Growth of Vertically Aligned CNTs with Ultra Thin Ni Catalysts

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We report on the growth mechanism of vertically aligned carbon nanotubes (VACNTs) using ultra thin Ni catalysts and direct current plasma enhanced chemical vapor deposition (PECVD) system. The CNTs were grown with -600 V bias to substrate electrode and catalyst thickness variation of 0.07 nm to 3 nm. The CNT density was reduced with catalyst thickness reduction and increased growth time. Cone like CNTs were grown with ultra thin Ni thickness, and it results from an etch of carbon network by reactive etchant species and continuous carbon precipitation on CNT walls. Vertically aligned sparse CNTs can be grown with ultra thin Ni catalyst.

Keywords : Carbon nanotube, Ultra thin Ni, Vertical alignment

1. INTRODUCTION

Carbon nanotubes (CNTs) are one of the most applicable field emitters for field emission displays (FED) because of their remarkable electron emission characteristics and current stability, which results from high aspect ratio and chemical inertness[1,2]. Vertically aligned and controlled density of CNT was most important parameter for display applications[3]. Well aligned CNT can reduce gate leakage of triode type CNT-FED[4] and the electron emission properties are enhanced with sparse CNT density by reduced field screening effects[5].

Vertically aligned and controlled density CNTs can be grown with various methods, such as e-beam lithograph [6], shadow mask[7], electrochemical deposition[8].

The plasma enhanced chemical vapor deposition (PECVD) is one of the best growth methods for vertically aligned and controlled densities of CNTs. The CNTs can grow on glass substrate directly and applicable to large area displays. In PECVD, the vertical alignment of CNTs is apparently induced by plasma effect and it could be due to the inherent electric field, formed by voltage drop in the ion sheath region[9]. The density can be controlled by changing size of catalytic particle such as Ni, Fe, etc., and the site of catalysts with thermal and plasma treatments. Generally, high density CNTs can be grown by PECVD.

In this study, we used ultra thin Ni catalyst (< 1 nm) and DC-PECVD for CNT growth. The CNT densities decreased with ultra thin Ni catalysts and aligned vertically. The CNT shows cone shape structure, and results from etching of carbon network underneath catalyst and continuous precipitation on the walls.

2. EXPERIMENTAL

A schematic diagram of dc-PECVD is reported on previous article[10]. Ultra thin Ni catalyst is deposited with Ni plasma treatment system and the thickness can be controlled by deposition time (~ 0.004 Å/s deposition rate). The nickel surface was 120 sec NH_3 plasma treated to granulate with NH_3 flow rate 75 sccm and RF power of 100 W. The CNTs grow with ammonia (NH_3) and acetylene (C_2H_2) source gases, C_2H_2 flow rate was changed from 15 sccm to 30 sccm and dc bias was fixed to -600 V on substrate. The substrate temperature and gas pressure was fixed at 580 °C and 2 Torr, respectively and growth time was changed from 1 min to 15 min.

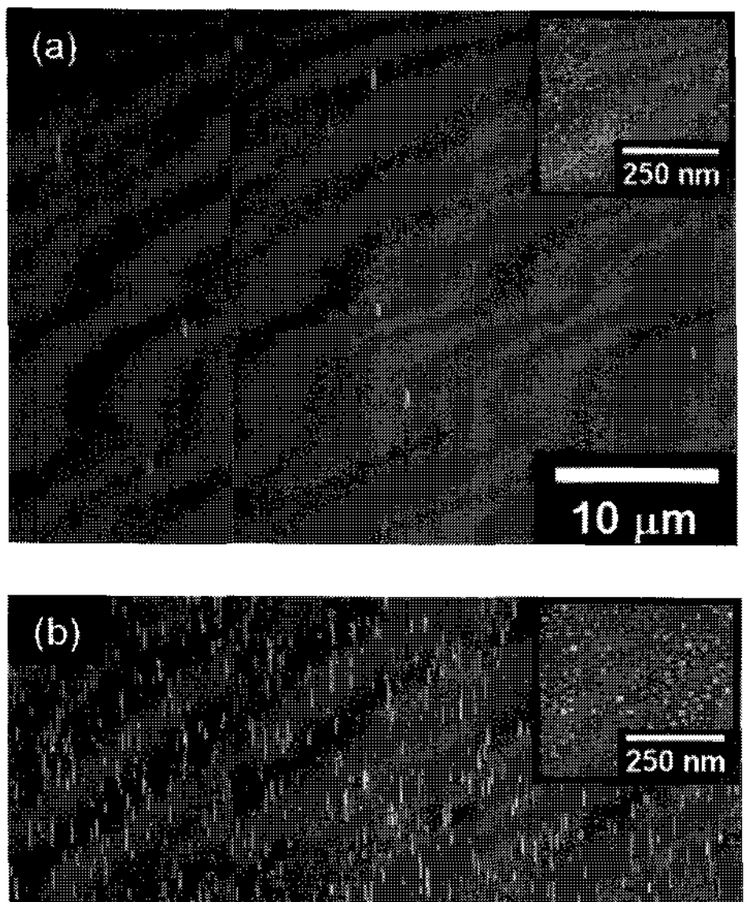

Fig. 1. The grown CNTs with nickel thickness of 0.7 Å (a), 3 Å (b) and 30 Å (c).

