



Effect of NH_3 and thickness of catalyst on growth of carbon nanotubes using thermal chemical vapor deposition

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Abstract

The growth behavior of carbon nanotubes synthesized from C_2H_2 using thermal chemical vapor deposition method has been investigated. The formation of catalytic cobalt nanoparticles was much enhanced when using NH_3 as the environment gas, whereas NH_3 introduced during nanotubes growth does not play a key role in growing the vertically aligned nanotubes. The role of NH_3 is to obtain the high density of nucleation sites for nanotube growth by inhibiting amorphous carbon generation in the initial stage of synthesis. We found unexpected behavior in terms of the length and growth time during nanotube growth. The length of the nanotubes is inversely proportional to the size of nanoparticle just in the initial stages of growth and thick catalyst.

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1. Introduction

Carbon nanotubes (CNTs) have attracted considerable interest because of their unique physical properties and may potential applications [1]. Different diameter and chirality of nanotubes give rise to diverse chemical, physical and mechanical properties. CNTs have been synthesized by numerous techniques, such as arc discharge [2], laser ablation [3], catalytic chemical vapor deposition (CVD) [4,5], etc. Compared to arc discharge and laser ablation, CVD has been used to produce

highly purified CNTs in large quantities and also to obtain CNTs vertically aligned on substrates for use as electron emitters. Moreover, this process makes it possible to control the size and growth density of CNTs by dispersing the catalyst on substrate and adjusting the reaction parameters. Especially, thermal CVD compared to plasma-enhanced CVD is better for large area synthesis. To research growth mechanism and realize device applications, controlled growth of well-aligned CNT is essential. The properties of CNTs critically depend on the catalyst thickness and reaction gas.

In this work, we describe experiments that systematically explore the effect of NH_3 on the catalyst film and vertical alignment of CNTs, and the

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effect of predeposited catalyst film on growth rate of CNTs with growth time.

2. Experimental details

In this study, the growth of CNTs was performed using a thermal CVD system already described in [6,7]. The standard pretreatment and growth conditions are shown in Fig. 1. Cobalt (Co) was deposited on the silicon wafer with thermally grown silicon oxide by r.f. magnetron sputtering. The specimen was placed into the quartz reactor for growing and the chamber was pumped down to less than $\sim 10^{-3}$ Torr using a mechanical pump. Before reaching the growth temperature at 750 °C, H₂ (80 sccm) and Ar (70 sccm) were fed into reactor. The synthesis temperature and pressure were about 750 °C and 50 Torr, respectively. After the temperature and the pressure were stabilized, NH₃ instead of H₂ was introduced for 10 min. C₂H₂ gas was then introduced with a flow rate of 5 sccm. The growth time was varied from 1 to 20 min. The samples were then cooled in Ar and H₂ flow ambient. The above standard pretreatment and the growth conditions might be replaced by various conditions according to the purpose of experiments. To investigate CNTs, high resolution scanning electron micro-

scopy (HRSEM, Hitachi S4300), high resolution transmission electron microscopy (HRTEM, JEOL, JEM-3000F), and atomic force microscopy (AFM, Veeco, CP-R) were used.

3. Results and discussion

We observed the effect of NH₃ gas on formation of Co nanoparticle during pretreatment. The scale is the same in all the images in Fig. 2. Figs. 2a–c are the SEM images of the morphology of Co layer annealed at 750 °C for 10 min in H₂ and Ar ambient. The corresponding thickness of the Co layer is 4, 8, and 10 nm in images a, b, and c, respectively. In 4 nm thick Co layer, the conglomeration effect was observed from the heating. As the thickness of the Co layer was increased, no remarkable change of Co layer was observed. Figs. 2d–f show the SEM images of the Co layer annealed at 750 °C for 10 min in NH₃ and Ar ambient. The Co layer was transformed into nanoparticles. As the thickness of the Co layer increased from 4 to 10 nm, an average diameter of Co particles increased and the density of nanoparticles decreased. These results suggested that Co layer agglomerated to become large

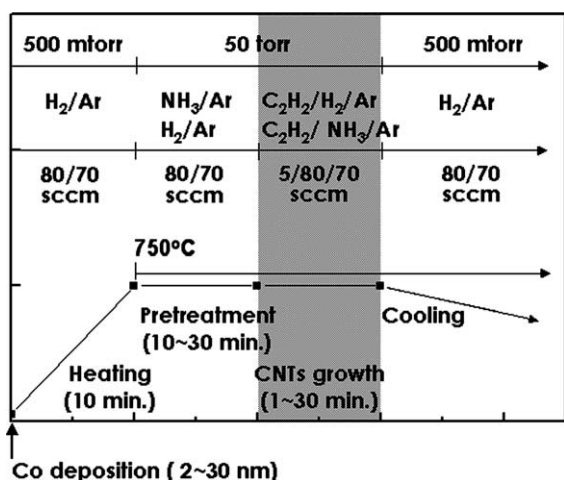


Fig. 1. Schematic diagram of pretreatment and growth conditions employed in this study.

