucleation delay. There have not been any studies on Co3O4 ALD that focus specifically on the nucleation stage. Therefore it is worth investigating the initial nucleation of the Co3O4 ALD films on relevant CNT substrates (SiO2)

![Fig. 2. Thickness of Co3O4 films during the initial 10 cycles on bare SiO2 and Al2O3 substrates as measured by spectroscopic ellipsometry (SE). In the first 5 cycles, the growth rate is slightly lower than the expected 0.05 nm/cycle. There is no significant difference in the growth rate on SiO2 and Al2O3. (A colour version of this figure can be viewed online.)](https://example.com/fig2.png)
and Al$_2$O$_3$) such that the thickness of the films can be estimated accurately from the number of cycles.

Fig. 2 shows the nucleation behaviour of the Co$_3$O$_4$ film (first 10 cycles) on SiO$_2$ and Al$_2$O$_3$ substrates. After every ALD cycle, an in-situ spectroscopic ellipsometry (SE) measurement is performed from which the Co$_3$O$_4$ thickness can be obtained. An apparent thickness of ~0.02 nm is already detectable after the first ALD cycle. There is no significant growth delay, however the growth rate is slightly slower initially, and a steady linear growth is only reached after about 5 cycles. While the accuracy of SE is debatable in this sub-monolayer regime, it still gives a useful estimate of the film thickness, and the growth rate of 0.05 nm/cycle that is eventually reached matches the previously reported value for thicker films [39]. The thickness of ~0.42 nm at 10 cycles was further verified by XPS measurements as shown in the Supplementary Info. The growth rate of 0.05 nm/cycle corresponds to approximately 66% surface coverage of the precursor (e.g. less than a monolayer) and is most likely limited by precursor adsorption site availability (e.g. surface hydroxyl groups), steric hindrance from neighbouring adsorbed precursor molecules and possibly surface poisoning from precursor ligands or reaction products.

There is no significant difference in the growth rate on SiO$_2$ and on Al$_2$O$_3$. However, it is important to note that the subsequent CNT synthesis depends greatly on the choice of substrate. Al$_2$O$_3$ typically yields very high density vertically aligned forests of CNTs, while identical catalysts on SiO$_2$ usually yield only random horizontal alignment at much lower densities. This has been attributed to the catalytic activity of the Al$_2$O$_3$ itself as well as the interaction of the Al$_2$O$_3$ with the catalyst material [25,35,47–50]. This work focuses primarily on SiO$_2$ substrates, however vertically aligned forests are indeed obtained on Al$_2$O$_3$ as will be shown in the next section and in the Supporting Information.

3.2. SEM analysis of SWCNT synthesis on SiO$_2$ and Al$_2$O$_3$

We have investigated the synthesis of CNTs from Co$_3$O$_4$ ALD films deposited by a varying number of cycles on SiO$_2$ and Al$_2$O$_3$ substrates. Fig. 3 shows scanning electron microscope (SEM)
images of SWCNTs synthesized on SiO$_2$ substrates, using 1, 2, 5, 10, 15 and 25 cycles of Co$_3$O$_4$ ALD. The SWCNTs grow in random orientation along the substrate surface. Remarkably even a single ALD cycle is sufficient to grow CNTs, which confirms the absence of any significant growth delay in the ALD process. The density of CNTs increases as the Co$_3$O$_4$ thickness increases. At a certain Co$_3$O$_4$ thickness (between 10 and 15 cycles), the CNT coverage exceeds a single layer and additional CNTs can be seen resting on top of a dense layer underneath. It should be noted that no CNTs were grown in control substrates on which no Co$_3$O$_4$ was deposited (0 ALD cycles). These substrates were introduced into the ALD reactor but were only exposed to the O$_2$ plasma and not to the CoCp$_2$ precursor, indicating that the CNTs originate from the Co$_3$O$_4$ and not from contamination of other species in the reactors.

