Chapter 4 Results and Discussion

4.1 Analysis of carbon-based nano materials by depositing with different parameters.

4.1.1 Negative bias effect

Before several sets of experiment, carbon nanotubes could be obtained under a gas mixture of CO_2/CH_4 with 30/30 sccm mixture and 10Torr pressure on Fe(100Å) deposited silicon substrate.Fig4.1 shows the SEM images of carbon nanotubes growth under various biases applied.

Obviously, the length of carbon nanotubes was enhanced with increasing bias voltage. When the bias voltage increased, the tube became more aligned and sharp. Until the negative voltage reached -200V, the tube turned to tip-like .It was due to carbonaceous ion accelerated near to the substrate and accumulated, meanwhile H^+ etching sharpened the top of tube.

It has been reported generally that applying negative bias could enhance the nucleation density of diamond. [59-61] In this experiment, the initial growing stage was the catalyst formed a carbon-sphered precursor and with the temperature raised, the tensile-forces induced the formation of short carbon nanotubes.

Electrostatic forces of the negative bias enhanced presented in the plasma drove the subsequent extension of the short carbon nanotubes to multiple-micron lengths. And, a key element to the mechanism proposed is defects in the carbon-sphered graphene-layers. Pentagon and heptagon rings are two types of defects found in graphene layers. Since the negative bias accelerated the growing rate of carbon nanotubes, defects on the tubes were accumulated more also. The basic tenets of the growth mechanism are as follows: Double [5-7] defects are in the equilibrium with the graphene layers in carbon nanotubes, via [6-6-6-6] to [5-7-7-5] Stone-Wales switches [62] .The [5-7] defects migrate thermally and at random. The [5-7] defects concentrated

at the location that are energetically favorable and, which is the stem of a nanotube under tensile strain. The higher concentration of [5-7] defects in the stem increases the probability of interactions in [5-7] defects that result in [5-7-7-5] to [6-6-6-6] reverse Stone-Wales switches. The net migration of [5-7] defects to the stem, and the subsequent generation of hexagons in the stem, result in the lengthening of stem.

The HRTEM (Fig.4.2) shows the structure of muti-walled carbon nanotubes with hollow inside and the outer surrounded amorphous carbon.