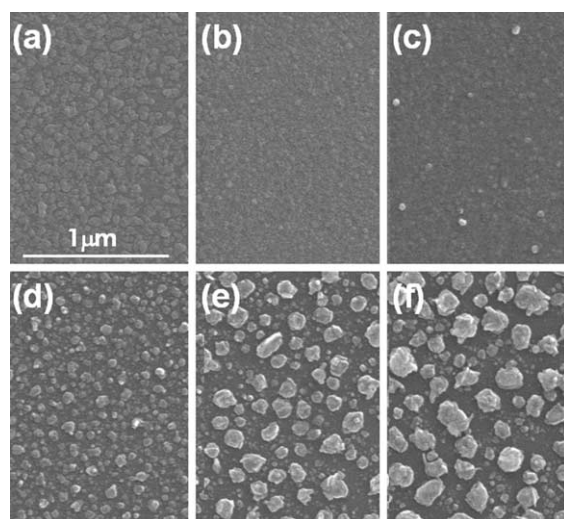


Fig. 2. SEM images of (a)–(c) the morphology of Co layer annealed in H₂/Ar ambient and (d)–(f) the Co layer annealed in NH₃/Ar ambient at 750 °C for 10 min: (a) and (d) Co layer of 4 nm; (b) and (e) Co layer of 8 nm; (c) and (f) Co layer of 10 nm.

particles by thermal energy during pretreatment. And both small nanoparticles and partially thin layers were etched and then removed by NH_3 gas.

Figs. 3a–c and d–f show the SEM images of CNTs grown on pretreated Co layers corresponding to Figs. 2d–f at 750°C for 10 min using a mixture of $\text{C}_2\text{H}_2/\text{NH}_3/\text{Ar}$ and a mixture of $\text{C}_2\text{H}_2/\text{H}_2/\text{Ar}$, respectively. The scale is the same in all the images in Fig. 3. The vertically aligned CNTs were grown on substrate when NH_3 was not introduced. By adding NH_3 gas, the growth rate of CNTs decreases [9]. Figs. 3g–i show the TEM images corresponding to Figs. 3d–f. The CNTs are multiwalled CNTs with outer diameter range from 25 to 35 nm and consists of hollow compartments, looking like a bamboo structure that is well known in the vertical growth of CNTs on a catalytic metal deposited substrate.

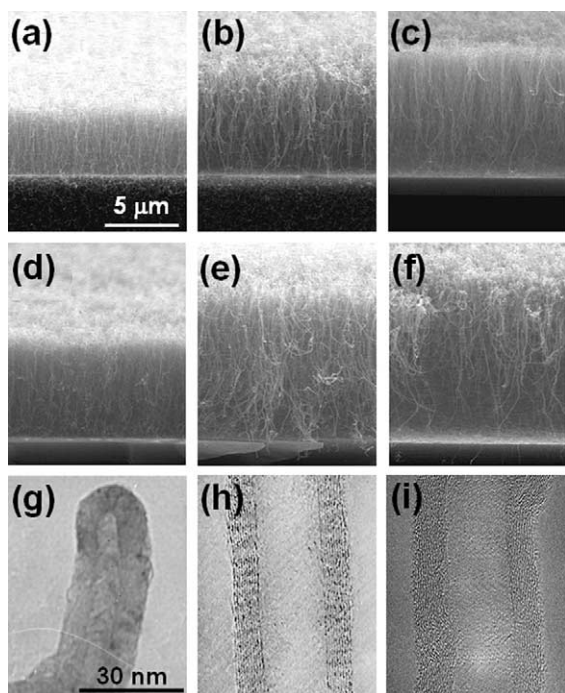


Fig. 3. (a)–(c) SEM images of CNTs grown using a mixture of $\text{C}_2\text{H}_2/\text{NH}_3/\text{Ar}$. (d)–(f) SEM images of CNTs grown using a mixture of $\text{C}_2\text{H}_2/\text{H}_2/\text{Ar}$: (a) and (d) grown on nanoparticles corresponding to Fig. 2d; (b) and (e) grown on nanoparticles corresponding to Fig. 2e; (c) and (f) grown on nanoparticles corresponding to Fig. 2f. (g)–(i) TEM images of CNTs corresponding to (d)–(f), respectively.

