Behavior of catalyst layer during the growth of carbon nanotubes for field emission application by thermal chemical vapor deposition

Jong-Bong Park[1], Dojin Kim
Dept. of Materials Engineering, Chungnam National University, 220 Gung-Dong, Yuseong-Gu, Dajeon, 305-764, Korea
Sung-Yool Choi, Seong-Deok Ahn, Jin Ho Lee[2]
Basic Research Lab., Electronics and Telecommunications Research Institute (ETRI), 161 Gajeong-Dong, Yuseong-Gu, Daejon, 305-350, Korea

Abstract
Growth behaviors of carbon nanotubes (CNTs) are studied in terms of catalyst by using scanning electron microscopy and transmission electron microscope (TEM). Catalyst films deposited on various substrates are agglomerated into nano-islands during the heat-up to the growth temperature. In particular, we focus on the direct investigation of the microstructures of the CNTs and the interface of CNTs-catalyst-substrate using cross-sectional TEM. We investigate relationship to the subsequent CNTs growth on each nucleation site. The growth of CNTs depends on the catalyst itself but not the silicide formation between the catalyst and the substrate.

1. Introduction
The synthesis of vertically aligned carbon nanotubes (CNTs) on a large-scale substrate has been one of the challenging issues for CNT-FED (field-emission display) in the field of flat panel display [1]. The preparation of CNTs typically involves a chemical vapor deposition (CVD) method on a substrate, which requires special treatments of the substrate [2] or separations of catalyst layer pre-deposited on the substrate [3]. This study directly investigates the behavior of catalyst layer during the growth of CNTs and the microstructures of the CNTs.

2. Experimental
CNTs were grown at 750~950°C using a thermal CVD method. Ni (15nm thick) and Fe (27nm thick) were deposited on various substrates, such as SiO_2, Si_3N_4, and bare Si. When a growth temperature stabilized, ammonia (NH_3) gas was introduced at a flow rate of 100 sccm for 5 min at atmospheric pressure, and acetylene (C_2H_2) gas was then supplied at 30 sccm for 10 min for the growth of CNTs. The furnace was cooled down to room temperature in an inert gas ambient.

To investigate the interface structure of a CNTs-catalyst-substrate, we have recently developed the ion polishing preparation as an effective method for the cross-sectional transmission electron microscopy (TEM) observations on the carbon nanotubes-catalyst-substrate. In brief, the key steps involved in the cross-sectional preparation are described. The first step is to peel off the grown-CNTs from both edges of the specimen. Once one drop of epoxy is applied to the peeled-off substrate, the epoxy permeates into the CNTs and covers the CNTs. Curing for the specimen was carried out at 60~70 ℃ for 5h at least to avoid the generation of air bubbles inside the epoxy. It would be expected to support the maintenance of the state of the CNTs as grown during the mechanical processes that follow. Two pieces were bonded face-to-face with the epoxy on a hot plate at 120 ℃ for 2h. The epoxy used for the covering and the bonding is M610 bond. The cross-sectional specimen for TEM was prepared using standard technique involving mechanical grinding, dimpling, and Ar-ion milling in a cold stage in order to minimize sample damage. Transmission electron microscopy (HRTEM) study was carried out in Philips CM20T/STEM equipment with a point resolution of 0.27nm at an accelerating voltage of 200kV.

3. Results and discussion
3.1 Ni-system
SEM images in Fig.1 show a top surface of CNTs grown on Ni/Si, and Ni/Si_3N_4/Si, revealing that the

[1] Corresponding Author. E-mail: pjb63036@etri.re.kr

grown CNTs depend on the substrate as well as the growth temperature. That is, CNTs are well grown on Ni/Si substrate at all growth temperature, while it is just at 950℃ that CNTs are grown on $Ni/Si_3N_4/Si$ substrate. We suggest that the reason for the poor growth of CNTs is due to an insufficient wettability of Ni particles on Si_3N_4 at below 850°C.