On Al$_2$O$_3$ substrates, the CNT growth characteristics are expected to be very different, and typically the CNTs form vertically aligned forests [25,35,47–50]. To investigate this behaviour, SiO$_2$ substrates were covered by ALD with 20 nm Al$_2$O$_3$ prior to deposition of Co$_3$O$_4$. Tall, vertically aligned CNT forests are indeed formed on these Al$_2$O$_3$ substrates when sufficient Co$_3$O$_4$ ALD cycles are used. Specifically, for 15 ALD cycles (~0.62 nm Co$_3$O$_4$), the CNT forest grows to approximately 200 µm in height. SEM images of CNTs grown on Al$_2$O$_3$ substrates are included in the Supplementary Info. Comparable results were previously reported by Sugime et al. [50] under very similar conditions: CNT forests ~200–300 µm tall were grown using ACCVD from a ~0.6 nm sputtered Co film, on a 16 nm Al$_2$O$_3$ film.

3.3. CNT growth around 3-dimensional features

To demonstrate uniform growth around 3-dimensional features, we have deposited Co catalyst by ALD on a dense forest of Si nanowires, and demonstrate CNT growth on these samples. The nanowires are 5 µm in height and were grown from Au particles at a pitch of 500 nm using the vapor-liquid-solid (VLS) technique. The nanowires are first uniformly coated with ~50 nm SiO$_2$ by ALD [46] to ensure substrate conditions similar to the planar SiO$_2$ substrates. Next, 10 cycles of Co$_3$O$_4$ ALD were performed for the catalyst deposition. Finally, CNTs were grown using the standard conditions. Fig. 4 (a) shows an SEM image of such a forest of nanowires after CNT growth. Fig. 4 (b) shows a TEM image of an individual nanowire, mechanically transferred to a TEM support grid by scratching the nanowire forest. It shows the Si nanowire (dark core) uniformly coated by SiO$_2$ ALD. Co nanoparticles are covering the nanowire uniformly along the length and on all sides of the nanowire. CNTs are mostly growing along the surface of the nanowire but sometimes become clearly visible when lifting up from the nanowire slightly. The bottom-right inset shows a close-up of the base of the nanowire demonstrating growth even at the bottom of the forest. The top-left inset shows a schematic illustration for clarity.

These results clearly indicate that Co$_3$O$_4$ ALD is able to uniformly deposit Co nanoparticles for CNT growth around 3-dimensional features. This is not achievable with conventional sputtering techniques, as the sputtered material would be hindered by shadowing from neighbouring nanowires. The sides of the nanowires would not be coated uniformly, and especially the bottom of the forest would likely remain devoid of catalyst particles.

3.4. Raman analysis of SWCNTs on SiO$_2$ substrates

Fig. 5 shows Raman spectra obtained from CNTs grown on SiO$_2$ using 2, 5, 10 and 15 cycles of Co$_3$O$_4$ ALD. All samples show typical SWCNT spectra and no evidence of MWCNTs: the appearance of
radial breathing modes (RBM), the split G' /G peak and a very low D peak \[51\]. The low D peak also indicates high quality CNTs with low defect densities. A zoom-in of the RBM region is shown in the inset of Fig. 5, and a zoom-in of the D and G peak region is included in the Supplementary Info. The increase in CNT density as seen in SEM is also observed in Raman as all peaks originating from the CNTs increase in intensity as the Co3O4 thickness increases. However, the peak intensities saturate around 15 cycles and similar Raman spectra are obtained from 25 cycles Co3O4 (Supplementary Info), indicating that the CNT density approaches a maximum at approximately 15 cycles for SiO2 substrates.

