4.4 Carbon Material Grown on Cr Film by Using MPCVD: CH_4/CO_2 Reactant Gas

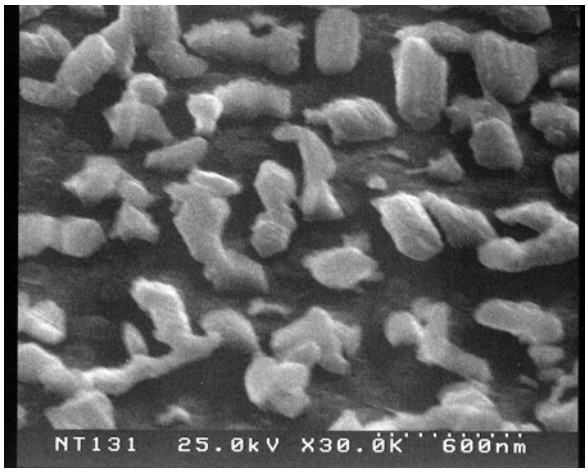
In this study, aligned carbon nanotubes were grown on a Cr film by bias-enhanced microwave plasma chemical vapor deposition, using CH_4/CO_2 as system source gases. The Cr film on a silicon wafer had a constant thickness of 100 nm, and bias-enhanced plasma pretreatment was performed for various biases to try growing carbon nanotubes on the Cr film.

4.4.1 Background

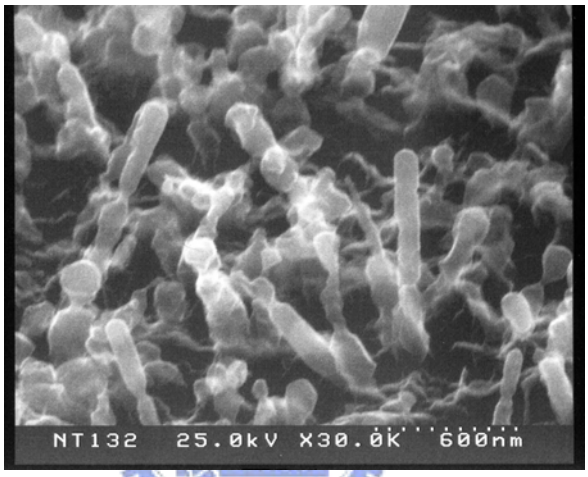
In this thesis, stainless steel 304, an Fe-Ni-Cr alloy with a high Cr content, was used as the substrate to grow CNTs. The top metal particles include only Fe and Ni, but not Cr when the carbon nanotubes are grown on the 304 alloy substrate. The Cr film was selected also because it adheres well to silicon wafers and it is a transition metal. CH_4/CO_2 system source gases were used due to the previous success in growing CNTs. In other words, we tried to study the possibility that if CNTs can grow on Cr films by bias-enhanced MPCVD using CH_4/CO_2

4.4.2 Characterization of Carbon Material

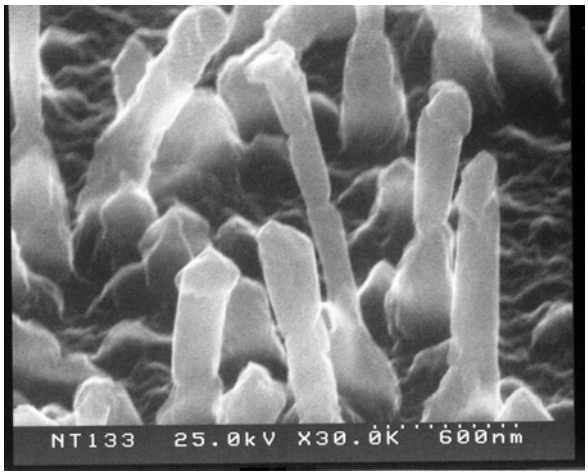
The applied microwave power and the working pressure were 400 W and 2666 Pa, respectively. When CH_4/CO_2 was used, the reactive gas mixture was used directly with a flow rate of 30/30 sccm, since pure CO_2 plasma damaged the quartz tube in the deposition system. The negative bias voltages applied to the substrates were 0 V, -150 V and -250 V. The growth continued for 30 min. Figure 48 shows carbon grown on Cr film by using CH_4/CO_2 gas system. No obvious CNTs were observed in these images, and the result was rod-like when bias voltage was over -150 V. Comparing the Fig. 48(b) and 48(c), exhibits the result grew to larger diameter but fewer under higher bias.



(a)



(b)



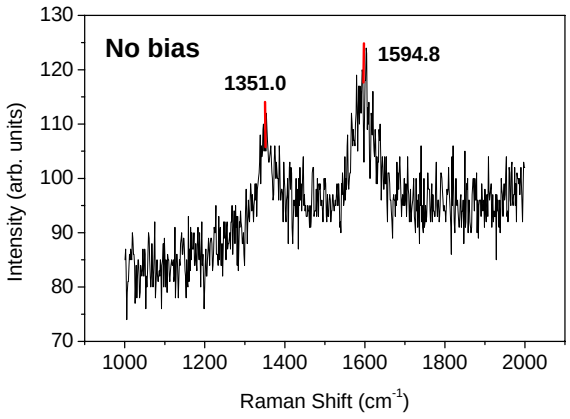
(c)

Fig. 48. SEM photographs of carbon grown on Cr film using the CH_4/CO_2 gas system at various biases; (a) No bias, (b) -150 V, and (c) -250 V.

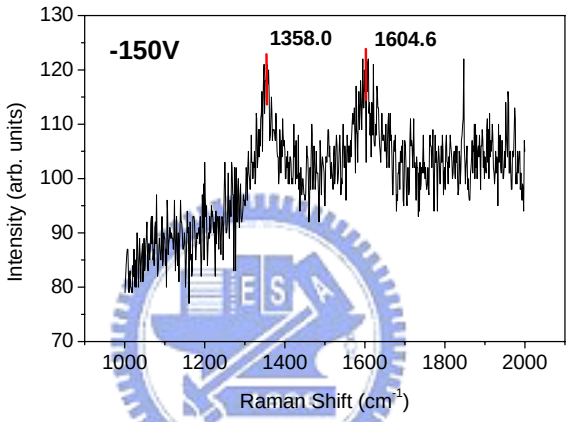
Figure 49 displays micro-Raman spectra of carbon grown on Cr film using the CH_4/CO_2 gas system at various biases. These samples have two sharp peaks located at around 1350 cm^{-1} and 1581 cm^{-1}. The relative intensities of the two peaks depend on the type of graphitic material.