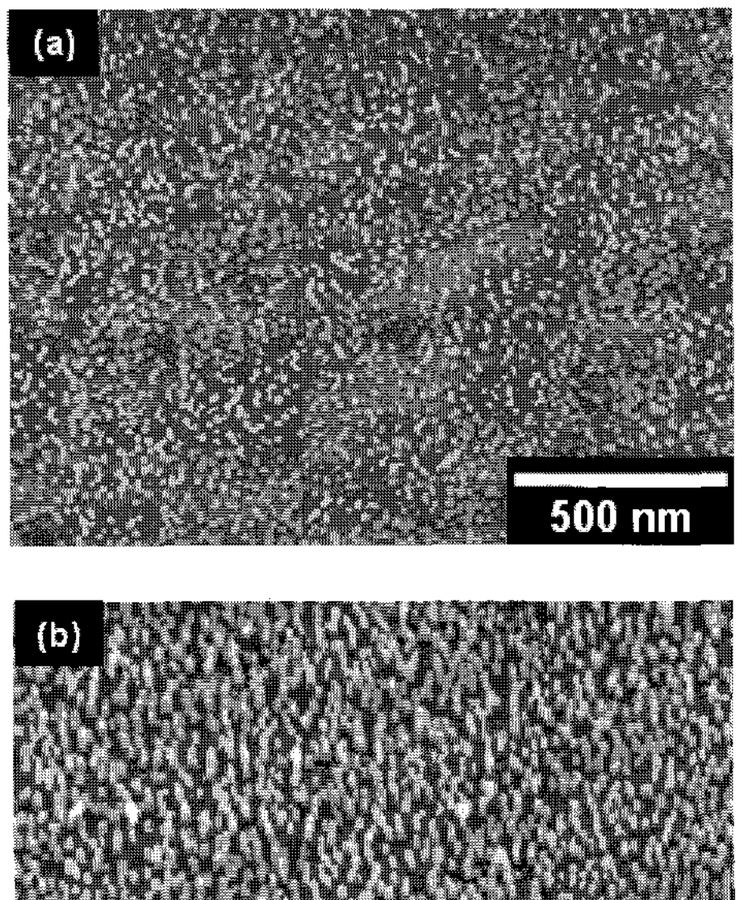

Fig. 2. CNTs with various growth time of 60 s (a), 180 s (b) and 900 s (c).

3. RESULTS AND DISCUSSION

The diameter of granules of Ni depends on the Ni catalyst thickness and the densities of granules increase as thickness decreases. In the case of nickel thickness of 0.7 Å, the diameter of the granule is near 1 nm and densities increased up to ~10^9/cm^2.

Figure 1 shows CNTs grown with the nickel thickness of 0.7 Å (a), 3 Å (b) and 30 Å (C). The SEM image of granulated nickel film was inserted in the figure. The growth time of the CNT was 20 min. The CNT density is decreased with decreasing nickel thickness. However, during granulation, the density increased with decreasing nickel thickness as shown in the figure. The CNT density decrease to ~10^3/cm^2 with 0.7 Å Ni catalyst.

Figure 2 shows CNTs with various growth time; 60 s (a), 180 s (b), and 900 s (c). The nickel thickness is 0.7 Å. Fig. 2 shows growth of CNTs with high density until 180 second growth time after then decreased density and increased diameter with increase growth time. The 900 s (c) grown sample shows bigger diameter of 38 nm and remarkably reduced densities of ~10^5/cm^2. We can see that density of CNTs can be varied by changing deposition time and controlling thickness of catalyst film. The decreased densities of CNTs with 900 s growth time appear to remove of most of all CNTs during etch dominated growing time, such as more than 180 s growth time.

Figure 3 shows SEM (a) and TEM (b) image of CNTs with catalyst on tip. We can see that some CNTs show larger diameter of metal compare with CNTs with smaller thickness.