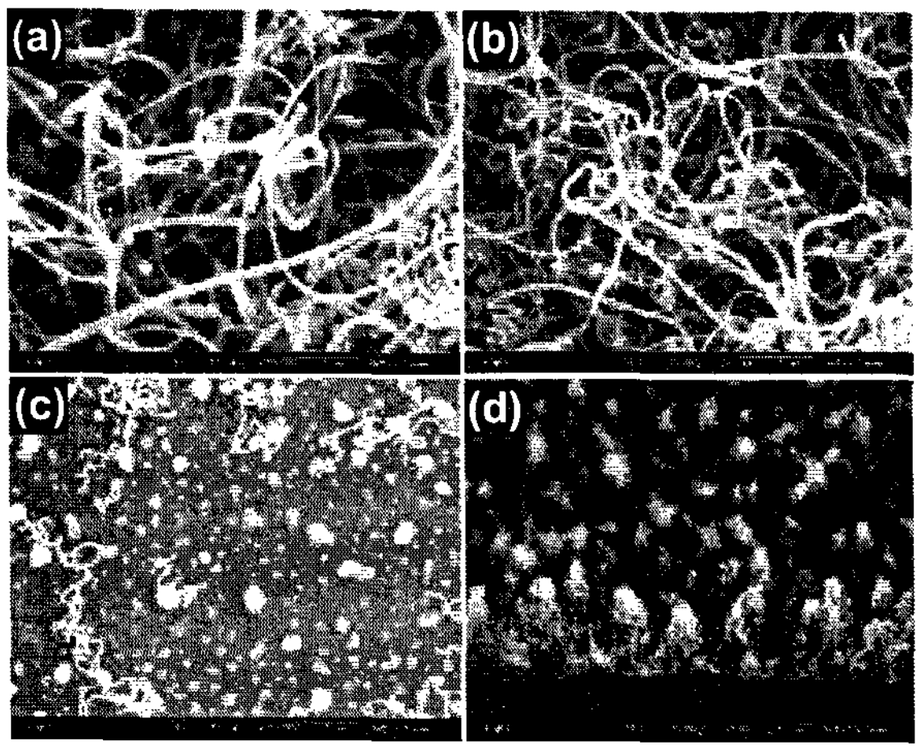

Fig. 1 SEM image showing a top surface of CNTs grown on (a) Ni/Si at 750℃, (b) Ni/Si at 850℃, (c) Ni/Si3N4/Si at 850℃, and (b) Ni/Si3N4/Si at 950℃.

To clarify the interface structure of a CNTs-catalyst-substrate, TEM analysis was performed. For 750℃-sample grown on Ni/Si, Ni particle has high wetting angle (Fig. 2(a)). The inset in Fig. 2(a) shows a selected area electron diffraction (SAED) pattern taken from the micrograph. It exhibits a characteristic reflection from the graphitic structure of the CNTs and spot pattern from pure Ni particle. Rare Ni-silicide is formed. For 850℃-sample grown on Ni/Si, Ni-silicide is formed <111> and <100> facets in our system as long as we observed (not shown here) [4]. Under the present TEM observations Ni-silicide is formed from the Si surface. Since the maximum of the Ni concentration exists at the surface, a strong flow of Ni diffusion from the surface to the inside during the growth governs the formation process of the Ni-silicide phase. The cross-sectional examination, however, enables us to distinguish the two areas. The CNTs are grown on the catalytic Ni particles remaining in the interface and the Ni-silicide is formed below the particles by diffusion of Ni into the Si substrate. On the other hand, the observation indicates that the silicide and the Ni particles, from which the CNTs grow, have sharp boundaries at the silicon surface suggesting the silicide formation is irrelevant with the CNTs growth.

