Single-step CVD growth of high-density carbon nanotube forests on metallic Ti
coatings through catalyst engineering

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Abstract

We demonstrate the direct growth of carbon nanotube (CNT) forests on metallic titanium (Ti) coatings by single-step chemical vapour deposition. This was achieved by catalyst engineering, which involves a novel design of Fe/Ti/Fe nanostructure sputtering coated on SiO₂/Si wafers. The Fe sublayer, an additional catalyst added to the conventional catalyst/support design, plays a key role in the growth of well aligned and highly dense CNT forests. Depth profile analysis of substrates by secondary ion mass spectroscopy shows that the Fe sublayer is thermally unstable at the Ti/SiO₂ interface under the growth conditions. Catalyst diffusion back to the surface from the Fe sublayer is much more significant than down towards the SiO₂/Si substrate from the surface Fe layer. This makes it possible to minimize the thickness of surface catalyst layer, and ensures the growth of well aligned and high-density CNT forests on Ti coatings. The filling factor of nanotubes on the substrate after liquid-induced compaction can be dramatically increased up to 57%, leading to an estimation of the areal density of around 10¹² cm⁻².

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1. Introduction

Currently, the most efficient way to produce vertically aligned carbon nanotubes (CNTs) is catalytic chemical vapour deposition (CVD) [1-7]. First, it usually involves the deposition of a thin catalyst layer as well as an underneath oxide support. A transition metal such as Fe, Co, Ni or their alloys is commonly used as catalyst, while Al_2O_3 , MgO and SiO_2 are the best oxide supports [8-11]. Then, a CVD pre-treatment or annealing is employed to convert the catalyst layer into active nanoparticles through catalyst reduction and dewetting. Finally, CVD growth of vertically aligned CNTs is carried out with a hydrocarbon source gas such as ethylene or acetylene, usually diluted in hydrogen or inert gases. The catalyst-oxide support interactions restrict the catalyst surface mobility, stabilizing small catalytic nanoparticles at elevated CVD temperatures and leading to a high nucleation density of CNTs. In recent years, great progress has been achieved in the growth of high-density (10^{12} - 10^{13} cm^{-2}) single-walled CNT (SWCNT) forests on Al_2O_3 support [12-15]. However, it is still challenging to reproduce the high-density CNT forests on conductive supports, especially on transition metal supports such as Cu, Ti and Ta. This is needed because of an urgent demand for nanotube applications as interconnects [16-18].

Studies have shown that the thickness of the surface catalyst has a decisive effect on the diameter and density of the as-grown CNT forests; the thickness of the surface catalyst should be prepared as thin as possible in order to increase the CNT density [11, 14]. In the case of a metal support, the challenges lie in: 1. A metal support has higher surface energy than an oxide support [19, 20], so that it is more difficult to form high-density and small catalytic nanoparticles on the metal surface through dewetting under the growth temperature. 2. The catalyst-support-gas interactions are

more complicated [21, 22]. The support may easily form alloys with the catalyst, and its grain may get coarsened during the CVD process [21]. In addition to Ostwald ripening and subsurface diffusion [8-10], alloying and grain boundary diffusion make the catalyst loss on the surface even faster. Furthermore, the metal support may also interact with the feeding and/or residual gases to form carbides and/or oxides, which significantly inhibit the growth of CNT forests and affect the contact between nanotubes and the support.

During the past decade, attempts have been made toward the growth of CNT forests on various metal substrates by different CVD methods [18, 19, 23-30]. However, the density and alignment of CNTs are far below that of the date-of-the-art high-density SWCNT forests grown on the Al_2O_3 support. Furthermore, most of the processes commonly use the Al_2O_3 coating (or Al coating, on which a passive oxide layer should be formed on exposure to air) between the catalyst and the metal support as a barrier layer [23-29]. In order to reduce the contact resistance between the nanotube and the support, it is essential to grow CNT forests directly on metal supports without the assistance of any insulating oxide coatings. Recently, encouraging progress has been made [18, 31-33]. Esconjauregui *et al.* succeeded in growing multi-walled CNT (MWCNT) forests ($4 \times 10^{11} \text{ cm}^{-2}$) on conductive substrates by tuning the nominal thickness of the Al_2O_3 support down to 0.5 nm, which allows a good electrical contact through tunnelling [33]. Yamazaki *et al.* reported the growth of almost closely packed MWCNT forests ($1 \times 10^{12} \text{ cm}^{-2}$) on 10 nm TaN by a multi-step growth method using plasma-assisted CVD [31]. In their process, plasma-assisted formation and immobilization of catalytic nanoparticles by a carbon film can be carried out only under very restricted pretreatment conditions in order to obtain the high-density CNT