Raman spectrum (Fig.4.3) revealed that carbon nanotubes are characteristic of graphite. The first-order of Raman spectrum of carbon nanotube shows strong peaks at $1591cm^{-1}$(G line), which is high frequency E_2g first –order mode and $1348cm^{-1}$(roughly corresponding to the D-line associated with disorder-allowed zone –edge modes of graphite)
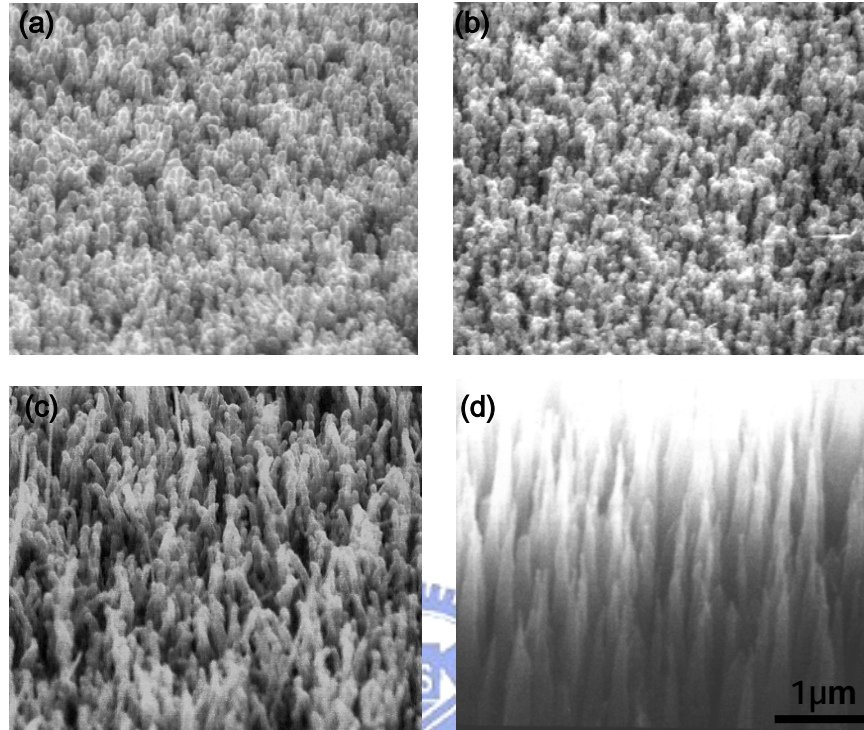
Fig.4.1 SEM images of changes negative bias voltage for synthesizing carbon nanotubes on silicon:
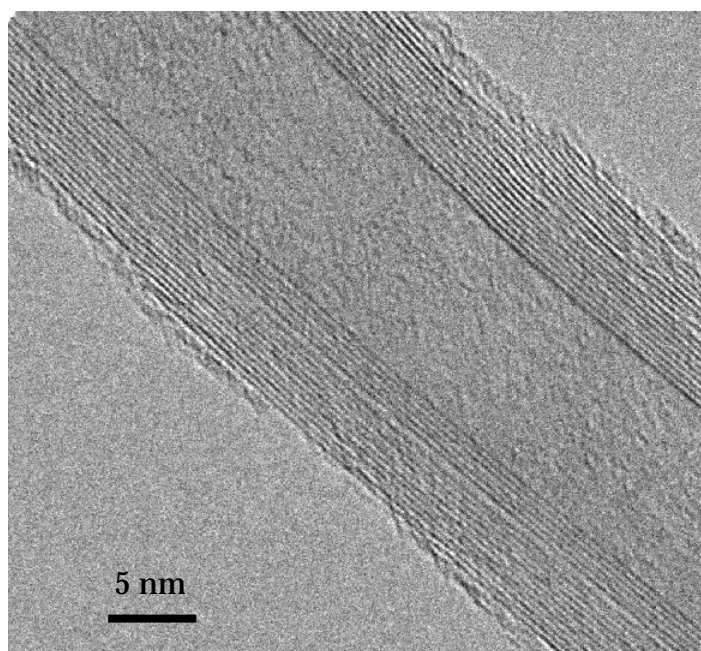**(a)-50V (b)-100V(c)-150V, and (d)-200V, each for 10mins**

Fig.4.2 HRTEM images of an individual carbon nanotube

I_D
(1330,2499)

I_G
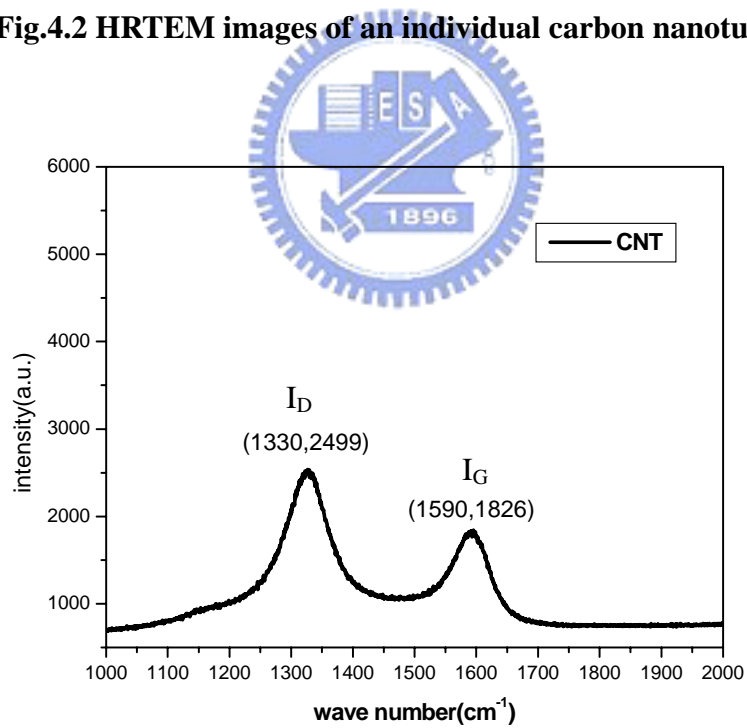(1590,1826)

intensity(a.u.)

wave number(cm^{-1})

CNT

Fig.4.3 Raman spectrum of CNT

4.1.2 Positive bias effect

The effect of positive bias was studied in this part. The positive bias was added after the negative bias applied. Since the negative bias might cause the straight shape of tube, the later applied positive bias could make different aspect change.

