Chapter 4

Modification of Si Nano Emitters by Diamond-clad Process

4.1. Introduction

The potential to achieve high-current devices is one of the most attractive issues of field emitters. Two important limitations of nanofabricated field emitters are their reliability and stability of individual emitter. In large part, these limitations can be traced to the inherent chemical/thermodynamic instability of clean, highly curved surfaces. Normal deposition processes, the contaminants are inevitably remained on the surface of emitters. These contaminants acting as tunnel barriers result in a larger work function and emitting instability, even leading to breakdown. Although pure Si tips have many processing and fabrication advantages [1-2], they are especially reactive chemically. A relatively unreactive coating compatible with other processing steps need to be developed to make Si tips maintain their desirable features.

The idea of using diamond and other wide band gap materials to improve filed emitters was proposed several years ago [3-4]. Diamond exhibits several unique properties such as negative electron affinity, chemical and physical stability. Furthermore, it is possible to generate SiC films on Si tips by surface reaction with gaseous hydrocarbon, rather than depositing a new layer on the emitter. However, the growth of SiC on a nanosized Si tips' surface is especially challenging due to the 20%

difference in lattice parameter between SiC and Si.

4.2. Experiment

Starting substrates were mirror-polish n-type, (100) oriented wafer with a resistivity of 4.5~5.5Ω/cm. The experimental procedure was initiated as follows. The substrates were first cleaned with organic solvents and washed with distilled water. The substrates were then dipped into a BOE solution for a few seconds to remove the native oxide about 100~200Å on the silicon and washed with distilled water. Finally, dried with nitrogen gas and placed into the CVD chamber. The chamber was then evacuated at a pressure of ~0.01 torr with a rotary pump. For synthesizing Si nanotips by hydrogen plasma etching the surface of substrate, the reactant gas hydrogen was only introduced into the chamber at a fixed flow rate of 200 sccm. The reactant gas pressure and microwave power were set at 15 torr and 300 W, respectively. The hydrogen plasma etching time lasted 15 minutes. The plasma's position was adjusted by the sliding short circuit to let the substrate was fully immersed in the plasma. Under these condition, the substrate temperature was about 700℃ measured by pyrometer.

For DLC-clad process, the reactive gases used in deposition were the conventional mixtures of CH_4-H_2 with a flow rate of 3.31/200 sccm. Normal deposition time was 1hour. During deposition, samples were subjected to a negative bias for enhancing the deposition rate.

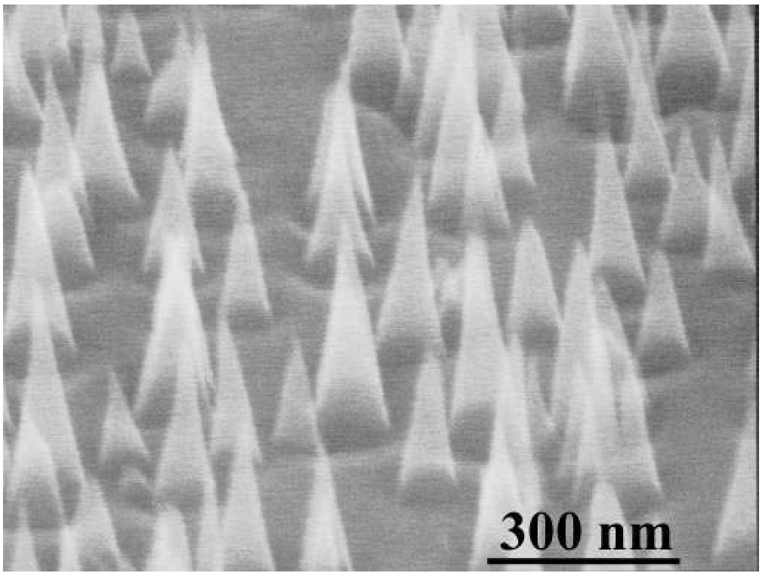
4.3. Results and Discussion

As shown in Fig. 4.1, Si tips with high aspect ratio has been realized. However, uniformity and distribution of Si tips show random tendency. This may be resulted from the non-uniformity surface of substrate on plasma ball. In addition, hydrogen plasma etching rate may vary on different position of plasma. The average diameter and height of Si tips are approximately 70 and 350 nm, respectively. It should be mentioned that the uniformity and intensity of hydrogen plasma would vary in different systems. These different parameters would lead to various diameter, height and density of Si tips. In spite of these parameters, the application of hydrogen plasma to induce Si tips is an easy method to produce high aspect ratio field emitters in many CVD systems.

Transmission electron microscope images shown in Fig. 4.2 indicate the nanostructure of Si. In Fig. 4.2 (b), it obviously displays the *d* spacing of Si (100) face equaled 0.314 nm.