4.4.3 Field Emission Properties

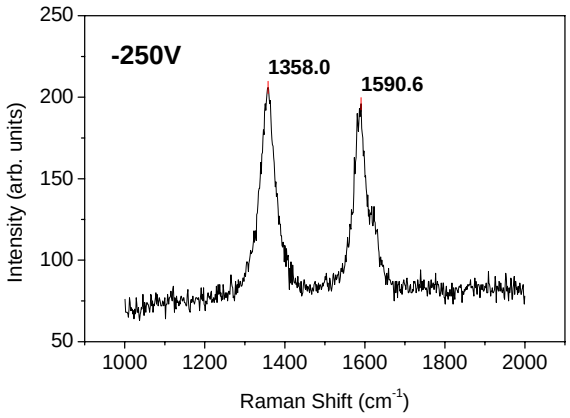
Even if not all of the tested sample surface may be full of CNTs, the defined area is still the whole of the sample (1×1 cm) to verify the overall effect of deposition conditions. Field emission properties are obtained using a diode structure. An anode, ITO glass, is separated by 500 μm from the CNTs cathode. The I-V properties are measured using an electrometer (Keithley 237) and analyzed through the Fowler-Nordheim (F-N) model. The F–N plot is used to confirm the field emission characteristics. Figure 50 displays the characterization of carbon grown using CH_4/CO_2 systems source gases. The emission currents at an applied voltage of 1000 V (2 V/μm) was 0.237 mA (0.237 mA/cm^2). Turn-on field was around 720 V (1.44 V/μm).



(a)

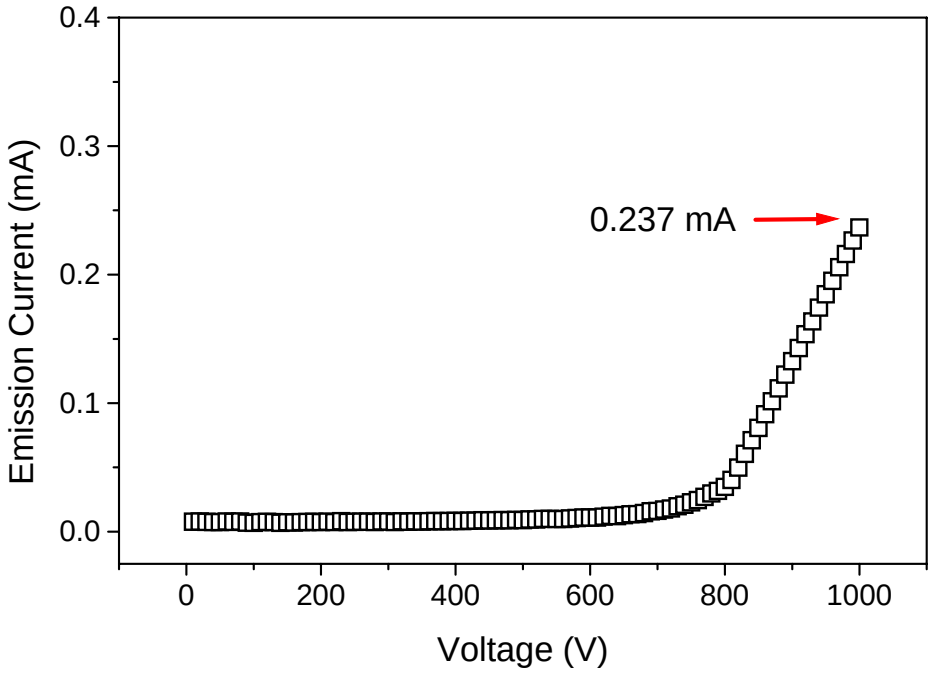


(b)

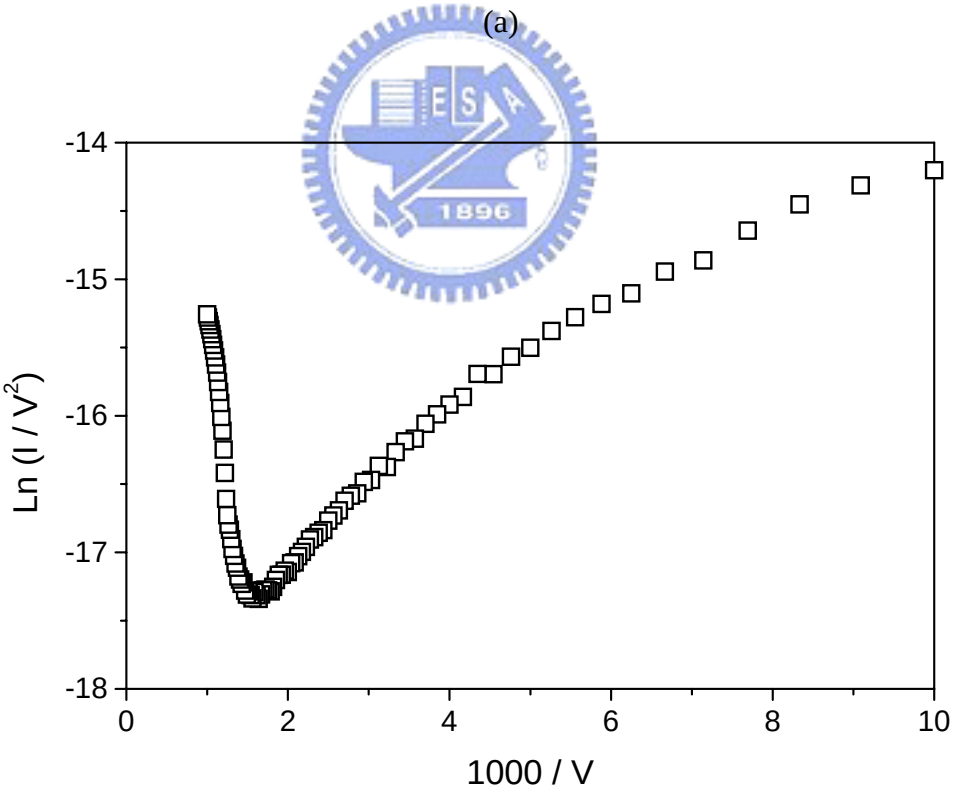


(c)

Fig. 49. Micro-Raman spectra of carbon grown on Cr film using the CH_4/CO_2 gas system at various biases; (a) No bias, (b) -150 V, and (c) -250 V.