Fig. 4a shows the SEM images of the 10 nm thick Co layer pretreated at 750°C for 30 min in H_2 and Ar ambient. The catalyst layer was agglomerate with increasing treatment time when NH_3 was not introduced. The size of nanoparticles was similar to that of Fig. 2f. We pumped out H_2 gas after pretreatment and introduced the chamber with NH_3 (80 sccm) for 0, 1 and 2 min, and then C_2H_2 (5 sccm) and H_2 (80 sccm) instead of NH_3 were introduced. Figs. 4b–d show the SEM images of CNTs grown for 10 min in $\text{C}_2\text{H}_2/\text{H}_2/\text{Ar}$ ambient after NH_3 introducing for 0, 1 and 2 min, respectively. It was not observed that the morphology of pretreated catalyst was abruptly changed. The alignment and density of CNTs was improved according to increase introducing time of NH_3 .

The above experimental results indicate that NH_3 gas introduced during CNTs growth doesn't play a key role in growing the vertically aligned CNTs. The vertical alignment of CNTs is due to van der Waals interactions between neighboring CNTs along the direction normal to the substrate. The appropriate density of nanoparticles on substrate is crucial in growing vertically aligned CNTs. A prior NH_3 treatment is necessary for obtaining high density of nucleation sites for CNT growth by inhibiting amorphous carbon genera-

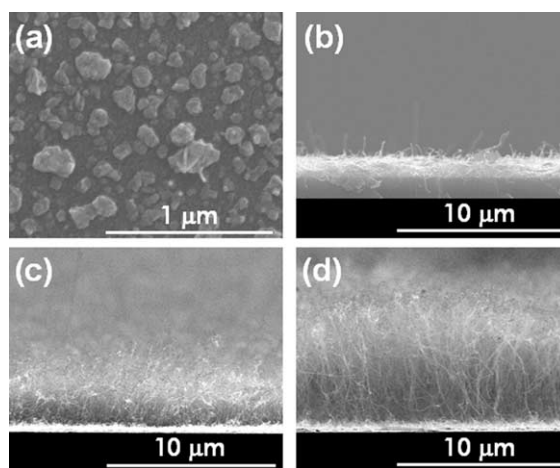


Fig. 4. SEM images of (a) the 10 nm thick Co layer pretreated at 750°C for 30 min in H_2/Ar ambient and CNTs grown for 10 min in $\text{C}_2\text{H}_2/\text{Ar}/\text{H}_2$ ambient after NH_3 introducing for (b) 0 min, (c) 1 min and (d) 2 min.

tion in the initial stage of synthesis, and thereby, protects the Co particles from the cover by amorphous carbon [10–13].

Fig. 5a shows the variations of an average diameter of CNTs and catalyst with thickness of Co layer. The diameters were measured using HRTEM and AFM. CNTs were grown at 750 °C for 10 min under $C_2H_2/H_2/Ar$ ambient after NH_3 pretreatment for 10 min. The catalyst was annealed at 750 °C for 10 min in NH_3 and Ar ambient. The average roughness increased with the thickness of Co layer. As the thickness of the Co layer was increased from 4 to 16 nm, an average diameter of Co nanoparticles was increased from

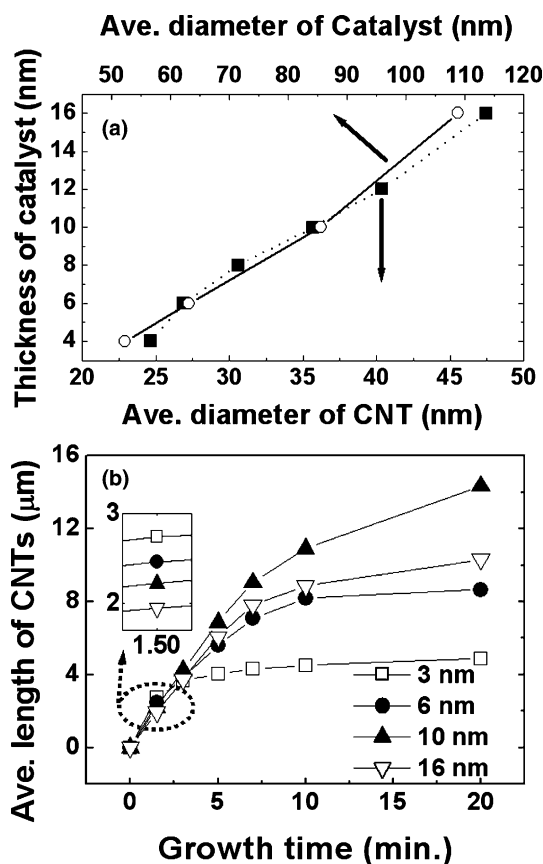


Fig. 5. (a) Dependence of the average diameter of CNTs and catalyst nanoparticles on thickness of Co layer. (b) Dependence of the length of CNTs on growth time. CNTs were grown at 750 °C in $C_2H_2/Ar/H_2$ ambient after NH_3 pretreatment for 10 min.