forests during the final growth step, which are not sensitive any more to the growth temperature in a large range. Dijon *et al.* claimed the growth nanotubes on metallic Al-Cu (99.5% Al) alloy with a density up to $2.5 \times 10^{12} \text{cm}^{-2}$ [32]. The latter also use plasma-assisted CVD under a low pressure of 1mbar. Very recently, Rao *et al.* even made a promising approach to grow CNT forests on Cu and other metals by using graphene as an atomically thin interface [34].

In this paper, we demonstrate a novel concept of catalyst engineering, which enables the growth of well aligned and high-density CNT forests on Ti coatings by using a single-step cold-wall CVD process. It requires neither a special plasma pre-treatment /annealing of catalyst nor an oxide barrier layer over the conductive support. Instead, only an additional Fe catalyst sublayer is added to the conventional catalyst/support design, i.e. we prepare δ nm Fe, 10 nm Ti and τ nm Fe sequentially by magnetron sputtering on Si wafers with 200 nm thermally grown SiO_2 as illustrated in Fig.1a. Our purpose is to minimize and sustain the surface catalyst during CVD process through a back diffusion of catalyst from the sublayer. Experiments indicate that a proper $\tau - \delta$ combination of the two catalyst layers can dramatically enhance the growth of well aligned and high-density CNT forests.

2. Experimental

Fe and Ti were used as the catalyst and the metal support, respectively, while Si wafers with 200 nm thermally grown SiO_2 were used as the substrates. Both Fe and Ti were sputtering coated using Ar as the sputtering gas. In order to accurately control the catalyst thickness, a low sputtering rate of about 1.1 nm/min was applied by using a low sputtering power of 20 W to a 4-inch Fe target under 3.5×10^{-3} mbar. First, δ nm

(0 - 2 nm) Fe was coated on a SiO₂/Si wafer; here, $\delta = 0$ nm means this step was skipped (equivalent to the conventional catalyst design). Following this step, 10 nm Ti and τ nm (0.5 - 2 nm) Fe were sequentially coated without breaking the vacuum (Fig. 1(a)). A single-step process was employed to grow nanotubes on the Ti coatings using a cold-wall CVD apparatus, which has been successfully used for the growth of high-density SWCNT forests [6, 14]. In the CVD process, the substrates were directly heated from room temperature to growth temperature under 15mbar, 40 sccm C₂H₂ + 460 sccm H₂, without any pre-annealing of the catalyst. The effect of pre-annealing of the substrates on the growth of nanotubes was also investigated. A method of liquid-induced compaction [35-37], which includes soaking the nanotube samples thoroughly in ethanol, and letting them dry in the air, was used to estimate the areal density of CNT forests [14, 38].

The nanotube samples were characterized by scanning electron microscopy (SEM, Philips XL30 SFEG and Carl Zeiss Sigma) and high resolution transmission electron microscopy (HRTEM, FEI Tecnai F20.) Element depth profile analysis on selected substrates by secondary ion mass spectroscopy (SIMS) was carried out as a service by Loughborough Surface Analysis Ltd. An ¹⁸O ion beam was used for the SIMS analysis. The electrical measurements were carried out on selected samples with a two-point probe station ((Keithley 4200-SCS). In order to get a good contact, 50 nm Au was pre-coated on selected substrates after the catalyst preparation and before the CVD growth of nanotubes. The probe spacing was set to a constant of 5 mm.