(a)



(b)

Fig. 50. (a) Relationship of emission current against applied voltage, and (b) F-N plot of the carbon nano-rods grown by using CH_4/CO_2 gas system.

4.5 Carbon Nanotubes Grown on Cr Film by Using MPCVD: CH_4/H_2 Reactant Gas

Using CH_4/H_2 source gases, vertically aligned carbon nanotubes were grown on a Cr film by microwave plasma chemical vapor deposition. The Cr film on a silicon wafer had a constant thickness of 100 nm, and bias-enhanced H_2 plasma pretreatment was performed for various periods to modify the surface of the Cr film. Bias voltage of -150 V was applied during both pretreatment and growth steps, the resultant carbon nanotubes on a Cr film, which had been pretreated in bias-enhanced H plasma for 5 min were vertically aligned. The field emission properties of the resultant carbon nanotubes included an emission current density of 0.305 mA/cm^2 at 2 V/μm; and a turn-on field of 1.34 V/μm.

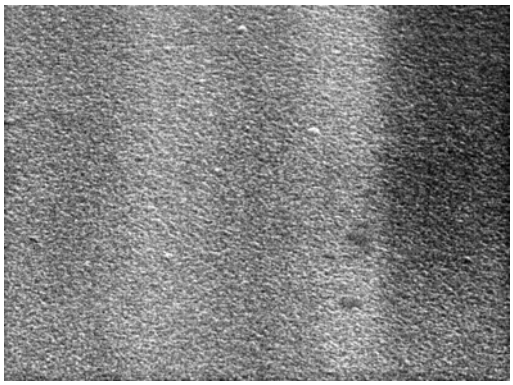
4.5.1 Background

Because no obvious CNTs were found in the previous study, we tried to find out the possible solution to grow high-aspect-ratio and vertical CNTs on Cr film. For growing CNTs *in situ* without pre-depositing a catalyst layer, one method uses a reactant gas that can act as a catalyst for growing CNTs on certain substrates [27]. Moreover, the power of the plasma may promote the generation of small metal particles from the metal substrate in a plasma-enhanced chemical vapor deposition [28]. Accordingly, the authors believe that CNTs grow due to a particular effect of a reactant gas on the surface condition of substrates, and these substrates have no way to provide proper catalytic particles for growing CNTs originally unless their surface is modified before or during the CNTs growth. Since pure CO_2 plasma damaged the quartz tube in the deposition system, therefore, this work develops vertically aligned CNTs grown on bias-enhanced hydrogen plasma-pretreated Cr films using MPCVD, and applies them to field emission. Bias-enhanced H_2 plasma pretreatment was performed for various periods to modify the surface conditions of the Cr film. Varying the pretreatment periods between 1 min and 30 min was found to form catalytic particles of different sizes. The size of the catalytic particles in turn determines the growth of vertically aligned CNTs.

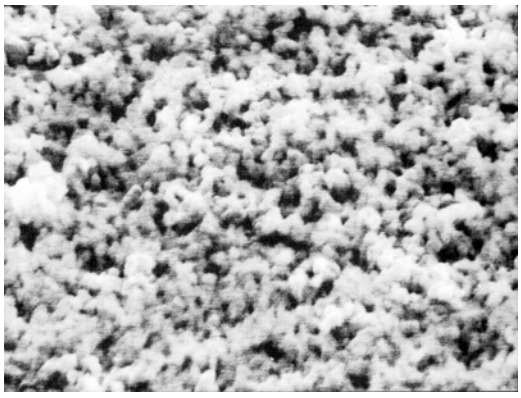
4.5.2 Bias-Enhanced H_2 Plasma Pretreatment of Cr Film

In this study, the deposition of CNTs proceeded in two steps: the pretreatment of Cr film with bias-enhanced H_2 plasma and the growth of CNTs. The applied microwave power and the working pressure were 400 W and 2666 Pa, respectively. During the Cr film pretreatment with H_2 plasma, the flow rate of H_2 was maintained at 300 sccm, and the negative bias voltage applied to the substrates was -150 V. The Cr surface was expected to be effectively treated by high capacity for etching. Thus, pretreatment was performed under bias to reduce the period over which the surface was modified. The resulting samples were examined by sampling, and they did not differ according to whether they underwent pretreatment and growth simultaneously or separately.

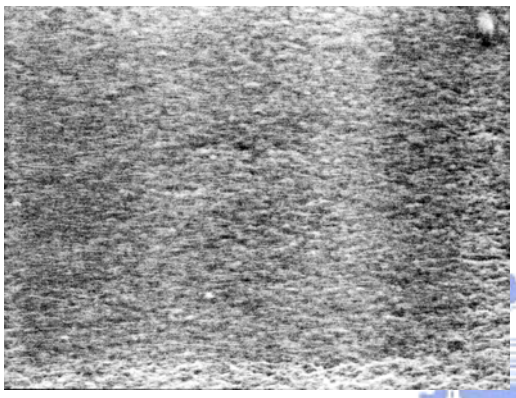
Figure 51 presents SEM photographs of Cr films pretreated with H_2 plasma for various periods. The surface of the silicon wafer, which was originally covered by a Cr film, appeared after 10 min, and etching seemed more severe after 30 min, as shown in Figs. 51(e) and (f). Hydrogen plasma has been used as an etching source in many applications. Thus, in this work, the accelerated active hydrogen radicals under bias yield anisotropic etching. However, this high capacity for etching may be appreciated even during short pretreatment. Unlike for the as-deposited Cr film sample, shown in Fig. 51(a), pretreatment periods between 1 and 5 min, Figs. 51(b)-1(d), resulted in obvious surface changes.