52.3 to 108.8 nm. And the diameter of the CNTs increases linearly because the diameter of the catalyst tends corresponding to the diameter of the MWNTs for thermal CVD [14].

Fig. 5b shows the length versus the growth time for the CNTs grown at 750 °C in $C_2H_2/H_2/Ar$ ambient. NH_3 pretreatment was carried out using Ar (70 sccm) and NH_3 (80 sccm) at 750 °C for 10 min. The thickness of Co layer is 3, 6, 10, and 16 nm, respectively. We observed that the length of CNTs varied according to the thickness of Co layer and growth time. When the CNT's growth time is below 3 min, the length of CNTs is inversely proportional to the CNT's diameter regardless of the catalyst's thickness. But, when the growth time surpasses 3 min, the length of the CNTs increases and then decreases with the thickness of Co layer. In a case when the catalyst's thickness is 3 nm, the growth rate rapidly decreases when the growth time reaches 3 min. But when the thickness is 6 nm and over 10 nm, there is a prominent decrease in the CNT's growth rate after 7 and 10 min, respectively. This result does not agree with previous report [8]. However, in our experimental conditions, CNT growth cannot occur when Co layer is much thicker than 25 nm. In general, the diffusion of carbon is mainly operative in the growth of CNTs. Therefore, in small and dense Co particle, the diffusion time for carbon atoms to arrive at the growth site would become short, resulting in accelerating the growth rate of CNTs. When the growth time is increased, carbon atoms cannot be adsorbed to the surface of Co particles due to the carbonaceous particles easily covering the surface of the Co particles and may not easily reach the bottom of the substrate due to the compact CNTs highly populated on the surface as shown in Fig. 3. In large Co particle, the diffusion length of carbon atoms increase and the growth rate decrease. Finally, when the size of Co particle is much larger than the diffusion length, CNTs growth cannot occur.

The above experimental results indicate there is critical thickness of catalyst showing the difference tendency in growth rate although the critical thickness of catalyst can be changed because the growth conditions are dependent on the equipment or research group.

4. Summary

We have grown the vertically aligned CNTs on Co deposited SiO₂ substrates using thermal at 750 °C. For the CNTs growth, the role of NH₃ is to obtain high density of nucleation sites for CNT growth by inhibiting amorphous carbon generation in the initial stage of synthesis. In case of using the Co film deposited in a large area, the diameter of CNTs always depends on the size of catalyst particles. But the length of CNTs inversely proportions to the size of catalyst particles just in that the catalyst that is thicker than 10 nm and the initial stage of CNTs growth though the critical thickness and time is changed according to research group. In order to realize better controllable growth of CNTs, the more quantitative analysis of catalyst and CNTs should be investigated in future study.

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References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, *Nature* 388 (1997) 756.
- [3] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fisher, R.E. Smalley, *Science* 273 (1996) 483.
- [4] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, *Science* 282 (1998) 1105.
- [5] W.Z. Li, S.S. Xie, L.X. Qain, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, *Science* 274 (1996) 1701.
- [6] Y.H. Lee, Y.T. Jang, D.H. Kim, J.H. Ahn, B.K. Ju, *Adv. Mater.* 13 (2001) 479.
- [7] Yoon-Taek Jang, Yun-Hi Lee, Byeong-Kwon Ju, Jin-Ho Ahn, Chang-Ki Go, Gong-Seog Park, *Vacuum* 68 (2003) 79.
- [8] C.J. Lee, S.C. Lyn, Y.R. Cho, J.H. Lee, K.I. Cho, *Chem. Phys. Lett.* 341 (2001) 245.
- [9] C.J. Lee, S.C. Lyu, H.W. Kim, J.H. Lee, K.I. Cho, *Chem. Phys. Lett.* 359 (2002) 115.
- [10] K.S. Choi, Y.S. Cho, S.Y. Hong, J.B. Park, D.J. Kim, *J. Eur. Ceram. Soc.* 21 (2001) 2095.
- [11] C.J. Lee, D.W. Kim, T.J. Lee, Y.C. Choi, Y.S. Park, Y.H. Lee, W.B. Choi, N.S. Lee, G.S. Park, J.M. Kim, *Chem. Phys. Lett.* 32 (1999) 461.
- [12] M.J. Jung, K.Y. Eun, J.K. Lee, Y.J. Baik, K.R. Lee, J.W. Park, *Diamond Relat. Mater.* 10 (2001) 1235.
- [13] Yih-Ming Shyu, Franklin Chau-Nan Hong, *Diamond Relat. Mater.* 10 (2001) 1241.
- [14] Y.Y. Wei, Gyula Eres, V.I. Merkulov, D.H. Lowndes, *Appl. Phys. Lett.* 78 (2001) 1394.