The Effect of Temperature on Properties of CNTs Grown by Chemical Vapor Deposition

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Abstract In this article, the carbon nanotubes (CNTs) grown at different temperature by thermal chemical vapor deposition (T-CVD) have been reported, while the effect of growing temperature and catalyst annealing on the quality of CNTs has also been investigated. The longest CNT bundles were grown at the temperature of 730°C by Scanning Electron Microscopy (SEM) images and the better quality of CNT bundles were achieved at higher temperatures of 850°C by Raman spectroscopy.

1. Introduction

CNTs have been widely reported in the gas pollution, water treatment or biomaterial sensing applications due to their small size, relative chemical inertness and large specific surface area. There are also various reports on CNTs in electrical applications because of its extraordinary electrical, mechanical and thermal properties [1-8].

Although many CNTs synthesis methods are available in the literatures [9-12], chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD) are still the most common used methods [13, 14]. However, the CNTs synthesis temperature is very high, normally varies from 650 to 900°C. This high temperature which can cause serious damages on the electronic components in integrated circuit (IC), become a significant barrier to handle and integrate CNT with microelectronic circuits or devices to form a completed system [15-17].

Therefore, a systematic study of the temperature parameter on both the length and quality of CNTs arrays grown by thermal CVD is carried out in this paper. The purpose of the study is to understand how the various synthesis parameters will affect CNTs growth, and determine which synthesis parameters can be used effectively to control the length and quality of the resulting CNTs. It is of great significance in the CNTs growth and silicon based Micro-electro-mechanical systems (MEMS), which will be integrated into through-wafer interconnects and biosensor [18-20].

2. Experimental

A low pressure thermal chemical vapor deposition (LP-TCVD) systems which consists of a 4 inch barrel quartz tube furnace and mass flow controllers was used to synthesis CNTs on Si substrate. 2 µm thick of silicon dioxide was first formed on the Si substrate before an electron beam evaporator was used to deposit a uniform layer of iron (Fe) which acted as the catalyst. After the catalyst pretreatment, C2H2 was introduced into the quartz tube to initiate the growth of CNTs. The flow rate of the process gas H2:Ar:C2H2 was fixed at the ratio of 1:4:1, respectively.

The surface morphology of the as grown CNTs on the Si wafer substrate was characterized using scanning electron microscopy (SEM). The root mean square (RMS) roughness of the substrate surface and the mean diameter of the catalyst particles after annealing treatment without CNTs growth were
measured. Raman spectroscopy (a 633 nm HeNe laser excitation, Renishaw Raman Microprobe-RM1000) was also used to study and characterize the graphitic ordering of the growing CNTs.

3. Results and Discussion

The CNTs growth was investigated as a function of the CVD growth temperature in the range of 650°C to 900°C. Fig. 1 showed a plot of CNTs length vs. growth temperature, and it could be seen that CNTs length was very temperature dependent, as a slight increase in the temperature range from 700°C to 730°C could increase the CNTs length by about 100 µm. It was also found that the drop in overall vertical CNT length was corresponded to the drop in the CNTs density, which was evident of the crowding effect that determined the overall vertical CNTs length [21].

![Figure 1. The CNTs length grown at different temperature by chemical vapor deposition](image-url)

The effect was more noticeable when CNTs synthesized at the temperature of 700°C, 800°C and 900°C compared with Fig. 2. The crowding effect could be explained by the differences in Fe catalyst particle density and the resulting CNTs density because of different temperature. The influence of growth temperature on the morphology of the Fe catalyst particles density could be investigated by simulating the condition of the catalyst layer. To investigate the reason, the prepared substrates with deposited Fe catalyst layer underwent annealing in vacuum with three different temperatures of 700°C, 800°C and 900°C without introducing acetylene gas into initiate CNTs growth. The surface topography of the resulting catalysts surface after annealing was then studied by SEM and RMS roughness.
Figure 2. Cross section SEM images of CNTs at different growth temperatures; (a) 168 µm long CNTs grown at 700°C (c) 40 µm long CNTs grown at 800°C, (e) 35 µm long CNTs grown at 900°C; The SEM images taken at the interface between the substrate and CNTs grown at (b) 700°C, (d) 800°C, (f) 900°C

The SEM images (Fig.2) showed that the RMS roughness (Fig.4) and the mean catalyst particles diameter (Fig.3) on the catalyst surface increased with increasing annealing temperature, which was similar to some results made by other papers[21, 22]. This was a result of a coalescence phenomenon, where the mobility of nanoparticles increased on the surface and agglomerated to form larger particles which reducing the surface energy as the result of temperature increasing [22, 23].