Fig.4.4 shows the SEM images of cross-sectional view of carbon nanoflakes. They were grown under positive biases adding after the negative bias applied each for symmetrical period of time.

The positive bias lead to another direction of net [5-7] migration since there exists the [5-7-7-5] to [6-6-6-6] reverse Stone-Wales switches under the negative bias applying. From Fig 4.4(a), the carbon nanotubes were fabricated and the catalyst migrated on their top. When the positive bias added, the carbon nanotubes had extended their lengths from the catalyst site which might be the secondary deposition. As the positive bias applying time increased, the graphite sheets extended to horizon direction and whole morphology turn to more spherical. This different carbon nano-material had petal-like graphite sheets was named carbon nanoflakes(CNF).A special difference from published carbon nanoflakes is its 3-D structure. This could lift application of its high surface areas and chemical activity.

From the HRTEM images of Fig.4.5, a small-angle rotation existing between the basal plane layers of the petal due to weak interlayer (van der Waals) interaction in graphitic layer. The occurrence of interlayer rotation might be also a result of the difference in layer curvature.

The spectrum of Raman shift (Fig.4.6) shows an additional weak peak at about 1615cm^{-1} (D'line). The origin of the D and D'lines in other forms of carbon materials has been explained as disorder-induced features, caused by the finite particle size effect or lattice distortion [63-65] Normally, the intensity of the 1350 cm^{-1} peak increases with an increase in the amount of unorganized carbon in the samples and with a decrease in the graphite crystal size.[66]
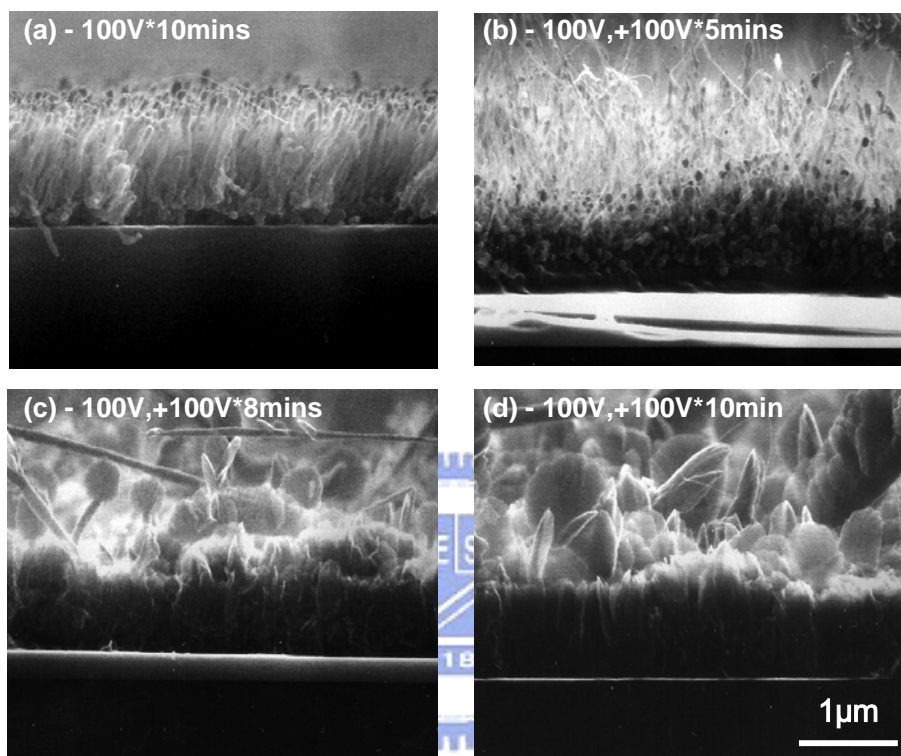
Fig.4.4 SEM images of changes from -100V to +100V in the symmetric period time

for synthesizing carbon flakes on silicon:

