Carbon Nanotube Growth for Field Emission Display Application

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Abstract

The role of NH_3 for vertical alignment of CNTs was investigated. The direct cause of the alignment was a dense distribution of catalytic metal particles, but which was kept catalytically active during the growth process by NH_3. This allows a dense nucleation of the CNTs, and consequently, assists vertical alignment through entanglement and mechanical leaning among the tubes. The CNTs grow in a base growth mode. Several evidences were presented including a direct cross-sectional TEM observation. Since Ni is consumed both by silicide reaction and by capture in the growing tube, the growth stops when Ni is completely depleted. This occurs faster for smaller particles, and thus a longer growth results in thin bottom with poor adhesion.

1. Introduction

Aligned carbon nanotubes (CNTs) have attracted great attention due to their potential application to tip materials for a next generation field-emission display (FED)[1]. For this purpose, thermal and plasma-enhanced chemical vapor deposition (CVD) methods were the first candidate for the synthesis due to the capability of uniform growth on large area. Considering the FED fabrication process, a few requirements such as selective and vertically aligned growth need to be satisfied. Thus far, the CVD techniques have used catalytic-metal-coated plane substrates[2,3] or catalytic-metal-embedded porous substrates[4,5]. For the thermal CVD synthesis of

CNTs, it is generally agreed with that NH_3 is a critical component for synthesizing aligned carbon nanotubes[2,3,6,7]. While, for the role of NH_3, it is controversial, the detailed examination of the role of NH_3 is still lacking. Moreover, for the proper control of the CNTs growth, in-depth understanding of the synthesis process is also a prerequisite. Including transmission electron microscopy (TEM) observation along the cross-sectional direction of the integral of CNTs-catalytic metal-substrate structure, we report a study on the role of NH_3 in the alignment of CNTs and the growth mode of CNTs in thermal CVD.

2. Experiment

Ni films of 10-40 nm were deposited on Si (100) substrates using dc magnetron sputtering method. The Si substrates coated with Ni films were placed in a 7.5 cm-diameter resistance heated quartz tube furnace at room temperature and were pumped down to less than $\sim 10^{-3}$ torr. The substrate was then heated to a synthesis temperature while introducing H_2 gas for a reducing environment. The synthesis temperature was in the range

of 500-900 °C. When the temperature was stabilized, NH_3 gas was introduced, when needed, followed by C_2H_2 or NH_3/C_2H_2 mixture gases. The gas pressure was ~1 atmosphere. At the end of the growth, the samples were slowly furnace-cooled in a hydrogen flowing environment. The morphologies of catalytic Ni films and CNTs were examined using SEM, high-resolution TEM, and Raman spectroscopy. In order to examine the local composition in the cross-section of the structures, EDX (electron diffraction x-ray spectroscopy) measurements were also made.

3. Results and Discussion

In order to investigate the role of NH_3 for the alignment of CNTs, the growth was varied in two ways; 1) NH_3 pretreatment + C_2H_2 flow, and 2) C_2H_2/NH_3 mixture flow without NH_3 pretreatment. Since the morphologies at and below 700 °C were such as of bent-grown CNTs with apparent thick amorphous carbon deposits, we concentrate on the growth above 800 °C, which is the temperature where NH_3 begins to play the role for alignment. For this purpose, a series of experiments was undertaken to reveal the role of NH_3 in CNTs alignment at ≥800 °C.

Since the morphology of the metal particles directly influences that of the grown CNTs, we examined the effect of NH_3 on the morphologies of Ni particles with varying heat-treatment temperature (700-900 °C) and time (up to 60 min). If there is a certain etching behavior by NH_3[3], a decrease in the particle diameter with etching time was expected. However, no noticeable differences in the Ni particle morphologies were observed between with and without NH_3. Moreover, the CNTs grown for different NH_3 pretreatment times, 1 to 60 min, revealed no remarkable differences in the grown tube diameters and distribution densities. This indicates that the etching effect of NH_3 is negligible. This result agrees with that of Jung et al.[6]

