Growth of individual vertically aligned nanotubes/ nanofibers with small diameter by PECVD on different metal underlayers

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ABSTRACT

The primary goal of this work is to achieve significant improvement of growth of carbon nanotubes (CNTs)/ carbon nanofibers (CNFs) on different metal underlayers that can provide a platform for electronic companies to adopt the technology into their existing manufacturing pipeline. In order to meet the requirements we have exploited a crucial component, inclusion of amorphous Si, as a buffer layer between the catalysts and the metal substrates to facilitate the growth of carbon nanotubes/fibers. Here we present some of the results on growth of carbon nanostructures on different metal underlayers for three different catalyst configurations: as film, as metal stripes and as dots of catalysts. Electrical characteristics of the grown structures as measured by STM are also addressed.

Keywords: cnf, cnt, vacnt, pecvd, ebl, stm.

1 INTRODUCTION

Carbon nanotubes have emerged as one of the most promising candidates for future nano-elements due to their one dimensional nature, and unique electrical, optical and mechanical properties. Hence, there is considerable interest on integrating carbon nanotubes into existing silicon based technology. Nanotubes have been used to demonstrate many applications including electronic applications: field emitters and/ or as sources for electron guns [1], NEMS [2], etc. For most of these and other applications, aligned /micro patterned carbon nanotubes are highly desirable [3]. Moreover, a prerequisite for exploring CNTs/ CNFs in an industrial process is to control mass production with high reproducibility. Controlled growth on patterned substrates is therefore an important issue and plasma enhanced chemical vapor deposition (PECVD) is perhaps the most promising technique to meet such requirements. To fully exploit this promising growth technique, it is necessary to investigate and optimize the growth of nanotubes on different types of metal and insulating substrates.

Cassell et al. have studied PECVD growth of CNFs on metal underlayers exploiting a combinatorial fabrication technique [4]. Recently we have performed a thorough investigation [5] on the effect of a thin intermediate a-Si layer for the PECVD-growth of nanotubes using Ni as catalyst on different metal underlayers. The Si/metal interaction occurring during growth plays a vital role in nanotube formation. One significant accomplishment achieved by a-Si insertion is the production of individual vertically aligned nanotubes/ nanofibers with diameters on the order of 10-20 nm, which is advantageous in many applications. Another important achievement with this technology is to be able to grow nanotubes on metal substrates which otherwise do not display CNF-growth with a Ni catalyst.

2 EXPERIMENTS

Oxidized silicon substrates, 1cm^2 in area, with an oxide thickness of 400 nm, were used. First the metal electrode layer was evaporated directly on the substrate by electron beam evaporation to a thickness of 50 nm. Sheet resistance measurements were carried out on the as-deposited films. An amorphous Si layer was evaporated before the Ni catalyst. For the case of stripe and dot patterns we used, electron beam lithography (EBL). A double layer resist, 10% co-polymer and 2% PMMA, was used as part of the lift off process.

A DC plasma-enhanced CVD chamber was used to grow the nanotubes. The experimental set-up and detailed growth procedure have been described previously [5]. The nanotube growth was carried out in a C_2H_2:NH_3 gaseous (1:5) mixture at 5 mbar chamber pressure at 700 ^{0}C for 10-20 minutes. After growth, the samples were cooled down to room temperature before air exposure. As-grown structures from pre-fabricated dots were then imaged with a JEOL JSM 6301F scanning electron microscope (SEM). All the experiments were performed repeatedly to verify the reproducibility. An STM probe was employed as the counter electrode to measure the electrical properties of the grown nanostructures.

3 RESULTS AND DISCUSSIONS

3.1 Growth from catalyst film

Figure 1 shows the results obtained after growth on different metal underlayers where amorphous Si was introduced between the metal layer and the catalyst. Significant improvement was achieved by introducing the Si layer. However, no growth was achieved for the case of Ti and Cr. The reason for lack of growth was attributed to Ti silicidation on the thick silicon oxide layer with a high release of oxygen that influences the Ni/Ti interface [5]. The rest of the metal underlayers seem to give growth of nanostrucures with reasonable density as depicted in Figure 2 (a). Pt gave very densely packed growth whereas Pd gave growth of vertical nanostructures together with many entangled nanotubes. These four metals reacted strongly with Ni and Si forming different kinds of silicides at the growth temperature. Therefore, silicidation processes occuring during the growth sequence are important for growing nanotubes on metal underslayers.