(a) -100V,10min (b)-100V* 5min,+100V*5min (c) 100V*8min,+100V*8min

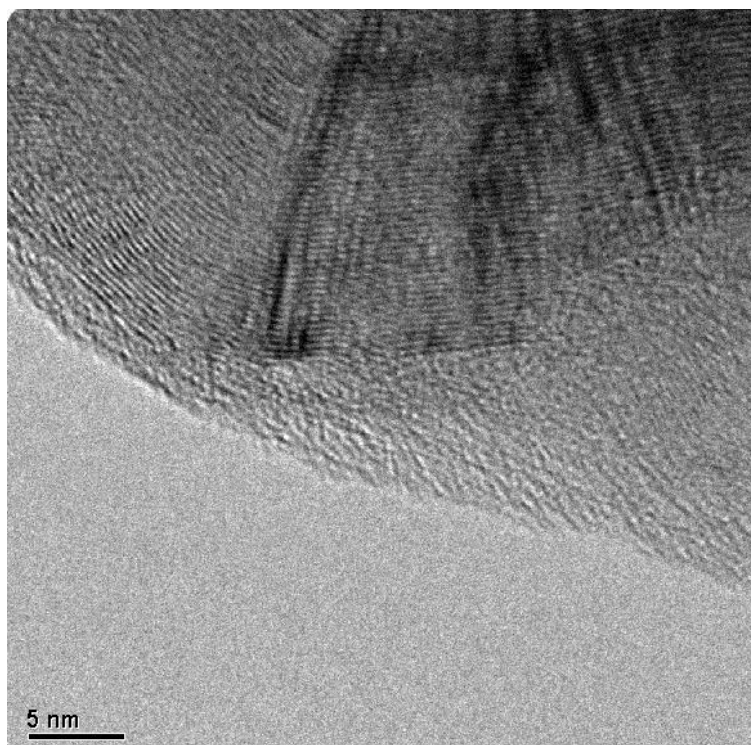**(d)-100V*10min, +100*10min**

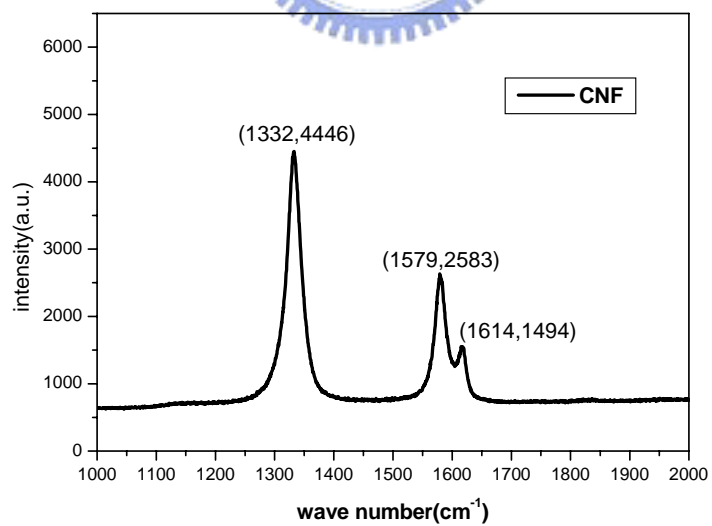**Fig.4.5 HRTEM of individual petal of carbon nanoflake**

Fig.4.6 Raman spectrum of carbon nanoflake under (-100, +100) V for 10mins

Fig.4.7 is the cross-sectional view of carbon nanoflakes grown under -100V for 10mins then switched to +100V for different period time. As the +100V period time from 5mins~20mins, it shows how surface morphology changes. When +100V period time extended, the curvature of surface which was formed porous structure became deep and wide. But when +100V period time reached 20mins, the balance was collapsed. It is because the different direction of carbonaceous ion accumulated and its speed is faster than electron striking.