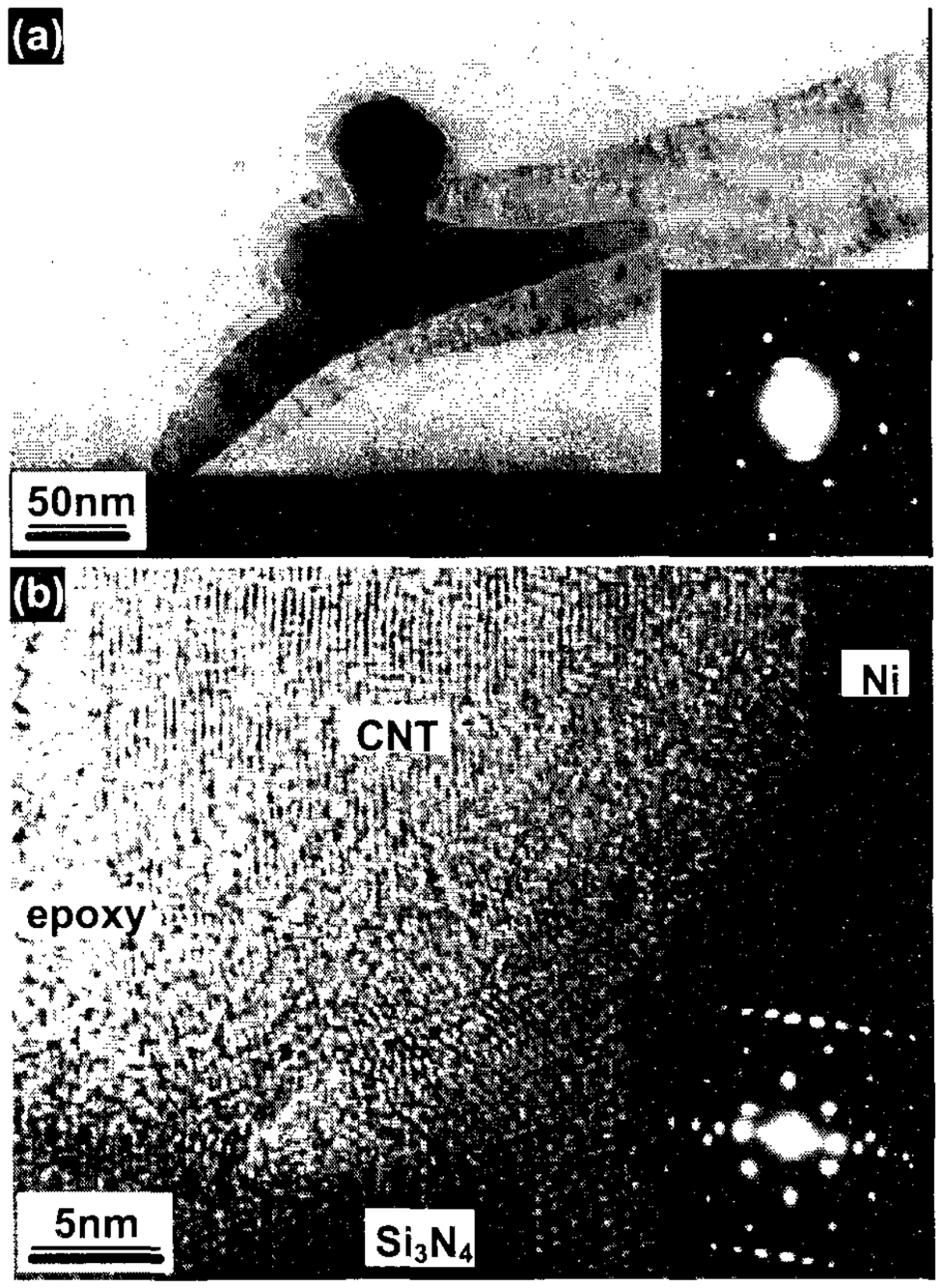

Fig. 2 (a) Cross-sectional TEM images of CNTs grown on Ni/Si at 750℃. (b) An HRTEM image at the interface between CNT and recrystallized-Si_3N_4 at 950℃.

For 850℃-sample grown on $Ni/Si_3N_4/Si$, we observe that Ni particles remain in the interface and mix with the Si_3N_4 near the interface in part (not shown here). As shown in Fig. 1(c), however, it couldn't be thought of any reason for not growing of CNTs. For 950℃-sample grown on $Ni/Si_3N_4/Si$, a noteworthy phenomenon is that amorphous Si_3N_4 is recrystallized. From SAED patterns inserted in Fig. 2(b), the c-axis of recrystallized Si_3N_4 is nearly perpendicular to Si (001). We speculate that transition metal (Ni) deposited on Si_3N_4 could result in decline of recrystallizing temperature during the growth of CNTs. Moreover, Ni-silicide is formed at Si substrate by diffusion through the recrystallized Si_3N_4.

3.2 Fe-system

In the earlier study, Baker et al. [5] have reported on

the catalytic activity of the iron subgroup (i.e. Fe, FeO, Fe_2O_3) for the formation of carbon filaments. Fan et al. [6] have obtained the vertically aligned CNTs by thermal CVD after the oxidation of iron-patterned porous Si substrates. In addition, they proposed that the iron oxide nano-particles are active catalyst for the formation of CNTs.