3.5. Diameter distributions

The distribution in diameters of both the catalyst particles and the CNTs was investigated in detail by TEM studies. We limited the study to substrates with a maximum of 10 ALD cycles, such that the density of CNTs is not so high to completely cover the surface. Fig. 6 (a) shows a TEM image of the catalyst particles formed from 5 cycles of Co3O4 ALD after the CNT synthesis process. To ensure similar growth conditions, the Si3N4 membrane typically used for TEM analysis was covered with 5 nm SiO2 by ALD \[46\] before Co3O4 deposition. Fig. 6 (b) shows a TEM image of SWCNTs grown from 10 ALD cycles of Co3O4. The CNTs are clean and straight indicating a low defect density. In this case, the CNTs were growing over a small gap (cut in the TEM membrane using a focused ion beam) so that the CNTs could more easily be imaged without contrast reduction by the underlying substrate. However, it was discovered that most CNTs tend to grow along the edges of the gap and only large diameter CNTs managed to cross the gap. Therefore, to avoid skewing statistics in favour of large diameter CNTs, these cut membranes were not used further. For measurements of the particle and CNT diameters, only images similar to Fig. 6 (a) were used.

TEM images similar to Fig. 6 (a) were used to determine the statistical distribution of the catalyst particle and CNT diameters to investigate how they evolve as a function of the initial Co3O4 film thickness. The catalyst particle distribution is shown in Fig. 7 (a) for 2, 5 and 10 ALD cycles. Both the mean particle diameter and the particle density increase as the number of ALD cycles is increased which demonstrates the control over the catalyst dimensions by ALD. Similarly, the CNT diameter distribution (shown in Fig. 7 (b) for 5 and 10 ALD cycles) also increases with the number of ALD cycles, which confirms that the control over the catalyst particles also translates into control over the CNT diameters. The diameters of CNTs grown from 2 ALD cycles could not be determined accurately as the CNT diameters were so small and the contrast so poor that it was not possible to distinguish individual CNTs from bundles of smaller CNTs. The mean nanoparticle diameter \(d_{np}\) and the mean CNT diameter \(d_{CNT}\) are determined using Gaussian fits (see Supplementary Info) and compared in Fig. 7 (c) as a function of the initial Co3O4 film thickness. The ratio of CNT diameter to particle diameter is the same for 5 and for 10 ALD cycles at \(d_{CNT}/d_{NP} = 0.36\) which indicates there could be a constant correlation between the CNT and particle diameter. Since the ratio is much smaller than 1 (the CNT diameters are smaller than the catalyst particle diameters) this could indicate a “perpendicular” rather than a “tangential” growth mode \[23\]. However, several factors make this interpretation difficult. First of all, the TEM images are recorded \textit{ex-situ} several days after the CNT synthesis, hence the particles have likely re-oxidized which could have increased their diameter as compared to their diameter during the CNT synthesis. XPS analysis of similar samples confirms the oxidized state of the particles (Supplementary Info). Secondly, the particle shape (e.g. contact angle) may be different during the growth at high temperature and during the TEM study at room temperature. Therefore the particle diameters measured here are likely different than the actual diameters during the growth process, although the trend should still be valid.

The total particle density (counting particles of all diameters) is somewhat higher than the density of CNTs. For example, for 5 ALD cycles, a particle density of \((1.1 \pm 0.1) \times 10^{11} \text{ cm}^{-2}\) is measured from the TEM images. The density of CNTs obtained from SEM (Fig. 3 (c)) however is only approximately \((2 \pm 1) \times 10^{10} \text{ cm}^{-2}\), estimated from manual counting in an area of \(1 \mu\text{m}^2\). In other words, only ~20% of the particles yield a CNT. A common cause for reduced yield is the encapsulation of catalyst particles by a carbon shell which renders them inactive \[52,53\]. This may be prevented by careful optimization of the synthesis conditions, however since this effect is unrelated to the catalyst deposition method this was not attempted in this work.