3. Results and discussions

3.1 Effect of catalyst engineering on CNT growth

Fig. 1 demonstrates that our novel catalyst design of τ nm Fe /10 nm Ti / δ nm Fe /SiO₂/Si can significantly enhance the growth of CNT forests on the Ti coating. Figs. 1(b-d) are nanotubes grown on substrates with the conventional catalyst design ($\delta = 0$); Figs. 1(e-l) are nanotubes obtained from our novel catalyst design but with different τ - δ combinations. All the samples were produced by the single-step CVD at 15mbar, 40sccm C₂H₂, 460sccm H₂ and 700°C, however, (b-h) were prepared in 10 min while (i-l) in 6 min. It can be seen that only disordered or less aligned nanotubes could be grown on the Ti coating without a catalyst sublayer; in contrast, aligned CNT forests could be prepared using our novel catalyst design. This proves that the catalyst sublayer plays a very important role in the growth of aligned CNT forests on the Ti coating. It can be also seen from Figs. 1(j-k) that the thin Fe sublayer in the range of 0.6-0.8 nm gives the best alignment of CNT forests. As CNT alignment is caused by a crowding effect of nanotubes [39], better alignment usually also means higher nanotube density if the nanotube diameter keeps the same [40]. An Fe sublayer thicker than 1.0 nm will produce nanotubes with larger diameters observed by SEM at high magnifications.

The electrical properties of the bare substrates and the as-grown high-density CNT samples were measured by using a two-point probe station. Fig. 2 shows the characteristic I-V curves and the derived resistances. The insets in Figure 2 illustrate how to contact the probes with samples. The overall resistance derived from an I-V curve includes not only the resistances of the as-grown nanotubes and the substrates, but also the contacts of probe to nanotube, nanotube to Ti, and/or probe to Au, Au to Ti. The I-V curve of the as-deposited bare substrate (coated with 0.8nm Fe/10nm Ti/0.8nm Fe on SiO₂) gives an electrical resistance about 180-195 Ω , similar to that of

a conductive CoSi_2 coating [19]. However, an annealing of the substrate in 15mbar pure H_2 at 700°C for 6 min resulted in an increase of the resistance to more than 10 $\text{k}\Omega$, as can be seen in Figs. 2(a-b). This implies that the Ti coating can also be partially oxidized under high temperature by the residual $\text{O}_2/\text{H}_2\text{O}$ in the CVD system even in a reducing environment just like a Ta coating [22]. To our surprise, the as-grown CNT forests showed almost linear I-V curves by contacting the two probes with CNT forests, or by contacting one probe with the forests and the other with a gold electrode (Figs. 2c-d). In the latter case, nanotubes surrounding the gold electrode were removed. The derived resistances are $\sim 1 \text{ k}\Omega$ for the CNT-Au contacts and $\sim 1.5 \text{ k}\Omega$ for the CNT-CNT contacts. Although the overall electrical resistance is similar to or up to 10 times higher than those CNTs grown on other conductive substrates [19, 33, 41, 42], it is still very promising if considering the high resistance of the annealed substrates. This implies nanotubes would have a fairly good contact with the Ti coating and Ti carbides may be formed during the growth of nanotubes, preventing the Ti coating from oxidation to some extent.

3.2 Depth profile analysis of selected substrates by SIMS

In order to disclose the role of the catalyst sublayer played in the growth, SIMS depth profiles were carried out on four substrates with the conventional catalyst design of 0.8 nm Fe/10 nm Ti ($/\text{SiO}_2/\text{Si}$) and the novel design of 0.8 nm Fe/10 nm Ti/1.0 nm Fe ($/\text{SiO}_2/\text{Si}$), see Fig. 3. Two were as-deposited and two annealed. The annealing was carried out by heating the substrates under 500 sccm pure H_2 , 15 mbar from room

temperature to 650°C in 3min, then switching off the heater power and letting the samples to cool down with the H₂ flow on.