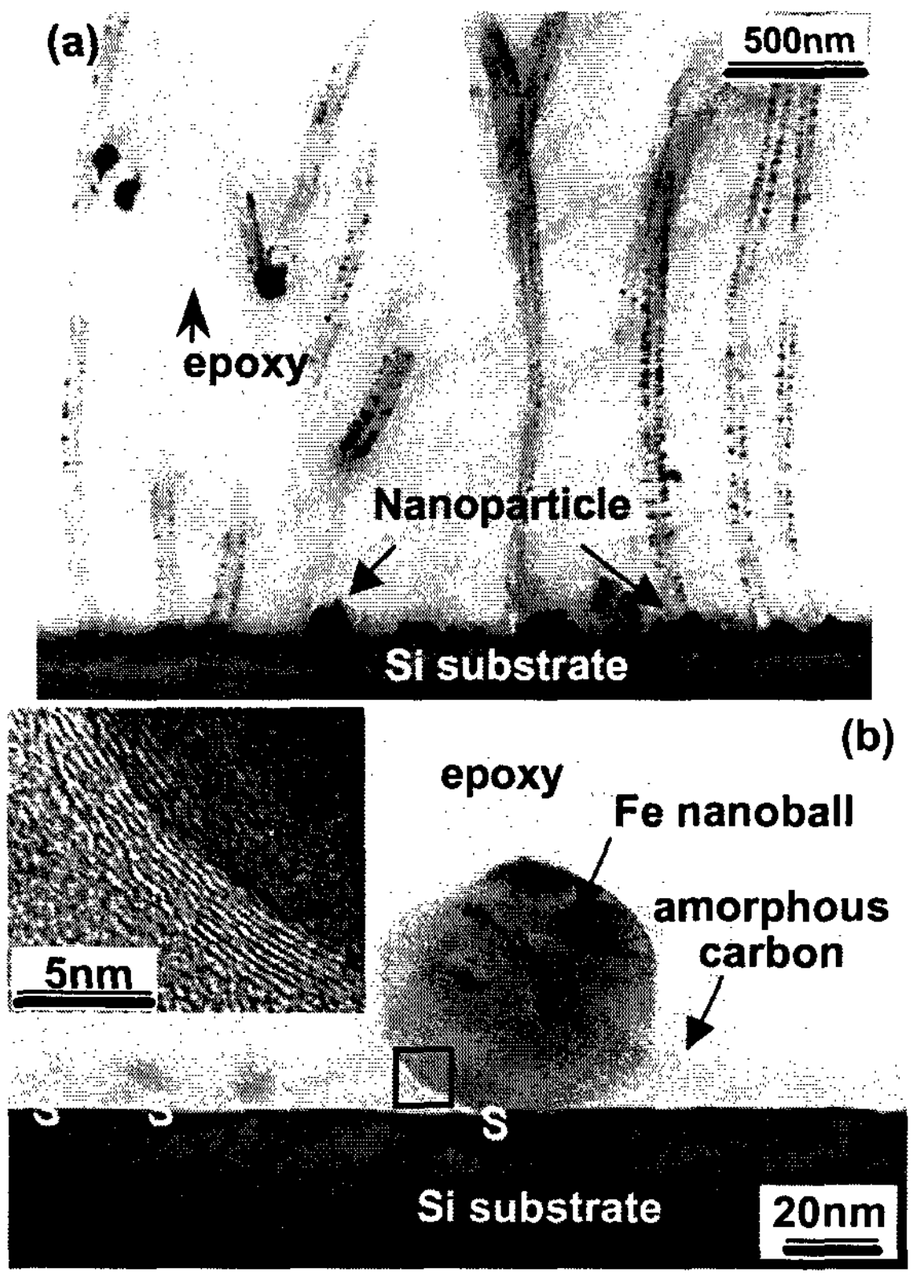

Fig. 3 (a) Low magnification image of the CNTs growing on the catalyst particles. (b) A cross-sectional TEM image of a Fe nanoball. The HRTEM image (insert) reveals that the nanoball is surrounded by graphene sheets. Fe-silicide is designated by 's' in (b).

A low magnification cross-sectional TEM image confirms that the CNTs originate only from the nanoparticles and the CNT diameters are correlated with the particle size (Fig. 3(a)). The particle size was significantly larger than the diameter of the corresponding nanotube grown with Fe catalyst. The nanoball is a small particle sitting on the substrate encapsulated by graphene sheets after the CNTs growth, but without CNT grown upon (Fig. 3(b)). The nanoball is determined to be in a-Fe from by the convergent beam electron diffraction measurements. The cross-sectional TEM, especially, reveals that Fe nano-island acts as a support and plays a role as the preferential site for the subsequent growth of the CNTs, while "nano-ball" in liquid phase looks like self-reformed droplets due to the high surface tension and relates to the formation of carbon shell at the initial stage of growth. The naked iron island is oxidized to form cubic Fe_2O_3, while the capsulated "nano-ball" is not oxidized at all.

4. Conclusion

The status of the nanoparticles during the carbon nanotube synthesis is examined by SEM and TEM. The cross-sectional TEM and CBED analysis, in particular, reveals that nanoparticles serve as the nucleation sites for the growth of CNTs. The growth of CNTs depends on the catalyst itself but not silicide formation between the catalyst and the substrate. It was also shown the general growth mode with Fe follows that with Ni particles.

5. References

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