POSITIONS EFFECT IN A CVD REACTOR ON THE GROWTH OF ALIGNED CARBON NANOTUBES

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1. Introduction

Recently, our research group developed a novel composite catalyst for oriented growth of CNT arrays[1], and succeeded to grow the longest multi-wall CNT forest (22 mm). The dependence of CNT growth on thermal CVD process parameters is of particular interest. A recent study by Bronikowski[2] and Jeong et al[3] have shown that the maximum nanotube length achieved in CVD growth depends also on the catalyst pattern size and spacing. Although much can be inferred based on previously published data, no comprehensive study of the substrate position effects in the CVD reactor on the growth of CNT arrays has yet been reported. Such investigation is critical for scaling up the production of CNTs from a small to a big size CVD reactor. For these reasons, we conducted a systematic study of the substrate position effect on the length of CNT arrays. Our objective in this study was to understand how various positions of the substrate could affect the growth of the CNT arrays, and from the gained knowledge to develop process approach for controlling the carbon nananotube quality and length.

2. Experimental

Multilayered silicon substrates (5000 Å ± 5% thermal oxide on surface) with aluminum oxide buffer layer (15nm Al_2O_3) and 2nm novel catalyst alloy on top were produced in a Clean Room and cut into square samples with dimensions 1cm$\times$1cm. The substrates were annealed for 5 hours at 400^{o}C. The CVD growth of CNT on top of the catalyst-coated substrates was conducted using two different in size reactors. The smaller one, EasyTube™ 1000, includes a 22 inch long quartz tube with 2 inch diameter, and 7 inch $\times$ 1 inch rectangular platform for placing the Si substrates. The bigger reactor, EasyTube™ 3000, accommodates a 24 inch long and 3 inch in diameter quartz tube, along with an 8 inch $\times$ 2 inch rectangular platform as shown in Figure 1 (a-b). The deposition process was conducted using a gas mixture of ethylene, hydrogen, argon and water vapor carried by a separate argon flow. The gas flow rates were programmed by using mass flow controllers and a graphical program for measurement and automation. The reactor total pressure was maintained about 760 Torr at a deposition temperature of 750º C for selected growth time of several hours.

3. Results and Discussions

The substrates were cut from a 4 inch wafer prepared with same multilayered structures and composition of the composite catalyst. The substrates were uniformly distributed on the platforms of the CVD reactors and processed at identical growth conditions such as gas flow rates, deposition temperature, and growth time. In this arrangement, the lengths of the CNT arrays only depend on the substrate position. We found similar behavior of the CNT arrays grown in a bigger EasyTube™ 3000 reactor and in a smaller one (EasyTube™ 1000) in terms of length distribution and quality. Since the EasyTube™ 3000 reactor is larger, 15 identical substrates were uniformly placed on the platform and grown in one experiment to study the position effect. Figure 1 (c) and (d) show the color contour plots of the CNT array lengths vs. different positions. The contour lines in Figure 1 (d) (5 hours deposition) are much closer to each other than in Figure 1 (c) (3 hours deposition), which indicates that the variation of CNT length becomes more significant at longer deposition time. Figures 1 (e) and (f) show the effects of the substrates positions along the platform's long and short side on the length of CNT arrays. These experiments revealed that substrates located in the middle of the platform's short side achieved maximum array lengths-Figure 1 (e). Similarly, substrates located at the second half of the platform away from the gas inlet yielded maximum nanotube length. As mentioned earlier, we believe that this non-uniformity in the CNT length is caused by the incoming cool gas flow which travels throughout the volume of the CVD reactor and heats up downstream. The Raman spectra and related I_D/I_G ratios of CNTs grown at different positions along the platform do not change much and are almost the same in spite of differences in the array's heights as shown in Figure 1 (g). This indicates that the purity, crystallinity, and degree of graphitization do not depend on the substrate position. SEM and HRTEM images of all the CNT samples are quite similar, which confirms the similarity in the nanotube quality as shown in Figure 1 (h) and (i). This may be related to the relatively steady growth environment. The growth conditions (substrate temperature, deposition time, gas mixture, and