As shown in Fig. 3a, for the conventional catalyst design, the abrupt and monotonous drop of the Fe signal of the as-deposited substrate (blue solid line), confirms that Fe is surface rich only. For our novel catalyst design, it is not only surface rich but also rich at the coating/SiO₂ interface as indicated by the sharp Fe peak at the interface (blue solid line) in Fig. 3b. This is just what we expected through catalyst engineering. For the conventional catalyst design, after 3 min rapid annealing, it can be seen that diffusion of Fe into the Ti coating resulted in about 40% loss of the Fe intensity on the surface. On the contrary, for our novel catalyst design, the Fe intensity on the surface increased by about 35% and the Fe peak at the coating/SiO₂ interface almost disappeared after the annealing. This strongly implies that the Fe sublayer between the Ti coating and the substrate is thermally unfavored, so that Fe diffusion back to the surface is more significant than that towards the substrate during the annealing.

It can be expected that a proper catalyst sublayer should be able to minimize and sustain the catalyst on the top surface during the nanotube growth without causing obvious loss or gain by diffusion. As the 1.0 nm Fe sublayer can already lead to the increase of surface Fe after the rapid annealing (Fig. 3b), a Fe sublayer thicker than 1.0 nm is in fact detrimental to the growth of high-density CNT forests. This is consistent with our SEM observations in Fig. 1. Experiments reveal that a catalyst combination of a 0.6-0.8 nm Fe top layer and a 0.6-0.8 nm Fe sublayer gives the best alignment of CNT forests by our single-step CVD process.

It can be noticed that the nanotubes demonstrated in Fig. 1 have different thicknesses, i. e. different growth rates. The reason is most probably related to the alignment of nanotubes. The higher is the alignment degree, the less is the strain occurred to nanotubes and the higher is the growth rate. Without the catalyst sublayer, the catalyst loses continuously through alloying and diffusion during the CVD process. This will result in a very low catalytic nanoparticle density, which may lead to the growth of low-density and randomly ordered nanotubes. If a proper catalyst sublayer exists, its back diffusion to the surface will dramatically hinder the loss of surface catalyst, which can sustain the high-density catalytic nanoparticles and lead to the growth of highly oriented high-density nanotube forests. Once the catalyst sublayer becomes too thick, its back diffusion will get too significant, which will finally result in the growth of nanotubes with large diameter, less density and less alignment.

3.3 Effect of pre-annealing on nanoparticle formation and CNT growth

The back diffusion of the Fe catalyst to the top surface was also confirmed by SEM observations of catalytic nanoparticles formed by a rapid annealing. Figs. 4(a-d) show the effect of 0, 0.6, 1.0 and 1.8 nm catalyst sublayers on the formation of catalytic nanoparticles; the surface catalyst and Ti layers were fixed to 0.8 and 10 nm, respectively, and the substrates were heated up from room temperature to 700°C in 15 mbar 500 sccm pure H₂ for a total time of 3 min. It can be seen that a 0.6 nm Fe sublayer resulted in the highest density of catalytic nanoparticles (Fig. 4b). For the sample without a catalyst sublayer, although the catalytic nanoparticles are similar to that of the 0.6 nm Fe sublayer, but its density is much lower. This is because the surface catalyst loss is too fast without the compensation of a sublayer catalyst

through its back diffusion. With the increase of sublayer thickness, catalytic nanoparticles become larger and larger, and their density becomes lower and lower. The coarsening of catalytic nanoparticles is evidence that there was a net catalyst back diffusion, which agrees well with the SIMS results.

In literature, most of the nanotubes were grown through a routine two-step CVD process: annealing + growth. Figs. 4(e-h) display the SEM images of nanotubes grown on the corresponding annealed substrates in Figs. 4(a-d). It can be seen that nanotubes are less aligned and their densities are terribly low. However, this is in consistent with the nanoparticle densities shown in Figs. 4(a-d). In Fig. 4b, even the highest density obtained from the 0.6 nm Fe sublayer can only approach 10^{11}cm^{-2} and it further drops down by half with the 1.8 nm Fe sublayer. As the overall density is much lower than that achieved by the single-step CVD process (Figs. 1(j-k)); it indicates that even a simple pre-annealing in H_2 had already resulted in catalyst loss and/or nanoparticle coarsening on the surface. A CVD process possessing a slow ramping rate may have the same negative effects as annealing. This is the main reason why we chose the single-step cold-wall CVD, which has the ability to heat the substrate to growth temperature in 2-3min. Single-step CVD also shows advantages on large scale and reproducible growth of aligned CNT forests over multi-step CVD.