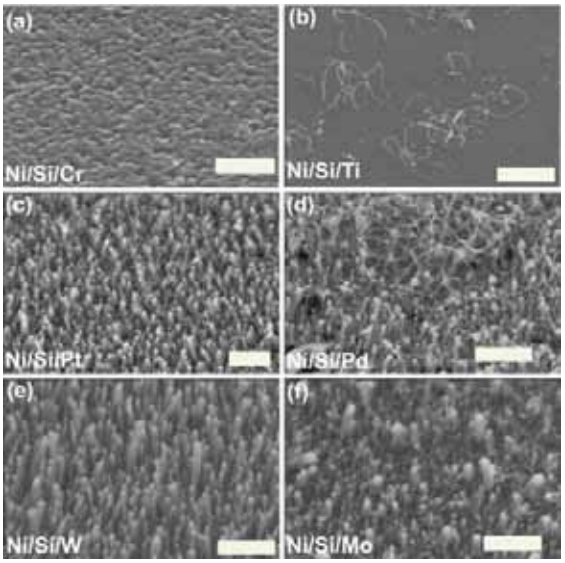

Figure 1: SEM micrograph of the samples after 15 minutes of CVD growth. The presence of Si facilitated the growth of nanotubes on some metal underlayers which was not possible in the other set of experiment (not shown here). All scale bars are 1μm.

The Density of the grown nanostructures is plotted for both the Si inclusion and Si exclusion cases. When the thin Si layer is included the density is much higher compared to no Si with a strong inclination towards forming structures with small diameters ≤ 20 nm. Only W and Mo metal underlayers show growth for the Si exclusion case with poor density and uniformity.

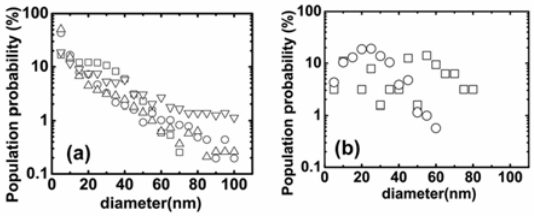

Figure 2: Size distribution of CNT: (a) metal underlayer with amorphous Si layer; square-Platinum-390 counts/μm^2; circle – Palladium – 226 counts/μm^2; up-triangle – Tungsten – 212 counts/μm^2; down triangle – Molybdenum – 89 counts/μm^2 and (b) metal underlayer without amorphous Si layer; square – Molybdenum – 5 counts/μm^2; circle – Tungsten – 73 counts/μm^2. No growth was achieved for other metal underlayers without the amorphous Si layer.

3.2 Growth on metal catalyst stripes

Growth from 1-10 μm wide catalyst stripes resembled the results obtained from films of catalyst as seen in Figure 3. CNTs/CNFs with small diameter and length are usually grown at the edges of the catalyst stripes. Though structures with large diameters are more visible in the figure, a large number of small diameter structures are present as can be seen in Figure 3 (b).

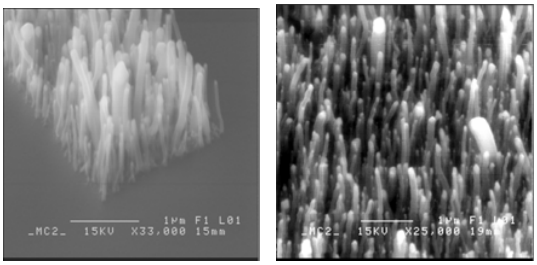

Figure 3: SEM micrograph of the samples after 15 minutes of CVD growth. Forest-like growth is observed. The length distribution is uneven (b) CNTs/CNFs grown on a 10 μm wide catalyst stripe.

The prevailing parameters that control the length distribution include the plasma power and gas ratio, the material below the plasma, species that are present in the plasma just above the material's surface due to secondary electron emission and different electric field distributions for different materials [6].

3.3 Growth on pre-fabricated dots

E-beam lithography (EBL) was employed for fabricating catalyst dots with different dimensions and pitches. Figure 4 portrays the results obtained from pre-fabricated catalyst dots of 100 nm and 50 nm diameter on a Mo metal underlayer. In each case there is a thin Si layer

inserted between the metal underlayer and the catalyst. For both 100 nm and 50 nm sized catalyst dots, there are some instances of multiple CNFs growing from a single dot (100% and 2% respectively). CNFs grown from 50 nm dots are well aligned vertically with respect to the substrate. Most of the fabricated dots (more than 95%) acted as nucleation centers for growth. It is found from our measurements that the base diameter of isolated VACNFs in most cases was slightly larger than the tip diameter. 100 nm catalyst islands tended to split into several islands resulting in the growth of more than one nanotube/ nanofiber. The verticality of the grown structures is not as pronounced as for 50 nm dots. The Inset of figure 4 (a) shows one of such dots where multiple fibers have grown. Diameters of the grown structures are of the order of 30 nm and in some cases even smaller. Typically length variations from 400 nm to 800 nm were observed.