Fig.4.8 is the enlarged image of Fig.4.7. It shows the different period of time with +100V affecting the porous size. It is due to the growing rate promoted by bias applied time while the petals grow up to form a larger pore. Besides, corresponding Raman spectrum shows in Fig.4.9 reveals the peak has narrow width which means more organized structure. According to the forward experiment analysis, the negative and positive voltages about period time have a balance status about 1:1, when the I_D / I_G has the smallest ratio and still has a lattice distortion. It means the better graphitic components that consist of micro-distortion to be nanoflake.

Fig.4.10 shows the SEM images of the cross-sectional view of carbon nanoflakes grown under various positive bias voltages adding after the negative bias applied. It reveals that along the stem body of the carbon nanotubes under the negative bias before, opposite ion bombardment and electrostatic force competing makes graphite sheets form a particular shape. With the positive bias voltage increasing, the pore formed of petaloid sheets became large until the competing forces lose the equilibrium.

The magnified observation is in Fig.4.11.Positive bias voltage variation from +50V to +200V shows pores formed of graphite grow in number per surface area. However the pore size is reduced due to the number increasing.

The Raman spectrum(Fig.4.12) indicates the same characteristic peak of D' line which means the lattice distortion and particle size limited corresponding to the particular shape of carbon nanoflakes, and they have uniform bonding components even

differ the bias. Besides, the I_D / I_G ratio raises as +100V period time increases which means the accumulated a-carbon for longer period time makes more defects in the graphitic structure.
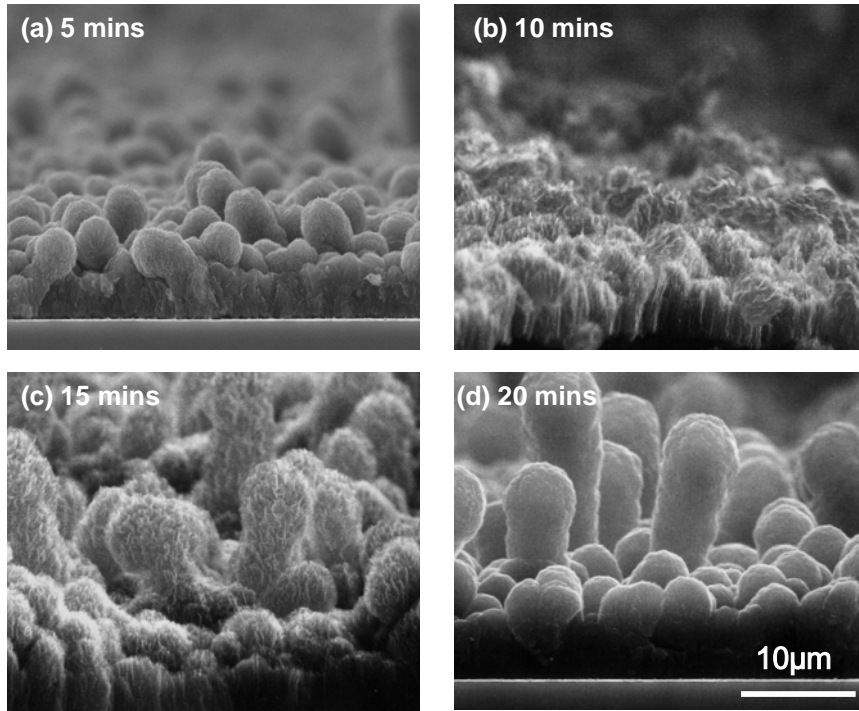
Fig. 4.7. SEM images of fixed -100V for10mins and switch to +100V in the different period time for synthesizing carbon flakes on silicon substrate: (a) 5mins (b) 10mins (c) 15mins (d) 20mins
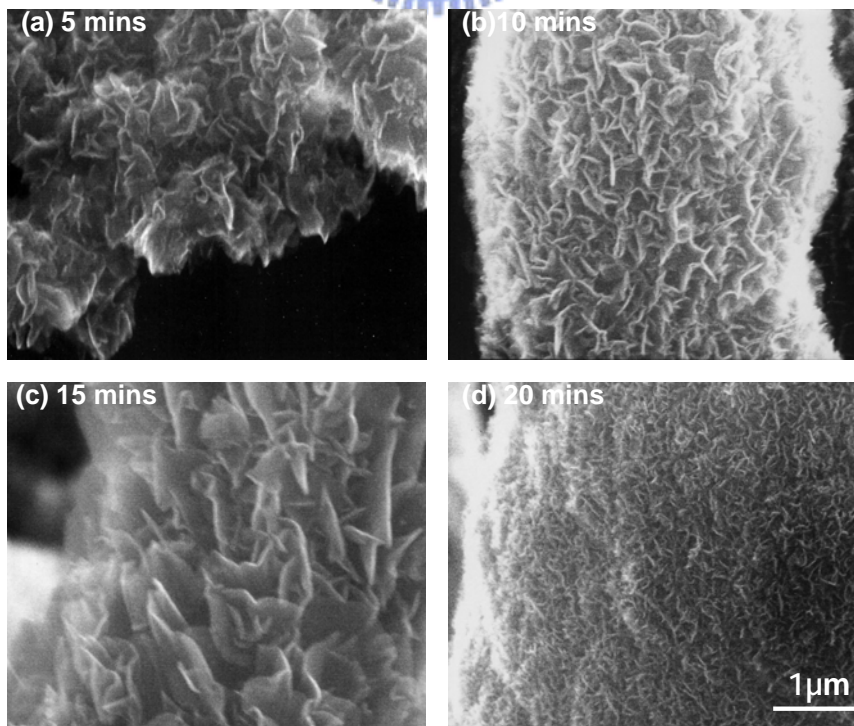