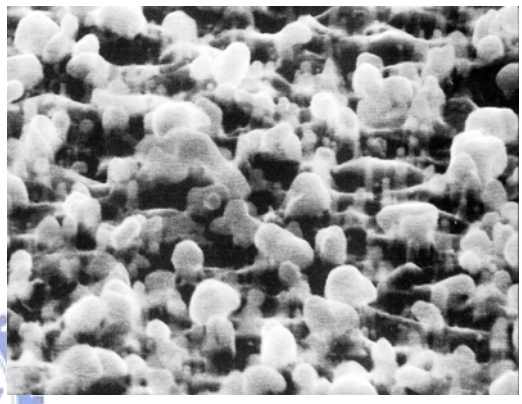
(a) 0 min



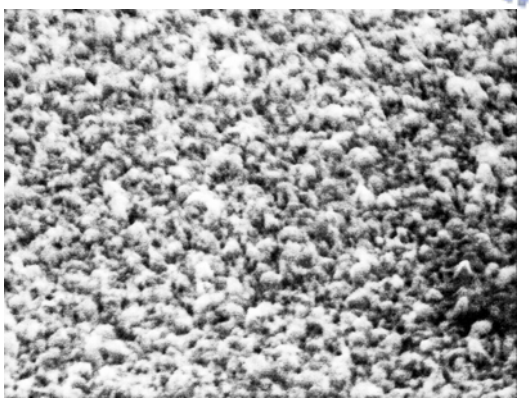
(d) 5 min



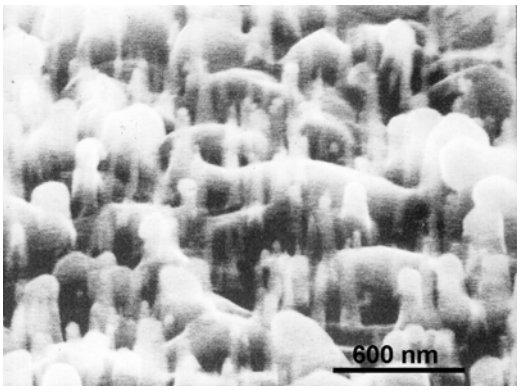
(b) 1 min



(e) 10 min



(c) 3 min



(f) 30 min

Fig. 51. SEM photographs of bias-enhanced H_2 plasma-pretreated Cr film, obtained for various periods of pretreatment; (a) 0 min, (b) 1 min, (c) 3 min, (d) 5 min, (e) 10 min, and (f) 30 min.

The surface roughness, average grain size and particle size of pretreated Cr films were analyzed by AFM. Figure 52 shows AFM images of bias-enhanced H_2 plasma-pretreated Cr film, obtained for various periods of pretreatment. According these images, one can make sure if the images conform to the real situation, and some useful surface conditions could be used calculated. Figure 53 shows the surface roughness, average grain size and particle size of Cr films for various periods of treatment with H_2 plasma. Longer pretreatment resulted in rougher surfaces and larger particles on the Cr film. The surface roughness, average grain size and particle size of a particular Cr film when growing CNTs were 26.871 nm, 928.74 nm^2 and 80.409 nm, respectively. These obtained analytic results show particle size to be the major factor that affects the growth of CNTs. CNTs were experimentally demonstrated to grow by precipitation of carbon from supersaturated transition metal particles and the diameter of CNTs was closely correlated with the size of dispersed metal particles [125,178]. However, the diffusion model for the growth of CNTs does not have universal significance and growth conditions can also significantly affect the formation of CNTs [180].