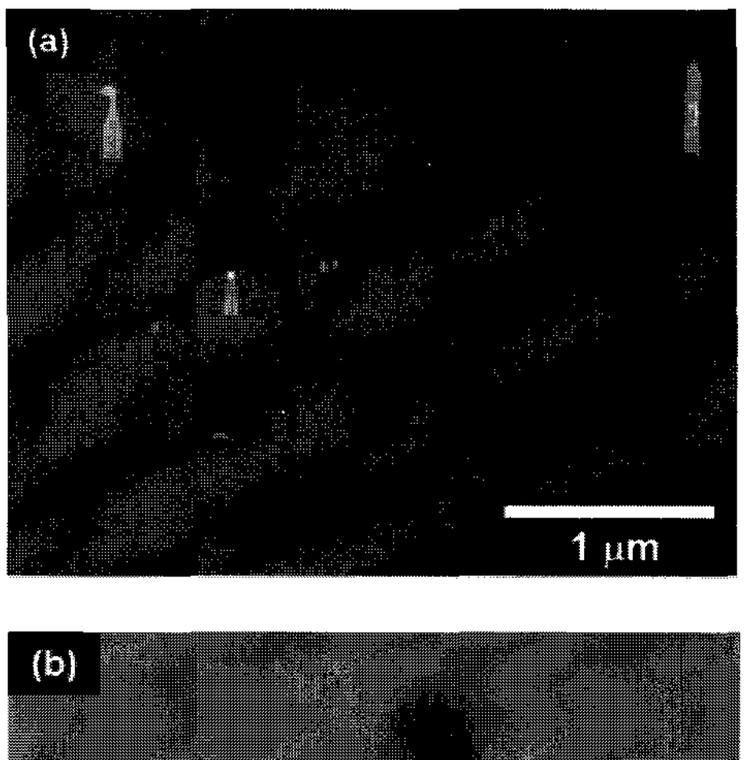

Fig. 3. TEM and SEM image of CNTs with catalyst on tip.

The TEM image of CNT with metal tip shows etched carbon networks underneath metal layer. If we increase growth time, the metal should be removed and then etch of carbon network then disappear the CNT.

Figure 4 shows CNTs with NH_3 and C_2H_2 gas ratio. The flow rate of C_2H_2:NH_3 was changed with 15:85 (a), 30:70 (b). The total flow rates are fixed at 100 sccm. Fig. 4(b) shows longer length of CNTs and denser CNTs comparing Fig. 4(a). However many CNTs show bended near the metal tip. Increase of flow rate of C_2H_2, much more carbon source, results in increasing growth rate of CNTs. The faster growth of CNT with much more carbon source can reduce etching of carbon network underneath metal tip and then result in increase of CNT length and density.

Figure 5 shows that TEM image of CNTs with catalyst thickness of 3 Å. The CNT was shaped like a 'cone' with cone angle of 18 degree. The diameter of bottom CNT was about 64 nm and that of tip was about 28 nm. So, the diameter of bottom CNTs increased comparing that of Ni granules and metal tips. The increase of diameter of bottom CNT was related to the precipitation of carbon source during growing CNTs, as Merkulove had reported[11]. The lager size of tip than that of initial catalyst granules is due to an agglomeration of nickels after granulation and before beginning of growth of CNTs.