Simultaneous flow of C_2H_2 and NH_3 in mixture without the pretreatment also established alignment. The results indicate that the metal films need not be *pre-treated* with NH_3 in order to synthesize aligned CNTs. If the NH_3 pretreatment is not immediately followed by CNT synthesis, or if CNTs were synthesized on NH_3 pretreated Ni films after pumping out NH_3 in the furnace

tube, alignment was not realized. The effect of the NH_3 pretreatment is, then, actually the effect mediated by a remnant of NH_3 existing right after switching to C_2H_2. Actually, NH_3 need not form the environment during the whole synthesis time for the alignment itself, but should exist at the initiation of the CNTs growth. The alignment of CNTs in atmospheric pressure thermal CVD is realized by a high density of the growing tubes. Namely, in a compact formation of the growing tubes, even in the situation where tubes are vulnerable to bent growth, mechanical leaning against neighboring tubes in contact can establish the morphology of vertical alignment. Therefore, for a dense growth of CNTs, a high density of Ni particles should play a role as nucleation sites in the initial stage of the growth. If C_2H_2 gas decomposes to form carboneous products and cover the surface of the metal particles, the amorphous carbon films deactivate the catalytic role of the metal particles probably by inhibiting the source gas from diffusing into the catalytic metal particles. The consequence is a sparse nucleation and growth of CNTs. Which in turn results in non-aligned morphology.

In relation with the above-explained way of the alignment, the NH_3 somehow provides clean metal surface at the initial stage of the CNT synthesis and allows CNTs to begin to nucleate from the metal particles. This is the situation realized right after the NH_3 pretreatment process. However, as the growth continues and NH_3 is flushed away from the environment, the continuously generating amorphous carbons will begin to cover and passivate the metal particles. This will terminate the lengthwise growth since the metal particles will no longer play a catalytic role. This was true, and in addition to that, amorphous carbon deposited on the surface of grown CNTs as shown in Fig. 1(a)-(c). Note that the CNTs grew radially thicker and thicker with synthesis time, about 50, 120, and 200 nm of growth of the diameter at 20, 40, and 60 min, respectively. TEM and Raman observation clearly revealed that the thickened layer is amorphous carbon (Fig. 2). The rate of thickening was higher at higher synthesis temperature, possibly due to higher decomposition rate of C_2H_2.

In contrast, the prolonged growth with C_2H_2/NH_3 mixture did not show such thickening by amorphous carbon because NH_3 had kept playing the role during the whole growth time. This result supports the interpretation of the results from the prolonged growth