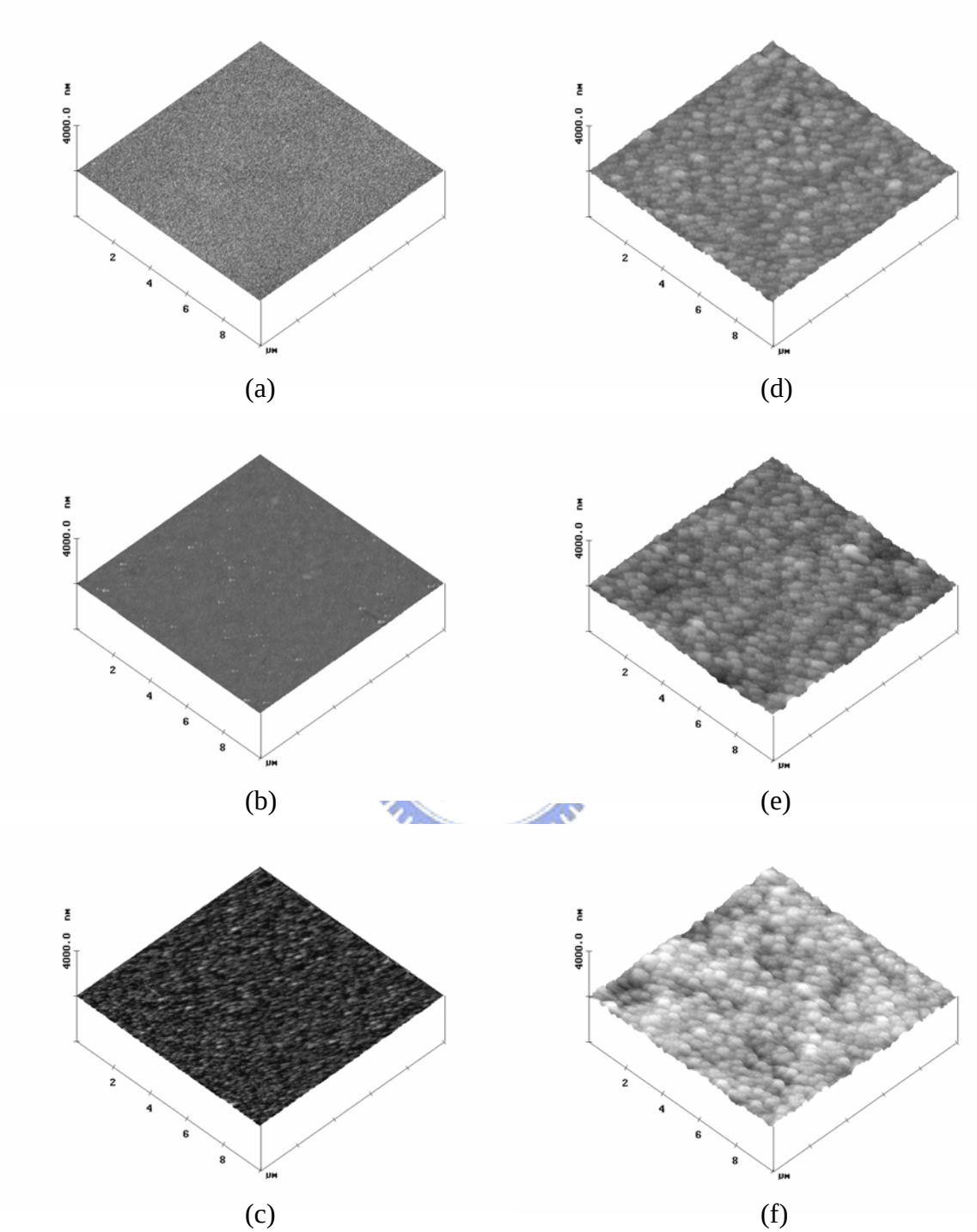
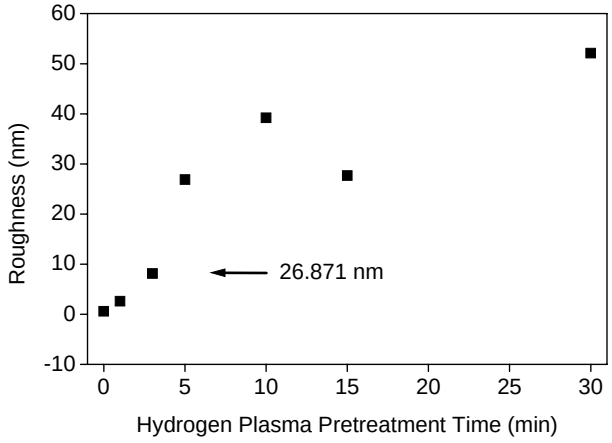
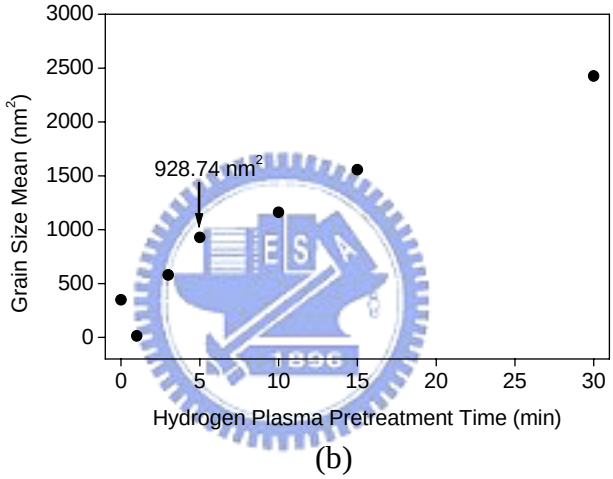


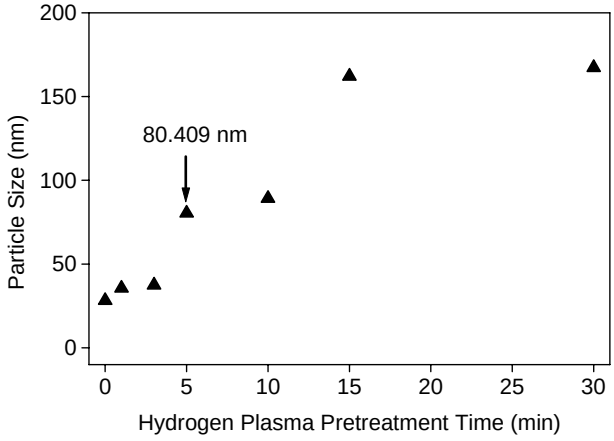
Fig. 52. AFM images of bias-enhanced H_2 plasma-pretreated Cr film, obtained for various periods of pretreatment; (a) 0 min, (b) 1 min, (c) 3 min, (d) 5 min, (e) 10 min, and (f) 30 min.



(a)



(b)



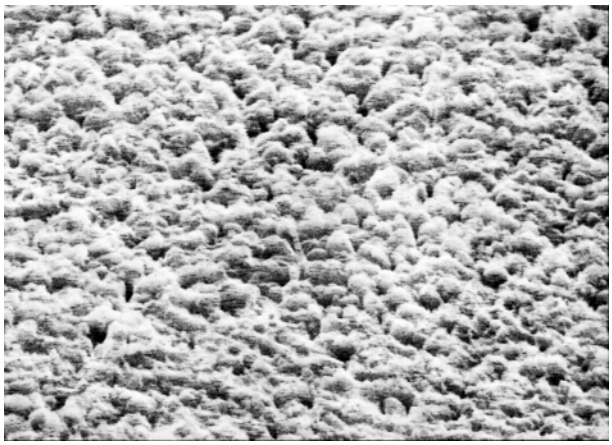
(c)

Fig. 53. (a) Surface roughness, (b) average grain size and (c) particle size of H_2 bias-enhanced plasma-pretreated Cr film, obtained for various periods of pretreatment.