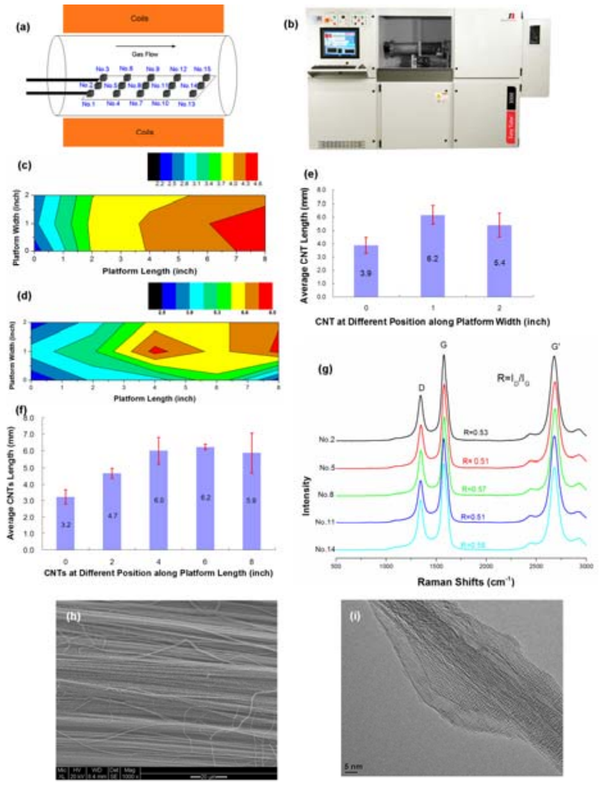

Figure 1. (a) Schematic of 15 substrates on the reactor platform; (b) EasyTube™ 3000 reactor; (c) Color contour plot of the CNT array lengths vs. substrate positions on the platform after 3 hours growth; (d) Color contour plot of the CNT array lengths vs. substrate positions on the platform after 5 hours growth; (e) CNT length along the platform; (f) CNT length within the platform's width; (g) Raman spectra of CNT arrays grown at 5 different positions along the platform; (h) SEM image of the CNT array; (i) HRTEM image of CNT array.

catalyst) around the substrates located at different positions on the platform are assumed to be the same. It is reasonable to speculate that the gas flow velocity would affect the local concentration of the gas species produced during the CVD reaction by changing the rate at which they are swept away from the growing CNTs. The gas mixture is inserted into the CVD reactor from an inlet with considerably smaller diameter compared to the tubular quartz reactor. This causes high inlet flow velocity. Right after the gas fluid starts running downstream the quartz tube, the flow velocity of the gas species including of those evolved during the CVD reaction, begins to decrease as the gas mixture travels towards the outlet. Higher flow velocity implies a lower steady state concentration of the CNT "feeding" species, which could cause lower CNT growth rate near by the gas inlet area of the platform. If the flow velocity is too low, the growth of CNTs is suppressed as the catalyst particles become passivated by the heavy hydrocarbons or graphitic carbon. Bronikowski[2] also reported similar flow rate effects on CNT growth. In addition, the relatively low temperature of the inlet gas flow may disturb the steady temperature profile of the tubular reactor and may also contribute to the length non-uniformity of the CNT arrays on the platform. Finally, we observed that the CNT arrays grow with a pretty good uniformity on a single substrate no matter of its position on the platform or of the substrate size. This is because the Al_2O_3 buffer layer on the Si substrate contributes to the surface diffusion of the carbon precursor and to its transportation to the catalyst sides, which results in homologous growth environment and uniform length of the CNTs.

4. Conclusions:

The position of the substrates located on the platform of the CVD reactor affects the length of the grown CNT arrays. This effect is more pronounced along the platform's length, although non-uniformity is also revealed across the width of the platform away from the gas inlet. Related factors such as gas flow velocity and temperature dependence of the gas mixture downstream the CVD reactor are the main reasons causing the observed non-uniformity of the CNT length. The quality of the CNTs was not affected significantly when changing the position of the substrates within the reactor's platform. The obtained knowledge could be applied to scale up the CVD growth of CNT arrays.

5. References:

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