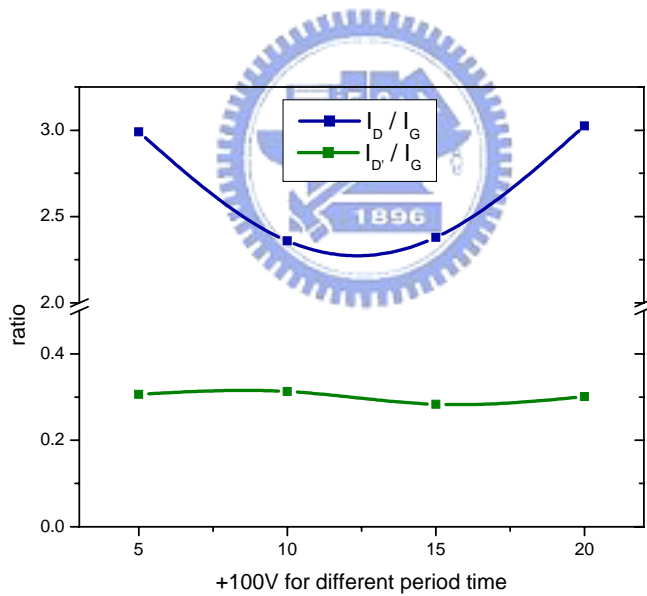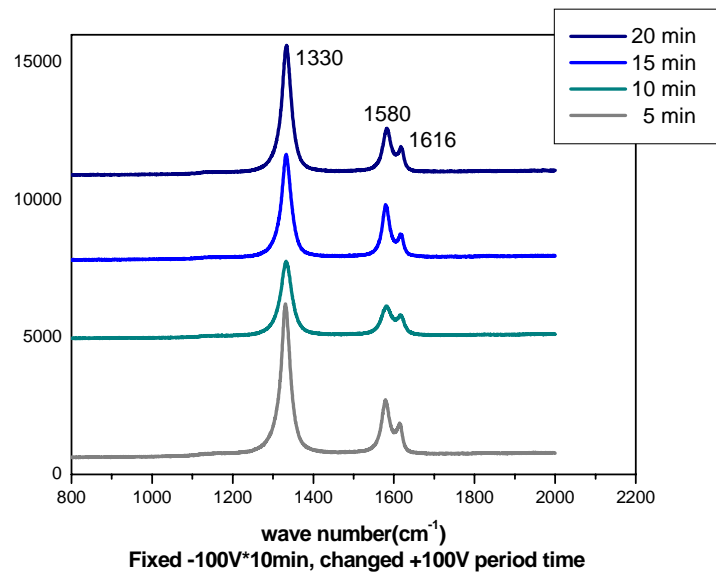**Fig. 4.8. Enlarged SEM image of Fig. 4.7**