with NH_3 pretreatment. When the C_2H_2/NH_3 mixing ratio was varied with 5/55, 15/45, 30/30, 45/15, and 55/5, the result is as follows; the mixing ratio greater than 1 or higher NH_3 flux than C_2H_2 achieved good alignment, and vice versa. For the growth with relatively very small NH_3 flux, amorphous carbon deposit over the substrate overwhelmed the CNTs growth. This indicates that the activity of NH_3 for the alignment is dependent on its flow rate, and suggests that the action of NH_3 maintaining the metal particles synthetically active is a chemical process. The reaction kinetic of the formation of amorphous carbon and its deposit and that of NH_3 to maintain the catalytic metal active compete in the growth process. Depending on the kinetics of the reactions in a condition of temperature and flux of the gases, the corresponding morphology will show up.
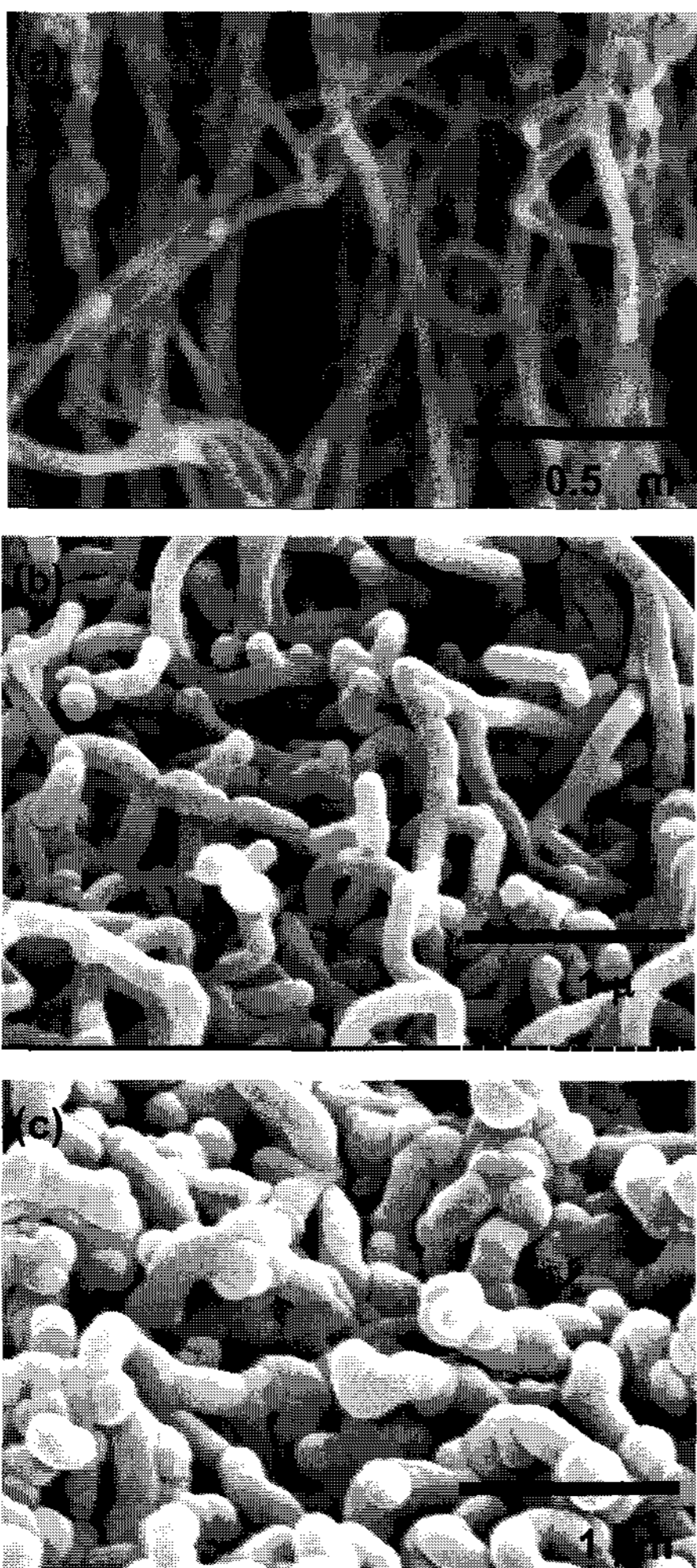

Fig. 1.   Morphologies of the CNTs synthesized on Ni films at 900 °C for (a) 20min, (b) 40min, (c) 60min after 5 min of NH_3 pretreatment.
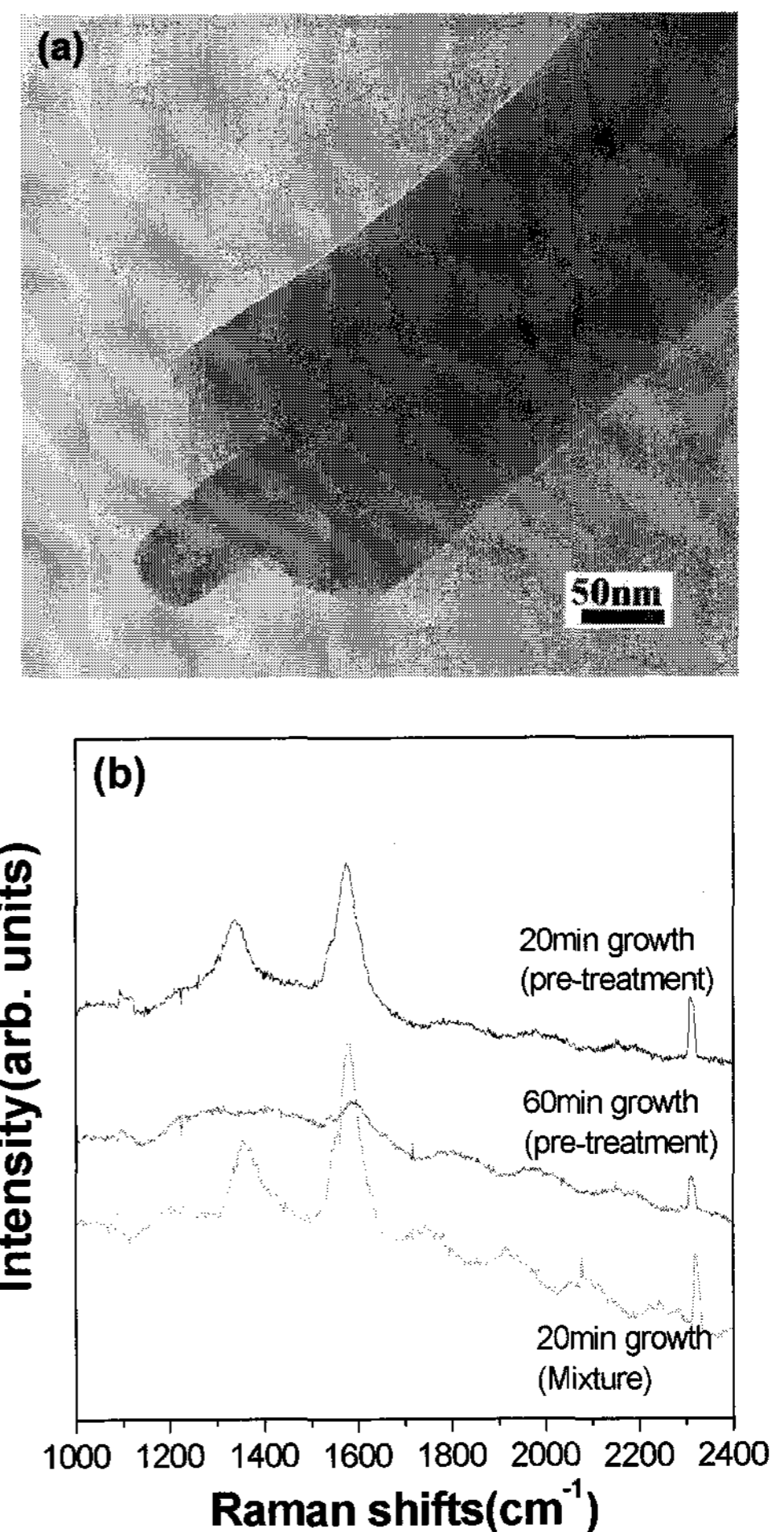