It is believed that a higher density of CNT forests is resulted from a higher density of catalytic nanoparticles. In addition to the novel catalyst design, the high concentration of C_2H_2 (8%), which has been proven to be the key growth precursor,[6] could probably have also played a very important role. Yamazaki [31] and Zhang [43] *et al.* have reported that a proper pretreatment of a catalytic thin film by CH_4 or C_2H_2 plasma could promote the formation of high density catalytic nanoparticles, which are

effectively immobilized by a carbon nano-film, leading to the growth of closely packed MWNT forests without causing the catalyst poisoning. High concentration C_2H_2 is also critical to grow ultra-high-density SWNT forests as reported in our previous study [14]. It is probably the same in our case. Once high density catalytic nanoparticles are formed on substrates with our novel catalyst design during the rapid ramping period, they are immediately immobilized and nucleated to grow nanotubes in the presence of C_2H_2 , hindering them from further coarsening or loss through surface and bulk diffusion. However, it is hard to obtain any direct evidence of the density of nanoparticles as the two-step CVD process does.

3.4 Density evaluation of aligned CNT forests

For the well aligned CNT forests, we used the liquid-induced compaction for fast density evaluation. Fig. 5 shows some comparative SEM images of the four samples shown in Figs 1(f-g and j-k) after compaction. Two different micro-structures were formed. For the low density samples (Figs. 5(a-b)), a cellular structure is usually formed, which agrees with that of low density MWCNT forests [35-37]. Due to the low density, most of the nanotubes were collapsed and densified on the surface except for those met from opposite directions forming the cell boundaries. For the high density CNT forests, CNT islands would be formed after densification (Fig. 5(c-d)). This is similar to our previous report for ultra-high-density SWCNT forests [14]. From these islands, a filling factor η termed as the area ratio of total islands to the substrate can be obtained, as labelled in Figs. 5(c-d). The higher is the filling factor, the higher is the CNT density. For the best of our samples, a filling factor as high as $\eta = 57\%$ can be reached. Figs 6(a-b) show the top-view and cross-sectional SEM images of such a sample, while Figs 6(c-d) are the high resolution SEM images taken

before and after the liquid-induced compaction. SEM observations under high magnifications disclose that well aligned and high-density nanotubes were almost compacted into solid blocks (Fig. 6d).

HRTEM observations reveal that the as-grown high-density CNT forests mainly consist of double-walled and triple-walled nanotubes with a mean diameter of 6.0 nm, as shown in Fig. 7. As we know that the areal density ρ of a nanotube forest is given by [12]:

$$\rho = \frac{1}{S} = \frac{2}{\sqrt{3}(D + \Delta)^2}$$

where, S is the average area occupied by one nanotube; D is the mean diameter of the nanotubes, and Δ is the average wall to wall spacing. The filling factor relates the density of nanotubes before and after the compaction as:

$$\eta = \frac{S_1}{S_0} = \frac{\rho_0}{\rho_1}$$

where, the subscripts of 0 and 1 represent the states before and after compaction, respectively. The density upper limit for nanotubes with a diameter of 6.0 nm can be calculated from ideally close-packed CNT forests [12], which is $2.87 \times 10^{12} \text{ cm}^{-2}$. Previous study has shown that compacted CNT forests could have a density up to 73% of that of ideally close-packed nanotubes [38]. Here we estimate a density close to 10^{12} cm^{-2} for our best samples prepared. This is similar to Yamazaki *et al.*'s work [31], which showed a slightly larger mean CNT diameter of 6-7nm, and an estimated filling factor of 30-40%. There may still have some room for density improvement by further

optimizing the catalyst/metal support/catalyst nanostructure and adopting plasma-assisted catalytic nanoparticle formation and immobilization [31, 43].