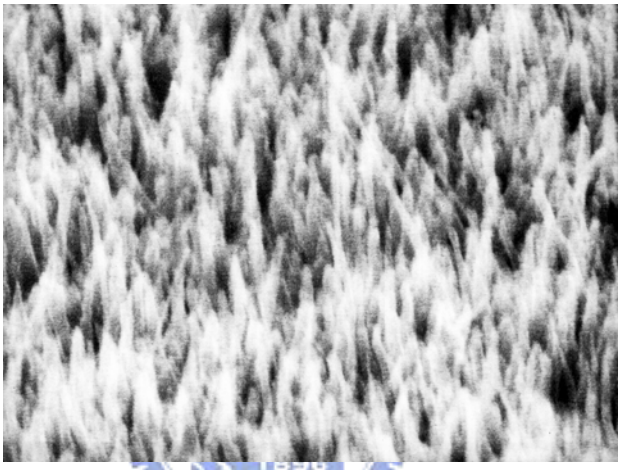
4.5.3 Growth of Vertically Aligned Carbon Nanotubes

Figure 54 shows SEM photographs of samples grown on H_2 plasma-pretreated Cr film pretreated for various periods. As shown in Fig. 54(a), no nanotube was found on the surface of a Cr film pretreated with H_2 plasma for 3 min. The vertically aligned CNTs seem only to have grown on the surface of Cr films pretreated with H_2 plasma-pretreated for 5 min or 10 min, as shown in Figs. 54(b) and 54(c), respectively. These CNTs possess a high-aspect-ratio, implying potential use as field emission devices.

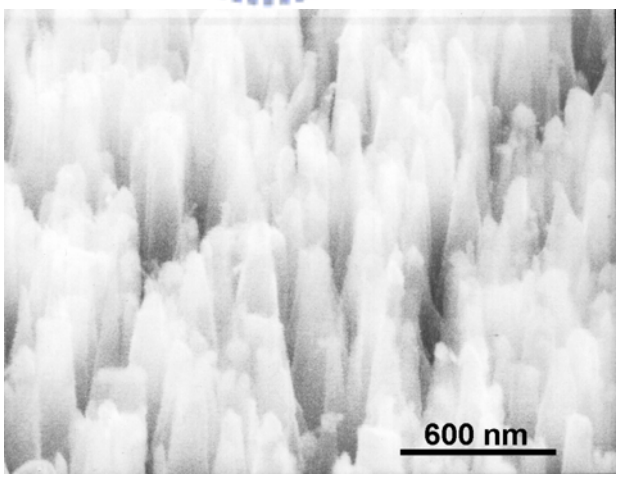
The first-order Raman spectrum of the CNTs includes strong, sharp peaks at 1581 cm^{-1} (G-line) and 1350 cm^{-1} (D-line). The peaks suggest that the CNTs are characteristic of microcrystalline graphite. Figure 55 displays the Raman spectra of the carbon grown on Cr film with various periods of pretreatment. As shown in Figs. 55(a) and 55(b), only samples pretreated for 3 min and 5 min showed two peaks at around 1350 cm^{-1} and 1581 cm^{-1}. The relative intensities of the two peaks depend on the type of graphitic material. However, the SEM photograph in Fig. 54(a) shows that no CNT grew on the sample with 3 min of H_2 pretreatment, the peaks seem to be associated with amorphous carbon since both resemble those in the Raman spectrum. Furthermore, as shown in Fig. 55(c), the Raman spectrum indicates that the sample with 10 min of H_2 pretreatment did not include carbon, which fact is interesting since this sample looks like carbon tips as shown in Fig. 54(c). After further characterized by X-ray diffraction, this sample was verified to be silicon. This maybe due to that the surface of the silicon wafer appeared after pretreatment. While in the growth step, lacking for the protection of Cr and the proper catalysts, the silicon sample suffered a more severely anisotropic etching. To improve the observation of growth of vertically aligned CNTs, SEM photographs of bias-enhanced H_2 plasma-pretreated Cr film and resultant samples grown, obtained for various periods of pretreatment, are rearrange in Fig. 56. It helps one could understand the growth or etching happened during the following stage.



(a) 3 min

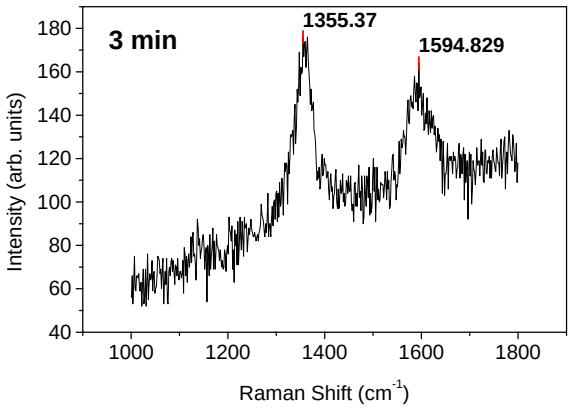


(b) 5 min

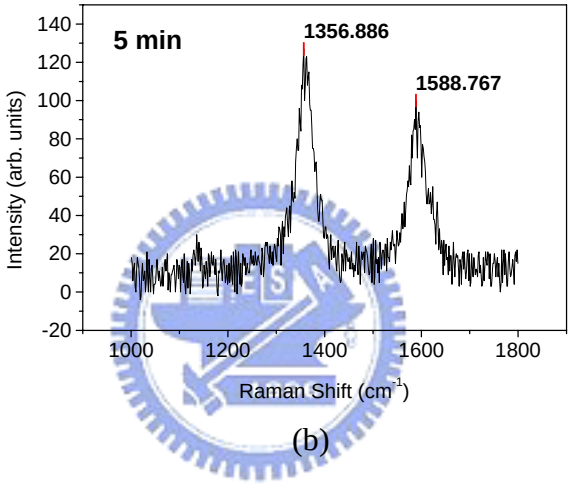


(c) 10 min

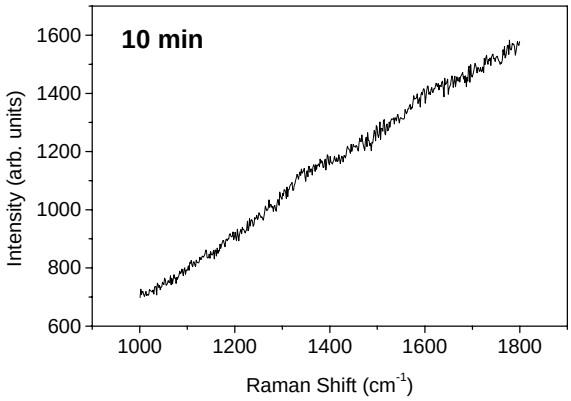
Fig. 54. SEM photographs of samples grown on H_2 plasma-pretreated Cr film pretreated for various periods; (a) 3 min, (b) 5 min, and (c) 10 min.