Finally, we note an interesting observation regarding the total volume of all the catalyst particles. Fig. 7 (d) shows the “total volume per unit area” of the particles, which is the sum of all individual particle volumes normalized to the imaged surface area. The volume of each particle was calculated from its diameter by assuming (partially) spherical particles with contact angle \(\theta\). The contact angle is unknown for these samples, hence Fig. 7 (d) shows a range of possible volumes between \(\theta = 180^\circ\) (full spheres) and \(\theta = 15^\circ\) (flat particles) as error bars. Assuming no loss of material and bulk mass densities, the total particle volume divided by the
by comparison with the initial film thickness (SE data) it is clear that the total volume of all particles is significantly less than the initial film volume, even at the maximum possible particle volume ($q = 180^\circ/C_{14}$), which indicates that a large fraction of the catalyst material is lost during CNT growth. The Co$_3$O$_4$ (or reduced Co) may have evaporated during the high-temperature anneal even though the temperature does not exceed the bulk melting temperature, as nanoparticles scaled down to below 10 nm exhibit greatly decreased melting temperatures [20,54] and increased vapor pressure [20]. XPS analysis shows a decrease in Co signal intensity by nearly a factor 3 after annealing (see Supplementary Info) which indeed suggests loss of material. Alternatively, material may be dissolved into the substrate [25,55]. The loss of material is likely only dependent on the CNT growth conditions and is not unique to atomic-layer-deposited catalysts.

### 3.6. Mixing ALD of Co$_3$O$_4$ and Fe$_2$O$_3$

**Fig. 7.** (a) Distribution of the Co$_3$O$_4$ particles diameters as obtained by TEM measurements using Si$_3$N$_4$/SiO$_2$ windows. $N$ is the number of particles measured. (b) Distribution of the CNT diameters as obtained by TEM measurements. $N$ is the number of CNTs measured. (c) Mean diameters of the Co$_3$O$_4$ particles and CNTs as a function of the initial Co$_3$O$_4$ film thickness. (d) Total volume (per unit area) of the oxidized Co particles derived from TEM data, compared to initial layer thickness as measured by SE. Data points indicate a contact angle of $\theta = 90^\circ$, while error bars indicate a possible volume range between $\theta = 180^\circ$ (full spheres) and $\theta = 15^\circ$ (very flat particles). (A colour version of this figure can be viewed online.)

Combined systems such as Fe/Co are known to increase the CNT yield and selectivity toward SWCNTs [20,21,56–58]. This effect is likely caused by a reduction in melting temperature and increase in carbon solubility of alloys as compared to individual catalysts [20]. The cyclic nature of ALD lends itself well to depositing bimetallic catalysts. Multilayers of metal-oxides can be deposited by alternating cycles of different materials and the ratio of the two materials can be accurately controlled by choosing the ratio of ALD cycles. As a demonstration, we have combined ALD of Co$_3$O$_4$ and Fe$_2$O$_3$ thin films to synthesize single-walled CNTs. During the H$_2$ anneal step in the CNT synthesis, the Co$_3$O$_4$ and Fe$_2$O$_3$ films are expected to mix and form Fe/Co alloyed catalyst particles. Fig. 8 (a) shows an SEM image of a very high density CNT film synthesized from a combination of 2 cycles Co$_3$O$_4$ and 25 cycles Fe$_2$O$_3$. Additionally, Fig. 8 (b) compares Raman spectra of CNTs synthesized from the addition of 2, 10 and 30 cycles Fe$_2$O$_3$ on top of 2 cycles Co$_3$O$_4$ films. The CNT density as seen in SEM as well as Raman (intensity of G$^+$ peak) for 25 and 30 ALD cycles of Fe$_2$O$_3$ is much higher than what could be achieved with just Co catalyst. It should be noted that, under the current CNT synthesis conditions, substrates with only Fe$_2$O$_3$ catalyst (and no Co$_3$O$_4$) do not yield any CNT
growth (see Supplementary Info). Furthermore, as shown previously in Fig. 3 (b), 2 cycles of CoO₄ without Fe₂O₃ results in a relatively low density of CNTs. These observations clearly demonstrate the synergistic effect of the combination of Fe and Co which cannot be achieved with either material by itself.