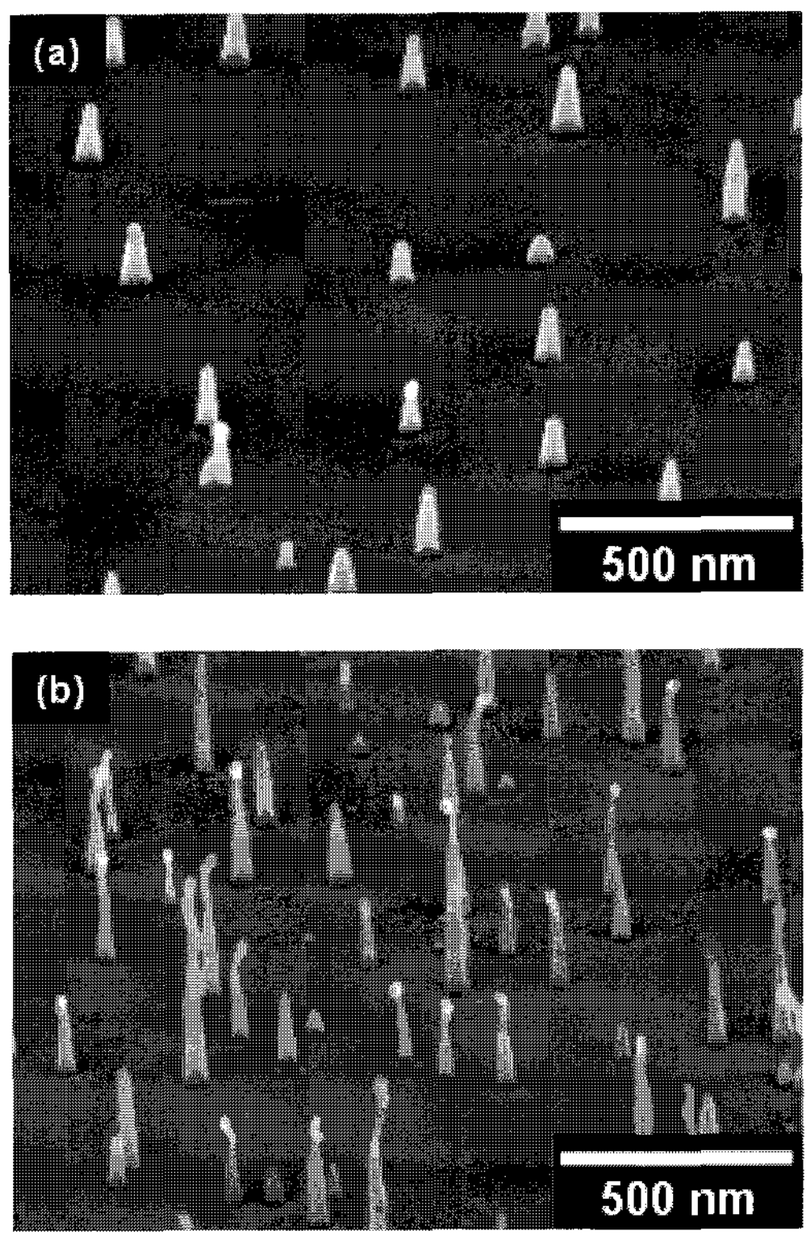

Fig. 4. CNTs with NH_3 and C_2H_2 gas ratio.

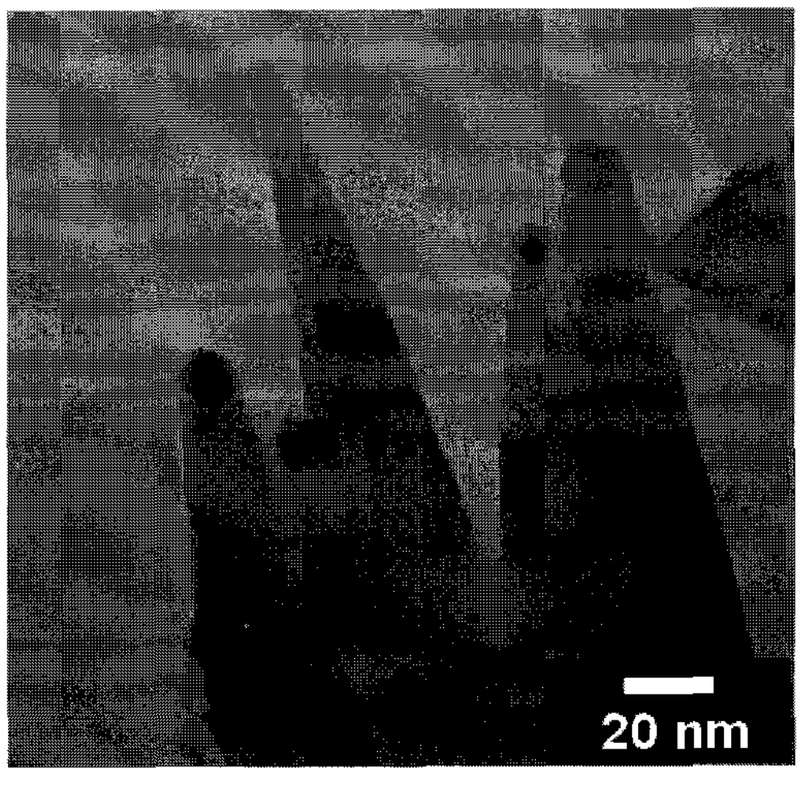

Fig. 5. TEM image of CNTs with 3 Å catalyst thickness.