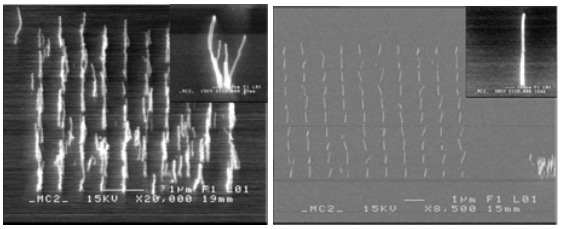

Figure 4: Multiwalled CNTs grown on pre-fabricated dots (a) 100 nm catalyst dots. Inset shows growth of multiple nanotubes. (b) 50 nm catalyst dots. Inset shows a high resolution image of an individual nanotube with ~50 nm diameter. In both cases a Mo metal substrate was used.

The inset of figure 4 (b) shows a high resolution image of an individual free standing CNF grown from a 50 nm catalyst dot. A tip growth mechanism prevails in all cases as the catalyst is riding at the top. The Mo underlayer provided a good base for the Ni and Si to interact and form catalyst particles which in most cases nucleated growth of free standing structures. However, size induced thermal expansion mismatch between the Ni/Si layer and the Mo layer let to break-up of the larger dots and subsequent growth of multiple structures As seen in the inset of figure 4 (b), the critical size for the nucleation of single CNTs was ~ 50 nm, which is much smaller than the previously published values [6].

3.4 Pitch limitations on growth

We performed a test on pitch induced limitations on growth and we find that it is possible to grow individual nanostructures down to 100 nm pitch for 50 nm dots, to a certain extent. Figure 5 portrays the obtained results. The grown structures are individual but tend to entangle with their nearest neighbors thereby putting a limit to the density attainable for growth of free standing individual carbon nanostructures.

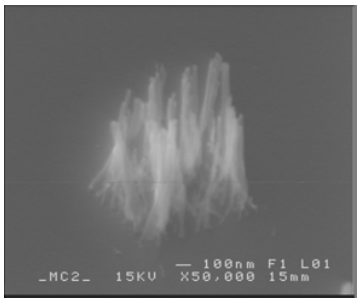

Figure 5: Pitch limitations for growing individual CNFs. 50 nm dot size with 100 nm pitch was used in this experiment.

3.5 STM study on grown structures

Since the majority of the structures grown here are CNFs, a metallic behavior is anticipated. We have used an STM probe station to investigate the two-terminal electrical resistance at room temperature.

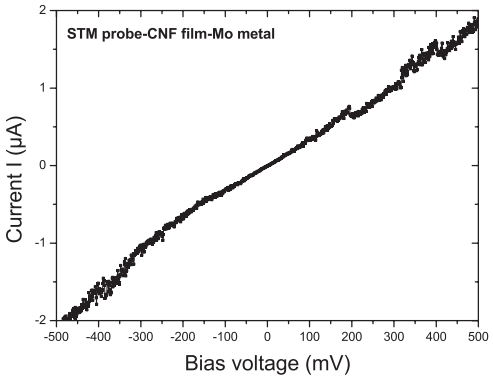

Figure 6: Typical IV characteristics of the measured CNF film after contacting the STM tip with the film

Figure 6 shows a typical current-voltage (*I-V*) measurement obtained from the CNF films. The measurements were carried out on grown structures from the 10 μm wide catalysts stripes. The resistance values were of the order of 200 kΩ which is slightly higher than the values reported by others for 4-probe measurements on individual structures removed from the substrates on which they were grown [4, 8].

Further measurements will be carried out to measure the conductivity of the free standing individual CNFs.

4 CONCLUSIONS

In conclusion, we have shown that it is possible to grow CNTs/ CNFs on different metal underlayers, a prerequisite for making electronic devices. The use of Si as an intermediate layer facilitated the growth of CNTs/ CNFs on

four metal underlayers. Catalyst metal stripes showed similarity with the film growth case. Moreover, we show successful growth of free standing vertically aligned individual CNFs from pre-fabricated catalyst dots. Vertical growth and linear IV characteristics make these grown structures promising for example as possible replacements for Cu interconnects for multilevel circuit manufacturing technology.

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