Fig. 2.   (a) TEM of CNTs in Fig.1(c). Amorphous carbon coat at the tip is broken during the specimen preparation and crystalline carbon nanotube inside is clearly shown. (b) Raman spectrum for a 20 min growth is compared with a 60 min growth. For the latter with thick amorphous carbon deposit, broad and featureless peaks are revealed. Mixture growth also shows some amorphous carbon deposit.

For the microscopic role of NH_3, while it is open to be resolved, a couple of possibilities can be tested. A possibility is that NH_3 suppresses the decomposition of C_2H_2 into amorphous carbon. However, as evidently shown in Raman spectra, no CNTs grown by thermal CVD showed a fully suppressed amorphous carbon peak even in the mixture growth (Fig. 2), and the possibility is low. More probably, NH_3 (and/or its decomposed forms) somehow inhibits sticking of amorphous carbon to the surfaces of the metal and CNTs. It is interesting to note that the temperature 800 °C, above which the alignment is achieved, is the temperature that NH_3 actively begins to decompose and generate atomic hydrogen[8]. Atomic nitrogen may be generated, but at very high temperature
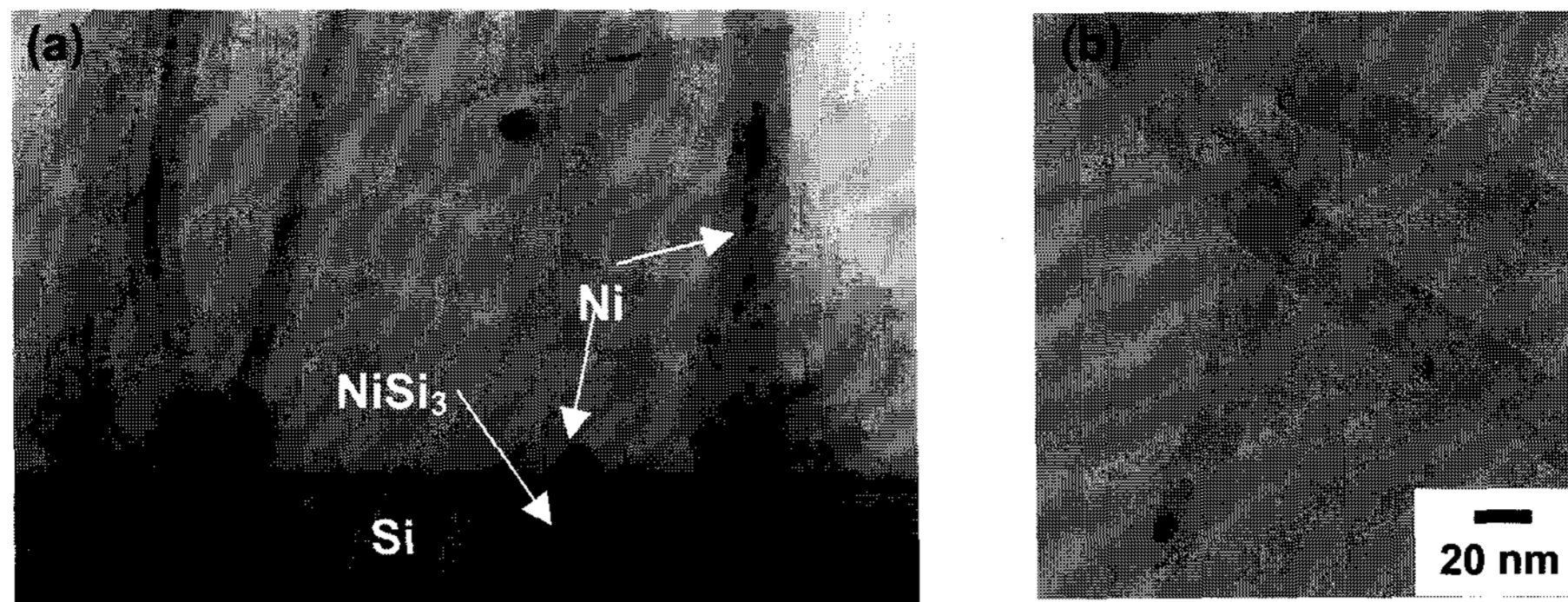
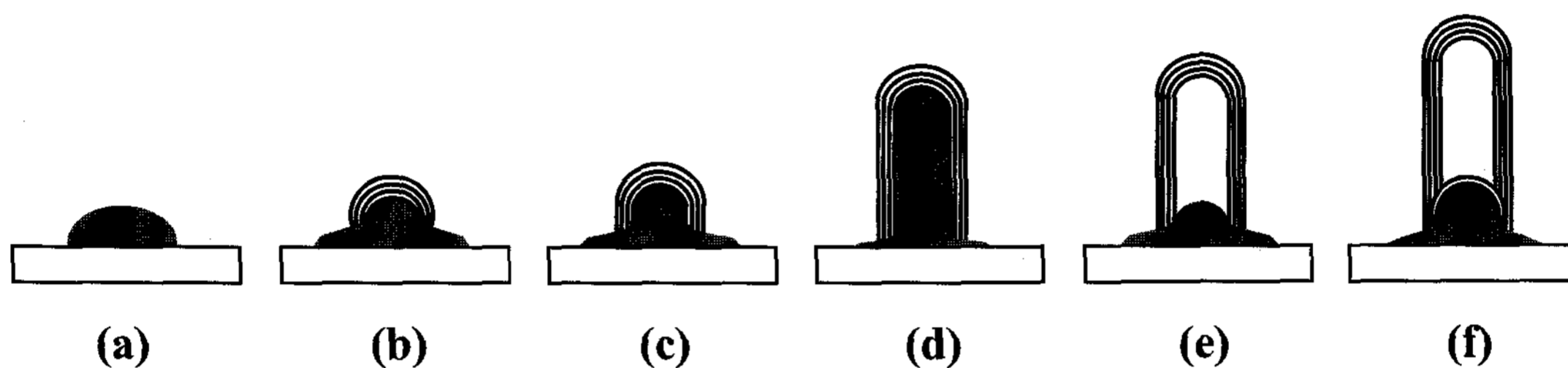**Fig. 3.** TEM image of CNTs grown at 850 °C with NH_3 pretreatment.

Fig. 4. The growth mode in the bamboo structure formation at high temperatures.

above 1200 °C[8]. Therefore, we propose that the atomic hydrogen may react with the amorphous carbon to form a volatile form and keep the metal surface clean. While this still needs further exploration of the detailed chemical processes involving NH_3 and others, the existence of NH_3 at the initiation of growth maintains many Ni particles being active state as nucleation sites, and consequently, the high-density growth of CNTs promotes their vertical alignment.