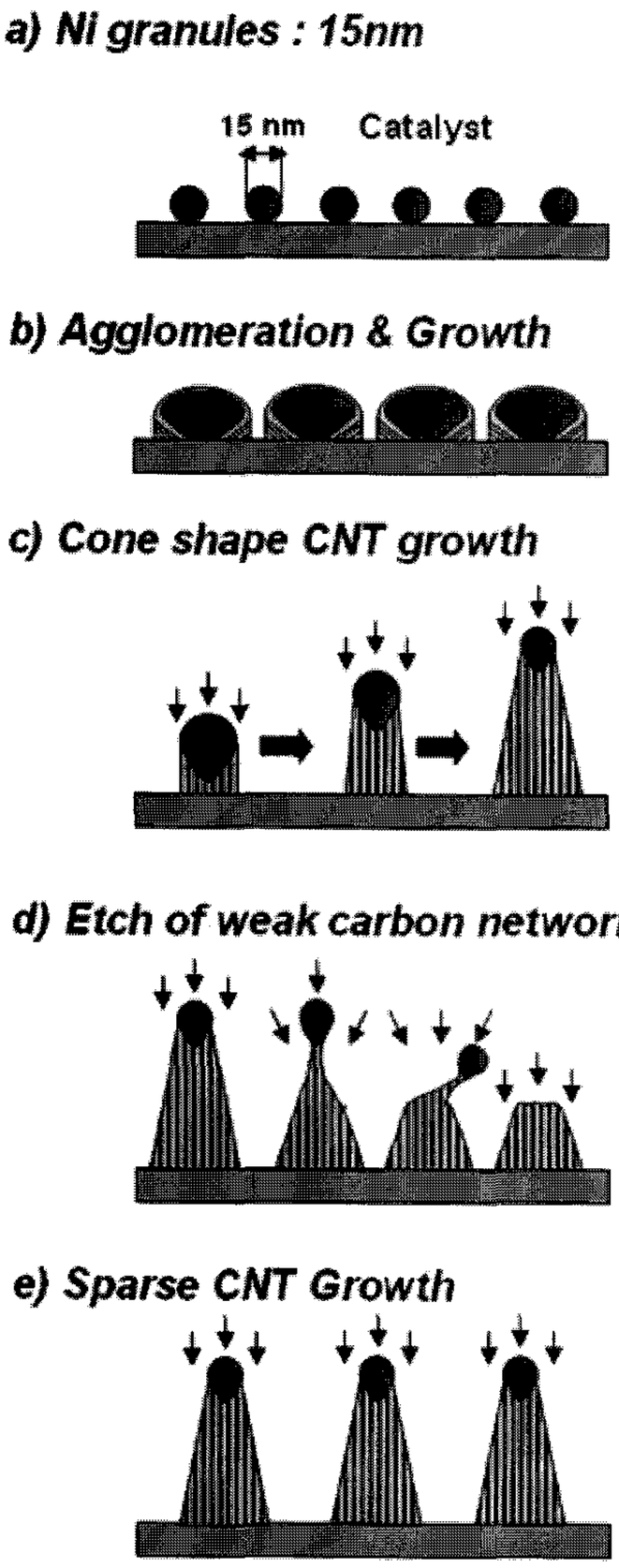

Fig. 6. Schematic diagram of sparse CNTs with ultra thin Ni catalytic layer.

Figure 6 shows the schematic diagram of sparse CNTs with ultra thin Ni catalytic layer. The CNT growth steps are divided to 5 steps. The nickel thin films are granulated to polycrystalline Ni (a) : granulation process, the poly crystalline nickels react with carbon and/or nearest Ni particles make to larger particle (b) : agglomeration and initial CNT growth process, the CNTs shows increased length by network growth and widen diameter, precipitation of amorphous carbon with increased growth time and the catalytic metals on tip (c), and concurrently, etch of carbon network underneath metal tip, firstly weakly bonded carbon network with metal tips (d) : growth and etch process, the CNT density decreases with increasing growth time, due to removal of weakly bonded CNTs, result in sparse CNT (e). The grown CNT densities depend on the growth time from etch dominated growth. The start of etch dominated growth time, Fig. 6(d), appear to depend on the catalyst thickness. The maximum thickness depends on the gas ratio and catalyst thickness. Higher C_2H_2 flow rate and thick catalyst will increase CNT thickness, Fig. 4(b).

4. CONCLUSION

We studied ultra thin nickel catalyst effect on CNT growth. The density and diameter of CNTs depend on the catalyst thickness and growth time. The growth mechanism of CNTs with ultra thin catalyst differ from general catalyst thickness (>1 nm). The cone shape CNTs were grown with ultra thin Ni catalyst. And CNT densities depend on the growth time, due to continuous etch of carbon network underneath metal tips and precipitation of amorphous carbon on CNT walls. The cone shape CNT shows a diameter of top particle is near 28 nm, bottom CNT diameter of ~ 64 nm size and cone angle of 18 degree. The particle size is larger than initial catalyst granules by agglomeration of polycrystalline Ni. We conclude that the vertically aligned cone shape CNTs with sparse density can be grown with ultra thin nickel catalysts.

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