(a)

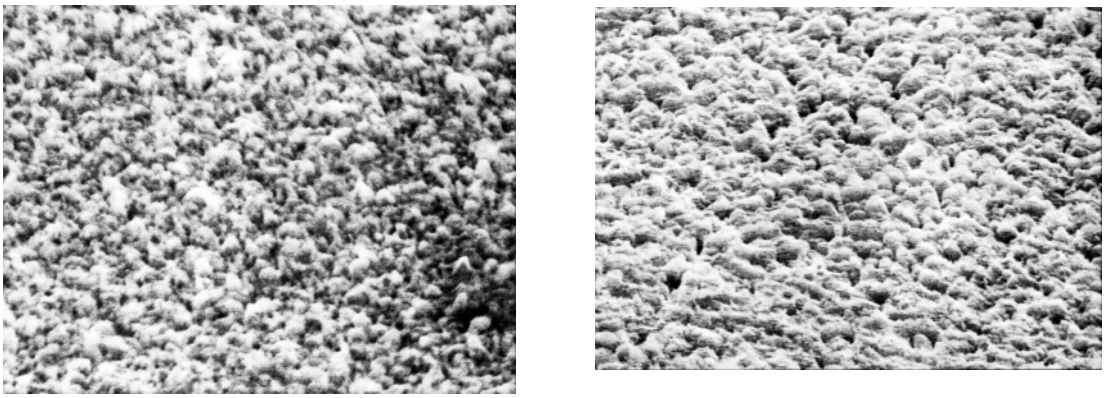


(b)

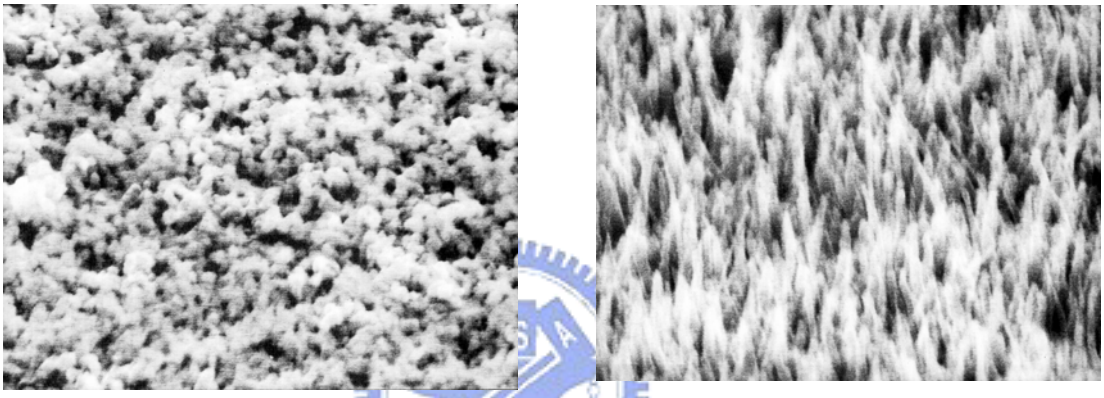


(c)

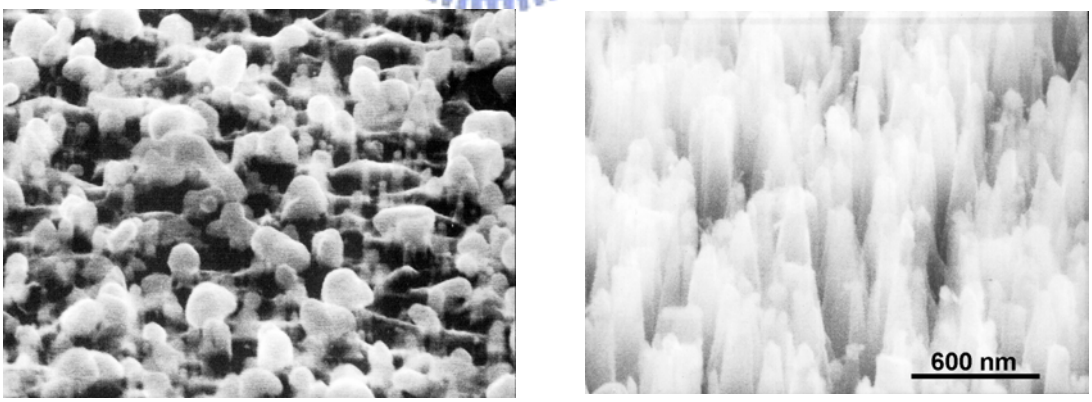
Fig. 55. Micro-Raman spectra of samples grown on H_2 plasma-pretreated Cr film pretreated for various periods; (a) 3 min, (b) 5 min, and (c) 10 min.



(a) 3 min



(b) 5 min



(c) 10 min

Fig. 56. SEM photographs of bias-enhanced H_2 plasma-pretreated Cr film and resultant samples grown, obtained for various periods of pretreatment; (a) 3 min, (b) 5 min, and (c) 10 min.

The CNTs were analyzed by TEM to confirm that they were truly CNTs, and not carbon fibers. Figure 57 displays the TEM image of an end section of an individual CNT. Comparing this image to those presented elsewhere [178] indicates that the tube is a multi-walled CNT. The darkness of the nanotube walls indicates that the nanotube is multi-walled and hollow rather than solid fibers. Figure 57 also reveals that the CNT has inner diameters of approximately 10 nm, and outer diameters of around 30 nm. The Cr was also observed by the EDX attached to the TEM, and is the darkest and teardrop-shaped part of this image. A comparison with the SEM photograph in Fig. 54(b) suggests that Cr is on the top of the CNT.