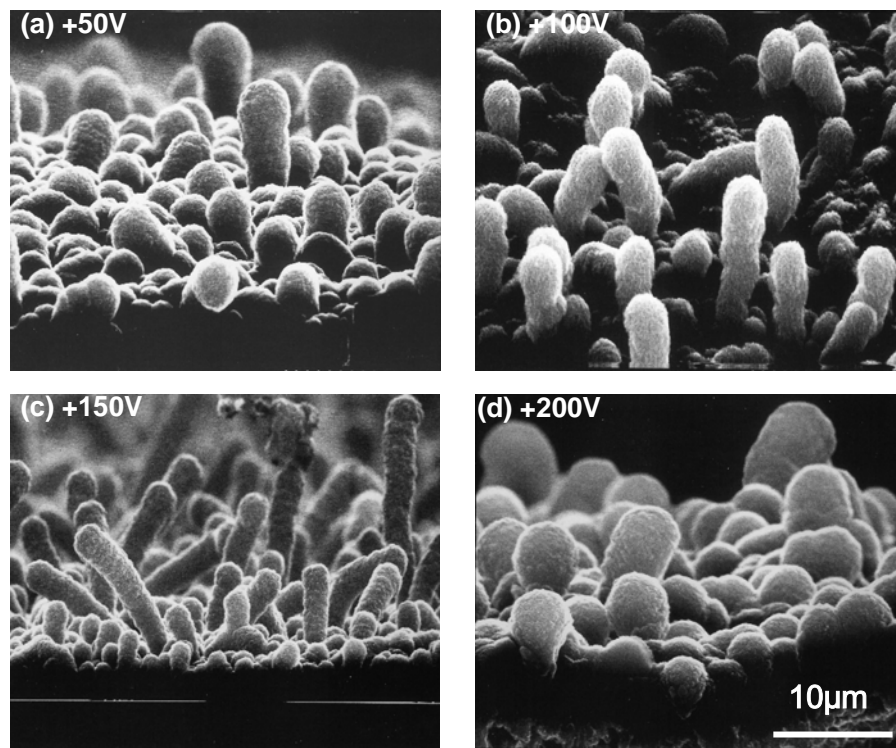**Fig.4.9 Raman spectrum and components ratio of fixed -100V for 10mins, changed +100V for 5~20mins.**