So far, various growth mechanisms or modes have been proposed for different synthesis methods in laboratories[9-11]. For thermal CVD method, it seems to converge on a base growth mode[3,7]. SEM and TEM have been useful tools in investigating the growth mechanisms[12,13]. A cross-sectional image shown in Fig. 3(a) clearly reveals that the tubes are growing from the sites of Ni particles. It can be seen that Ni of the particles climbs up from the bottom into the tubes. Note, also, that silicide forms and its composition was determined to $NiSi_3$ by EDX. The CNTs grown at 850 °C with NH_3 pretreatment mostly revealed a bamboo structure[14,15] with short bell-shaped compartments [Fig. 3(b)]. The top of the tubes usually begins with an empty bamboo compartment and successive regular bamboo compartments were all empty. The closed-cap features suggest

that the relevant segregation and graphene sheets formation occurs uniformly over the Ni particle surface in the initial growth stage. In a radially heated furnace tube, a uniform radial diffusion and segregation through out the entire surface of the metal hemisphere may take place [Fig. 4(b)]. When the graphene multi-wall cap is formed and blocks the source gas incorporation, the periphery of the metal particle in contact with the substrate would be the only conceivable diffusion path. As the peripheral is concentrated with the source, tubular extension from the graphene sheets of the cap is favored [Fig. 4(c)-(d)]. The tendency of vertical growth will be maintained unless an inhomogeneity in the process, such as defect formation[16], causes the CNT to change the growth direction. The tube bending with Ni inclusion shown in Fig. 3(b) should be an example. With the base growth mode, the metal-substrate interface will be apt to offer vulnerable sites for defects generation. Returning to the growth, as the tube grows, the liquid Ni is pulled into the hollow cap of vacuum forming a Ni rod. After a little of growth, the liquid Ni rod falls down to form a hemisphere [Fig. 4(e)]. To explane this process, terms such as bonding energy of the metal liquid, metal-substrate interface energy, metal-CNT interface energy, etc. may have to be included. This microscopic issue is

should be solved. Now, the cap formation repeats to form a bamboo partition wall [Fig. 4(f)].
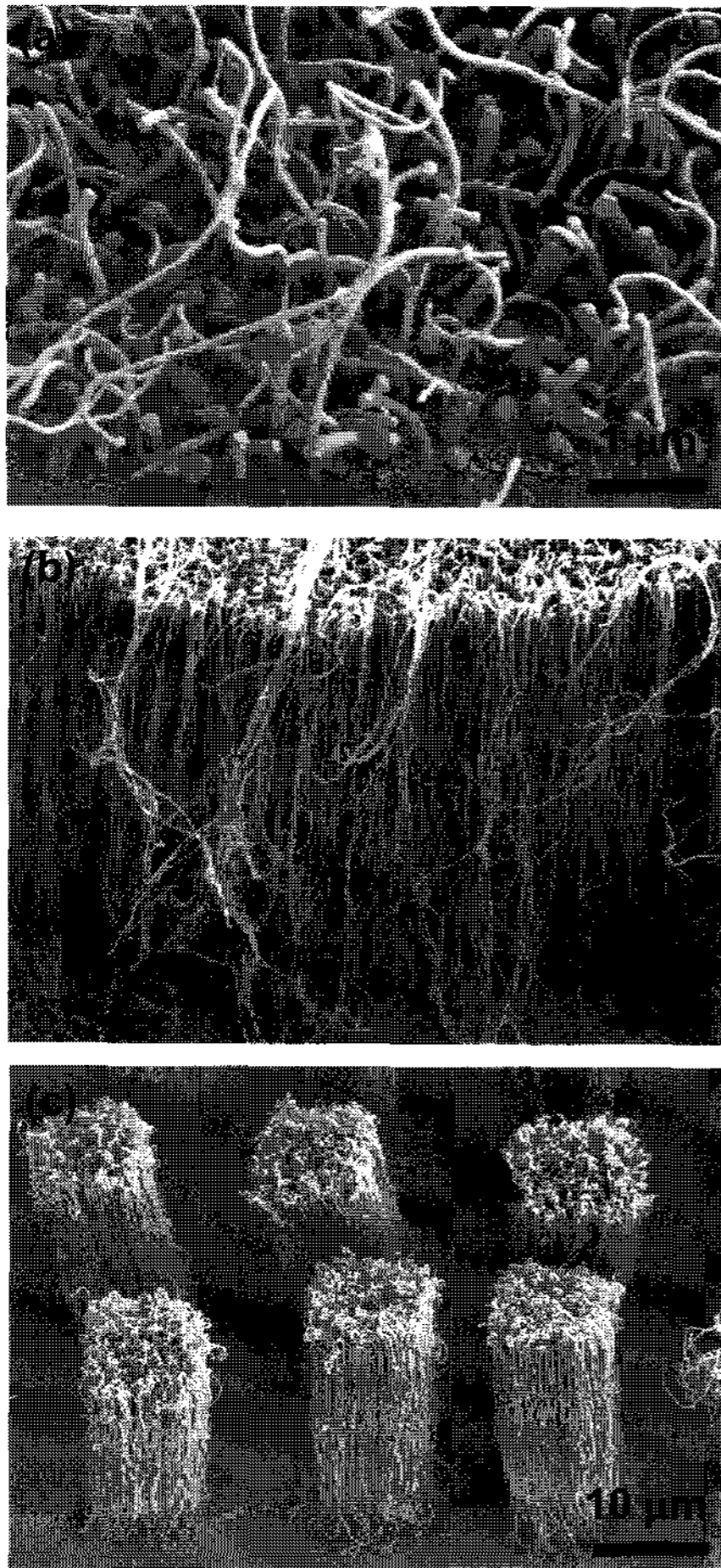