Higher temperatures could encourage the formation of bigger Fe catalyst particles which were less uniformly distributed with lower catalyst particles density. At higher temperatures of 800°C and 900°C, the catalyst particles were less dense, thus the resulting CNTs growth was also less dense. The higher rate of reaction and increase in the dissolution, diffusion and precipitation of carbon provided by higher temperatures were not ignored, but this effect was seriously weighed down by the decrease in CNTs density. The low CNTs density allowed more space for the CNTs to grow laterally and in random directions as they suffered from a lack of crowding effect or mechanical leaning between neighboring CNTs. As a result the overall vertical length was much shorter for higher temperatures. Conversely the CNTs synthesized at 700°C formed from dense Fe catalyst particles were denser, and more aligned which explained the long overall vertical length of 168µm. This was similar what was being reported in several papers [15, 20], which investigated the effect of temperature on CNTs growth.
Figure 3. The catalyst surface SEM images (a) before annealing and after annealing pretreatment of at (b) 700°C, (c) 800°C, (d) 900°C.

It was widely accepted that the CNTs diameter was determined by the catalyst particle diameter. However, it was very difficult to directly correlate the CNTs diameter to measured particle diameter because the diameter of the CNTs was so small, and the variation in CNTs diameter could not be verified within the limits of the SEM pictures. It was observed that the distribution of CNTs diameter was wider at 900°C, with some CNTs of significantly bigger diameters (Fig. 3f). It can be stated that these thicker CNTs were formed from the bigger size catalyst particles that coalescence at the higher temperature of 900°C. The larger surface of larger Fe particle permitted more adsorption of carbon atoms, and the diffusion rate increased with the higher temperature and this result in large diameters CNTs [23].

Figure 4. (a) RMS roughness of catalyst surface and (b) Mean diameter of particles on catalyst surface as a function of catalyst annealing temperature

Raman characterization had demonstrated that the crystallinity of graphitic CNTs improved with increasing temperature, and the degree of defectiveness in the CNTs decreased with the growth temperature which was also reported in other papers [15, 17, 21]. Fig.5 showed the relationship of the peak intensity ratio of the G band and the D band as a function of growth temperatures. As the growth temperatures increased, the Raman I_G/I_D ratio reaching a maximum at 850°C showed that highly ordered graphitic tubular structures of the CNTs grown at this temperature.

As the growing CNTs were mainly multi-wall CNT (MWCNT) at lower temperatures, the radial breathing mode of single-wall CNT (SWCNT) started to appear in the lower parts of the spectrum at
The highest temperature of 900°C (Fig. 5). This point to the presence of SWCNT at higher temperature similar to that reported in some studies [21]. The high temperature at 900°C could have provide the needed activation energy for the nucleation of SWCNT, and the high surface roughness of the catalyst surface after annealing at 900°C (Fig. 4) could also help to stabilize the catalyst particle with smaller size and promote the growth of SWCNT [21]. The results show that not only the density and length of CNTs growth by the thermal CVD system could be controlled by adjusting the temperature, but also the type, structure and quality of CNTs is also greatly affected by the temperature. Vertically aligned MWCNT with the longest length were best synthesized at around 730°C while CNTs with better quality were achieved at higher temperatures of 900°C.

![Figure 5. Peak intensity Raman ratio I_G/I_D of CNTs grown at different temperatures](image)

### 4. Conclusion

In summary, the CNTs grown at different temperatures by thermal chemical vapor deposition have been reported, and the surfaces of catalysts annealed at different temperature were investigated. The SEM pictures and the Raman characterization demonstrated that the longest of CNTs bundle were grown at the temperature of 730°C, and the better quality were achieved at higher temperatures of 900°C by chemical vapor deposition.

### 5. References

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