Besides Fe and Co, almost all popular CNT catalyst materials can be deposited by ALD [59]. For example, ALD processes exist for the deposition of Ni [60,61] or NiO [62], MoO₃ [63,64], Pt [65,66] and WO₃ [67,68] which may be used to form any combination such as Fe/Ni, Co/Mo, Fe/Pt, Co/W, etc. While a plethora of possibilities exists, the combination of Fe and Co was chosen in this work as proof of principle that alloying is feasible with ALD.

3.7. Catalyst patterning by EBL

As a final demonstration, we have investigated the possibility of patterning the CoO₄ ALD catalyst. With conventional catalyst preparation techniques (e.g. sputtering), patterning is relatively trivial to achieve by standard lithography. However, one disadvantage of ALD processes in general is that they are often incompatible with lithography. The substrate temperatures required are often too high causing reflowing of the resist films [42]. Furthermore, possible deposition on the side-walls of the resist hinders lift-off, and the use of plasmas as the reactant can cause etching of the resist film. Contrary to many ALD processes however, the current ALD process of CoO₄ is compatible with standard lithography techniques. The possibility of low temperature deposition (~100 °C) prevents reflowing and enables the use of conventional resists such as polymethyl methacrylate (PMMA). Furthermore, since only few cycles are required, etching of the resist by the oxygen reactant (O₂ plasma in this case) is insignificant. As an example, we used electron-beam lithography (EBL) to pattern CoO₄ catalyst deposited by ALD, and subsequently grow CNTs in these patterns. Patterns were developed in PMMA resist by EBL, after which CoO₄ was deposited using 15 ALD cycles at a substrate temperature of 100 °C. Acetone is used to lift-off the remaining resist which leaves patterned CoO₄ on the substrate. While the CoO₄ may also be deposited on the resist, the film is so thin that it does not hinder the lift-off process.

Fig. 9 shows an SEM image of the patterned substrate after CNT synthesis. To make the demonstration more clear, in this case an Al₂O₃ substrate was used resulting in a vertically aligned forest of CNTs, as explained previously in Section 3.2. No CNTs have grown outside of the pattern where the substrate was covered by the resist film. Furthermore, the edge between the clean substrate and CNT forest is very sharp and abrupt, demonstrating that the relatively low temperature deposition prevents reflowing of the resist.

4. Conclusions

In summary, we have studied CoO₄ ALD as a method to prepare catalyst nanoparticles for the synthesis of SWCNTs. CoO₄ films were annealed in H₂ during which they dewet into metallic Co catalyst particles which were active for SWCNT growth. We have confirmed that ALD is an ideal catalyst preparation technique due to its excellent thickness control and reproducibility even for depositions of ultrathin films and for depositions around 3-dimensional features, all of which can be challenging for other deposition techniques such as sputtering or evaporation. The effect of the CoO₄ film thickness was investigated in detail, and it was shown that the density and diameter distribution of the catalyst particles as well as the resulting SWCNTs could be controlled by the number of ALD cycles. SWCNTs of high quality with low amounts of defects and impurities were obtained over a large window of 1–25 ALD cycles. Additionally, the density of the SWCNTs could be
further increased by growth from Fe/Co bimetallic catalysts prepared by combining Co3O4 ALD with FeO2 ALD. Compared to more common studies on ALD of Fe and Ni oxides, we have shown that the facile Co3O4 ALD offers significant advantages for SWCNT growth. Because there is no significant nucleation delay, SWCNTs can be grown reproducibly from Co3O4 films deposited by single-digit number of ALD cycles, even down to a single cycle. Furthermore, Co3O4 ALD is possible over a very large temperature window (100–400 °C) which improves the flexibility of the technique. Specifically, the possibility of low deposition temperature (100 °C) allowed us to demonstrate patterned deposition by masking parts of the substrate with standard electron-beam lithography patterning. The combination of low cycle number and low temperature deposition avoids common issues such as resist etching and reflowing. Our results highlight that this novel ALD catalyst offers further possibilities for reproducible and controlled SWCNT growth.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbonyl.2017.06.001.

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