Fig. 5. Surface morphology of the CNTs. (a) Initial stage of the growth of 1 min on 30 nm Ni film. (b) Lift-up at the tubes bottom, and (c) tilted pillars due to a lift-up.

It is well known that the particle size distributes[17] and controls the tube diameter. We observed that the difference in particle size causes a difference in the growth rates of CNTs [Fig. 5(a)]. It shows that outgrowth of thinner tubes is dominated in the initial stage of the synthesis. If the synthesis of CNTs progresses with diffusion and segregation of carbon or its compound via the Ni particles, the incubation time to the growth initiation will be different for different particle size. This is because, in zeroth order approximation, the diffusion flux is proportional to its surface area of the Ni particle while the segregation begins when the particle is saturated with source gases. Therefore, the smaller particles, having higher surface-to-volume ratios, will be saturated in shorter time leading to earlier initiation of

the tube growth. The thin out-growing tubes in a condition vulnerable to crooked growth lie over the surface without finding tubes nearby to lean on, but note that the tubes underneath with an average size are growing vertically.

Since the metal particle is consumed partly by silicide formation and partly by inclusions into the tube during the growth as revealed in Fig. 3(a) and (b), they will finally be totally depleted from the Si substrate. The growth then stops. In the meantime, nearby tubes of larger diameter keep growing to tear up the thin tubes from the substrate and lift upward, because the tubes are entangled with one another. As the growth proceeds, the number of growth sites or the metal particles keeps decreasing. This will result in a sparse distribution of CNTs at the bottom [Fig. 5(b) and (c)]. Such occurrance in patterned growth can cause tilted pillars of CNTs as shown in Fig. 5(c), which is very detrimental to the field-emitter array applications that require solid contact of the CNTs to the substrates. The floating CNTs decisively prove that the carbon nanotubes grow in a base growth mode in thermal CVD.

4. Conclusions

In thermal chemical vapor deposition method for synthesis of carbon nanotubes, NH_3 plays a critical role in vertical alignment of CNTs. NH_3 prevents the Ni particles from being passivated by amorphous carbon deposit and keeps the Ni particles catalytically active during growth. Thus, densely nucleated graphene sheets form spherical cap in the initial stage and confine the path for diffusion to the peripheral of the particle at the contact with the substrate. Now the tubular graphene sheets begin to form and grow vertically. Even with bent-growth, the mechanical leaning against nearby tubes establishes the vertical alignment in overall. For the synthesis on Si substrate with Ni films, silicide reaction and capture by the tube consume the Ni particle during growth. Therefore, in a growth taking place at a long enough time, Ni of the small particles is completely consumed away and the growth stops. While CNTs keep growing on the larger Ni particles, they lift up the growth-stopped thin tubes causing sparse tube density at the bottom. This induces a poor adhesion of the tubes, and is detrimental to field-emitter tip application. All the

morphological investigations including the cross-sectional TEM prove that the CNTs grows with a base growth mode.

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