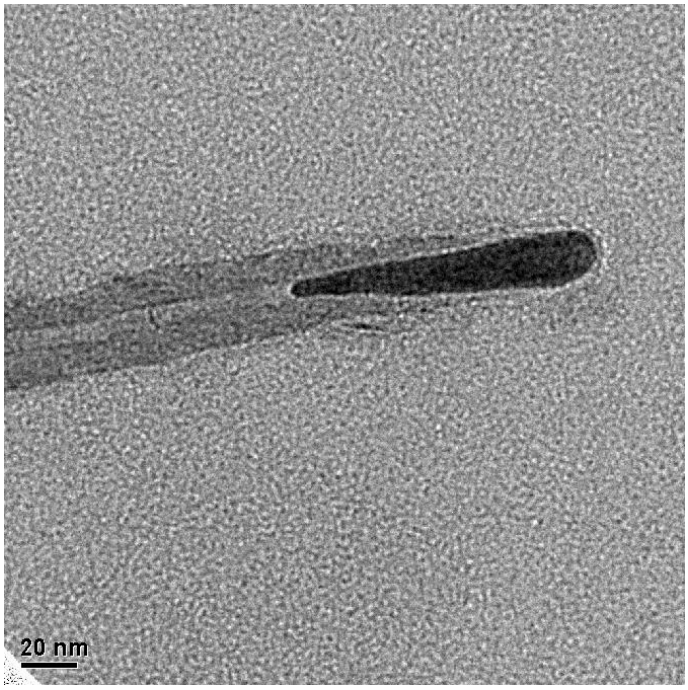


Fig. 57. TEM image of the end section of an individual CNT.

Most of the existing models of the chemical vapor deposition growth of carbon nanotubes are based on the model first proposed by Baker *et al.* [181]: the hydrocarbon molecules decompose at the surface of the catalyst, and the carbon atoms dissolve into the metal, forming a solid solution. When this solution becomes supersaturated, C precipitates at

the surface of the particle in its stable form, as crystalline graphitic layers. Several reported alignment mechanisms were reviewed to explain the possible mechanism in the deposition process performed here. Bower *et al.* [121] reported that the alignment is mainly induced by the electrical self-bias field imposed on the substrate surface from the plasma environment. However, they used heavier ammonia plasma, rather than hydrogen plasma, promoting the establishment of a stronger local field at the surface. They used this fact to explain why others have grown randomly oriented nanotubes in a similar microwave plasma enhanced chemical vapor deposition system using hydrogen-based plasma [113,160]. A high concentration of hydrogen plasma and a high negative bias applied to the substrate were found to enable the randomly oriented carbon nanotubes to be easily removed by anisotropic etching. Such a mechanism can remove all carbon nanotubes that are not parallel to the hydrogen plasma attracted to the substrate under a negative dc bias [178]. Similarly, Murakami *et al.* [120] developed a process that involved depositing and patterning a nickel-based metal line on a glass substrate, followed by bias-enhanced microwave plasma chemical vapor deposition to grow well-aligned carbon nanotubes. During nanotube growth, a negative voltage of -250 V was applied to the substrate. Merkulov *et al.* [182] reported that the crowing effect could assist the alignment of CNTs. However, in this study, it could not be decided crowing effect or anisotropic etching which was the main mechanism to assist the alignment of CNTs.

4.5.4 Field Emission Properties

Field emission properties are obtained using a diode structure. An anode, made of indium tin oxide glass, was separated by 500 μm from the tip of a cathode made of CNTs. The *I-V* properties were measured using an electrometer (Keithley 237) and analyzed using the Fowler-Nordheim (F-N) model. The F–N plot is used to confirm the field emission characteristics. Figure 58 characterizes the vertically aligned CNTs grown on Cr film pretreated for 5 min. The emission current at an applied voltage of 1000 V (2 V/μm) was 0.305 mA/cm^2 (0.305 mA/cm^2). The macroscopic turn-on voltage was 670 (1.34 V/μm).

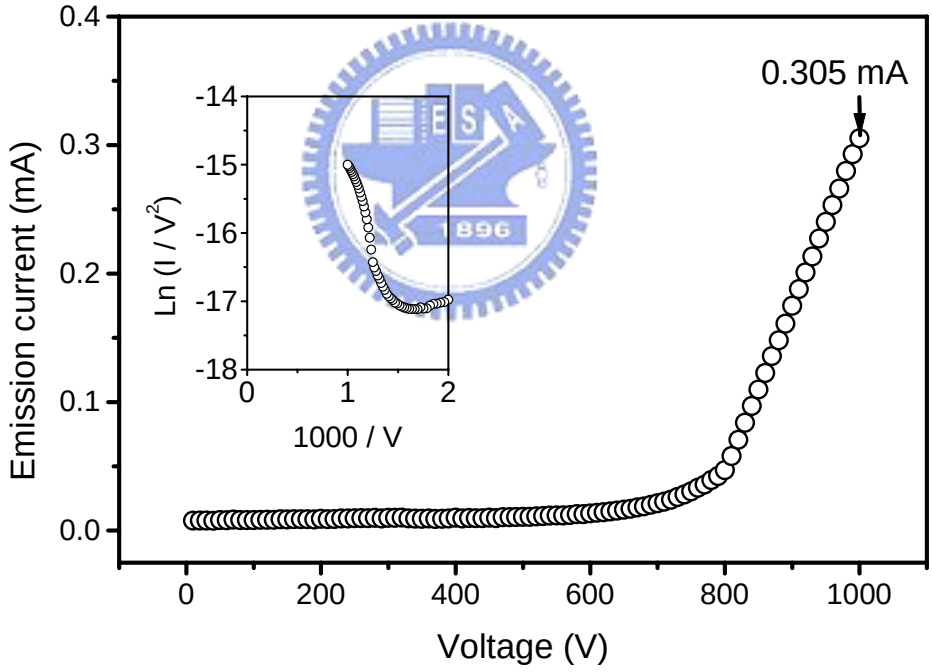


Fig. 58. Emission current against applied voltage, and F-N plot for CNTs grown by using CH_4/H_2 gas system.