SEM observation also shows that high-density CNT forests could only grow a few microns in height. We find this is a common feature for CNT forests with high filling factors [14, 31, 43]. The most probable reason is that a high filling factor means very high packing density of nanotubes, which will strongly block the growth precursors from reaching the catalytic nanoparticles localized at the nanotube/support interface.

4. Summary

In summary, catalyst engineering, by adding an additional catalyst sublayer to the conventional catalyst/support design, is a very efficient way to promote the growth of high-density CNT forests on metal support. In our case, the surface catalyst can be minimized to 0.6 - 0.8 nm and sustained without remarkable loss or gain during the growth of CNT forests by adding a sublayer of 0.6 - 0.8 nm Fe catalyst beneath the 10 nm Ti coating. SIMS depth profile analysis and SEM observation indicate that the catalyst diffusion back to the surface from the sublayer overtake that down to the sublayer from the surface. HRTEM observations show that the high-density CNT forests consist of mainly double-walled and triple-walled nanotubes with a mean diameter of 6.0 nm. By using the liquid-induced compaction method, a filling factor up to 57% was achieved, and areal density around 10^{12} cm^{-2} was estimated for our best samples.

Acknowledgement

The authors are grateful to the EC funding of Viacarbon and Technotubes projects.

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Figure Captions

Fig. 1. Comparative growth of carbon nanotubes on Ti coatings using the conventional and our novel catalyst designs, respectively. (a) Schematic diagram of our novel catalyst design of τ nm Fe / 10 nm Ti / δ nm Fe on SiO₂/Si; it is equivalent to the conventional catalyst design if $\delta = 0$. (b-l) Cross-sectional SEM images of

nanotubes grown on Ti coatings with different τ - δ combinations. All the samples were produced by the single-step CVD at 15mbar, 40sccm C_2H_2 , 460sccm H_2 and 700°C, however, (b-h) were prepared in 10 min while (i-l) in 6 min.

Fig. 2 Electrical properties measured by a two-point probe station from (a-b) bare substrates coated with 0.8 nm Fe /10 nm Ti /0.8 nm Fe on SiO_2 and (c-d) the as-grown CNT forests. The insets illustrate how to contact the probes with the samples.

Fig. 3. SIMS depth profiles of the as-deposited (solid lines) and annealed (dash lines) substrates with (a) the conventional catalyst design and (b) our novel catalyst design, respectively. The annealing was carried out by heating the substrates under 500 sccm pure H_2 , 15mbar from room temperature to 650°C for 3min, then switching off the heater power and letting the samples to cool down with the H_2 flow on.

Fig. 4. SEM observations of (a-d) catalytic nanoparticles formed by a rapid annealing and (e-h) nanotubes subsequently grown from the corresponding nanoparticles. The annealing was performed by heating the substrates under 500 sccm pure H_2 , 15mbar from room temperature to 700°C for 3min; the growth lasted 3 min by introducing 8% C_2H_2 in H_2 immediately after the annealing. Substrate: 0.8 nm Fe /10 nm Ti / δ nm Fe/ SiO_2 .

Fig. 5. Top-view images (a-d) of the CNT forest samples shown in Figs. 1(f-g, and j-k) after liquid-induced compaction by soaking the samples thoroughly in ethanol and letting them dry in the air. The nanotube filling factors η were also given in (c-d).

Fig. 6. SEM images of one CNT forest sample showing the best alignment and highest density of nanotubes. (a) Top-view and (b) cross-sectional SEM images of the

sample after liquid-induced compaction. (c-d) High resolution cross-sectional SEM images before and after the compaction.

Fig. 7. HRTEM images of the high-density CNT forests and the diameter/wall number distributions.

Fig.1

Fig. 2

Fig.3

Fig.4

Fig. 5

Fig.6

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Fig.7