Fig. 4.10. SEM images of fixed -100V for10mins and changed positive bias voltage from +50V~+200V, each for 10mins for synthesizing CNFs on silicon: (a) +50V (b) +100V (c) +150V (d) +200V
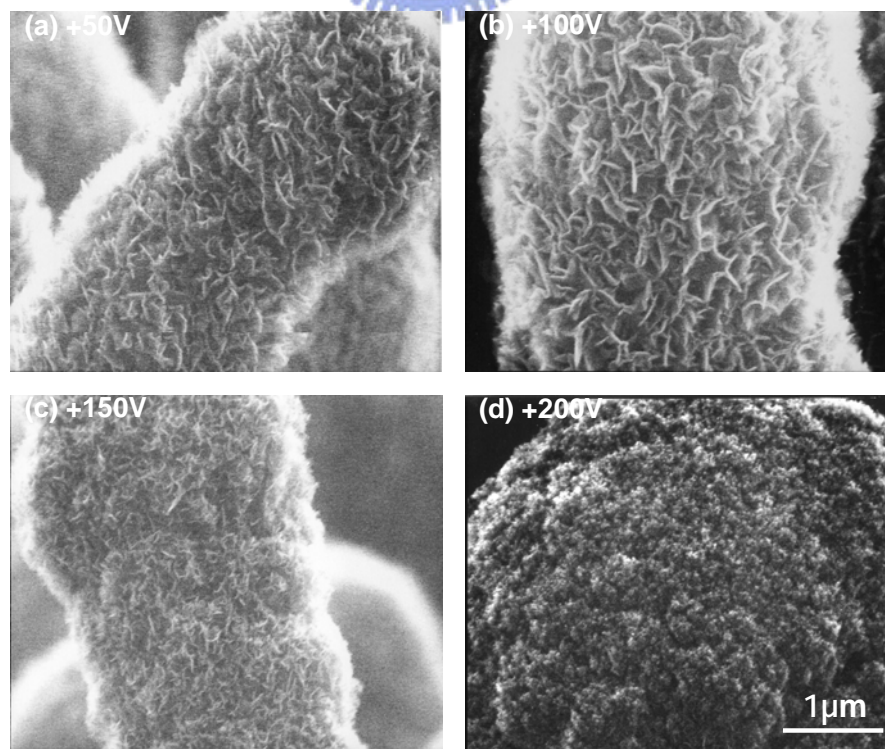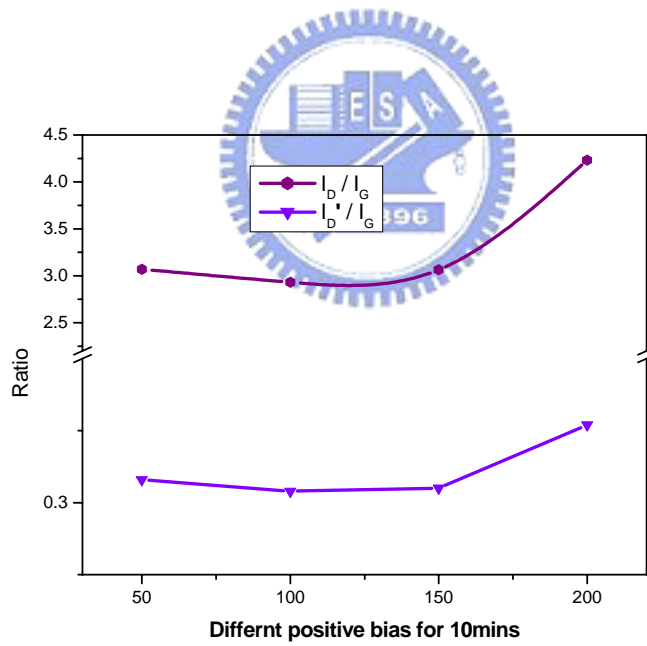

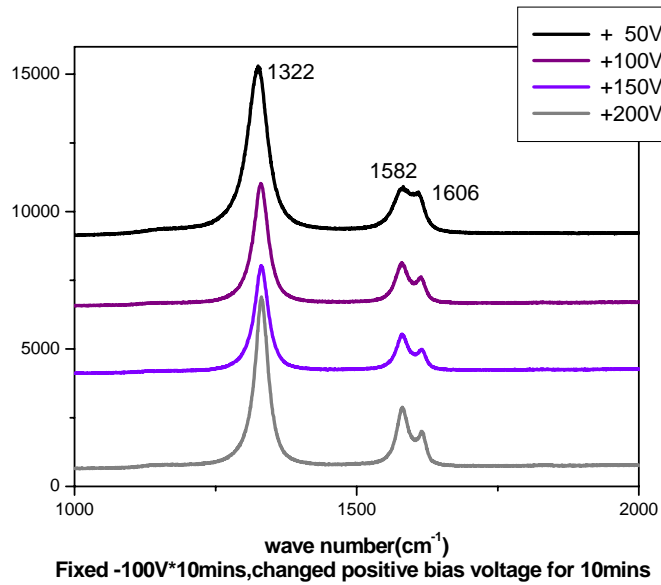**Fig.4.11 Enlarged SEM images of Fig.4.10**

Fig.4.12 Raman spectrum and components ratio of fixed -100V for 10mins, changed +50~200V, each for 10mins.