Figure 4.3 shows the SEM photographs of DLC-clad Si tips with high and low magnification, respectively. The as-deposited carbons exhibit circle-shaped particles on the top of Si tips. According to SEM observation, carbon particles favor the growth on the surface of cone-shaped structures. The reason that the carbon is preferentially

(a)



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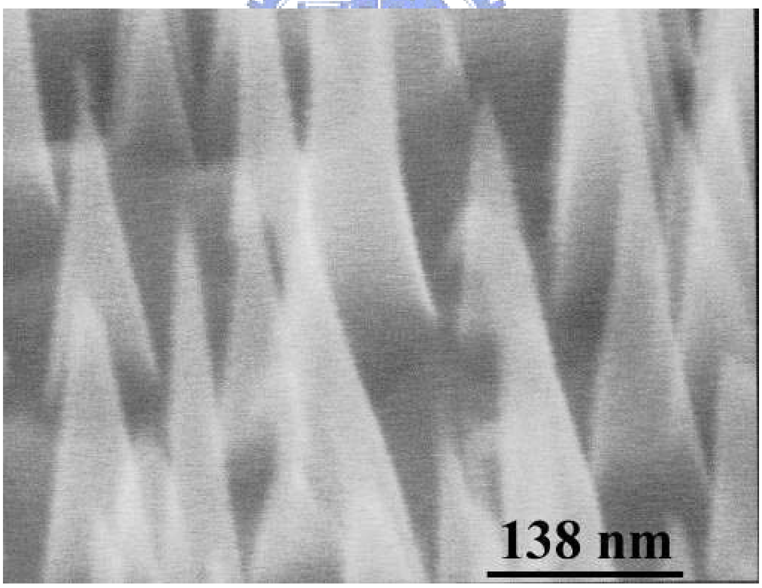
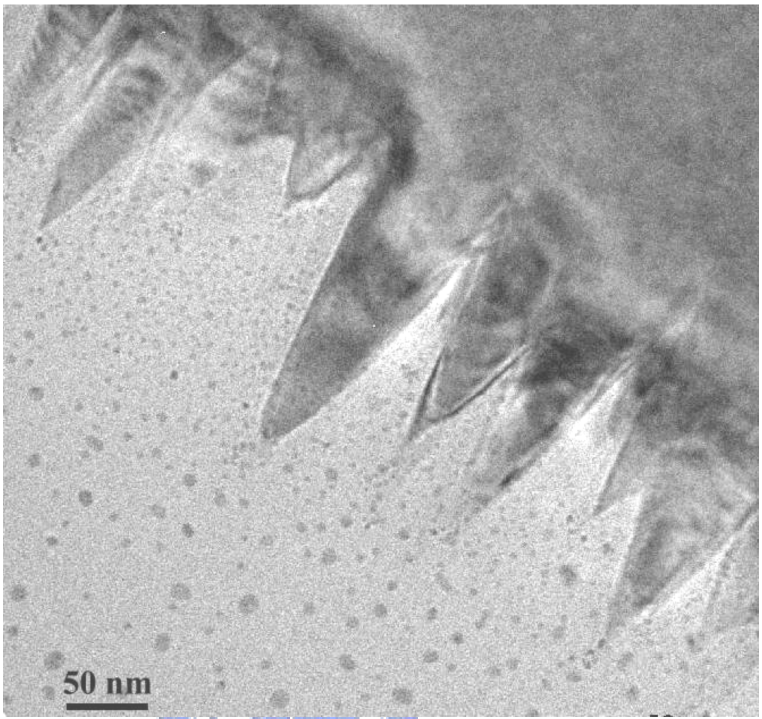


Fig. 4.1 (a) High and (b) low magnification of SEM photographs of Si nanotips

(a)



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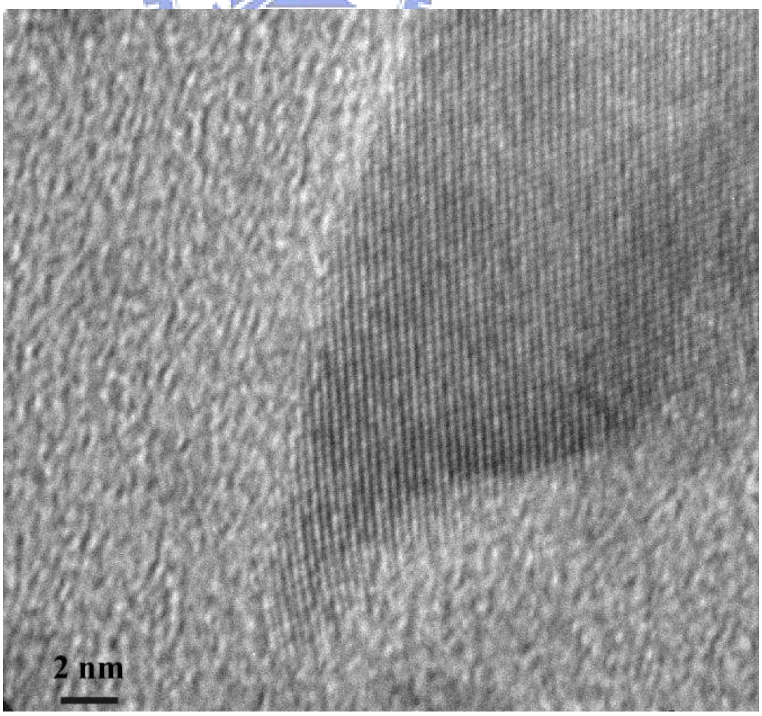
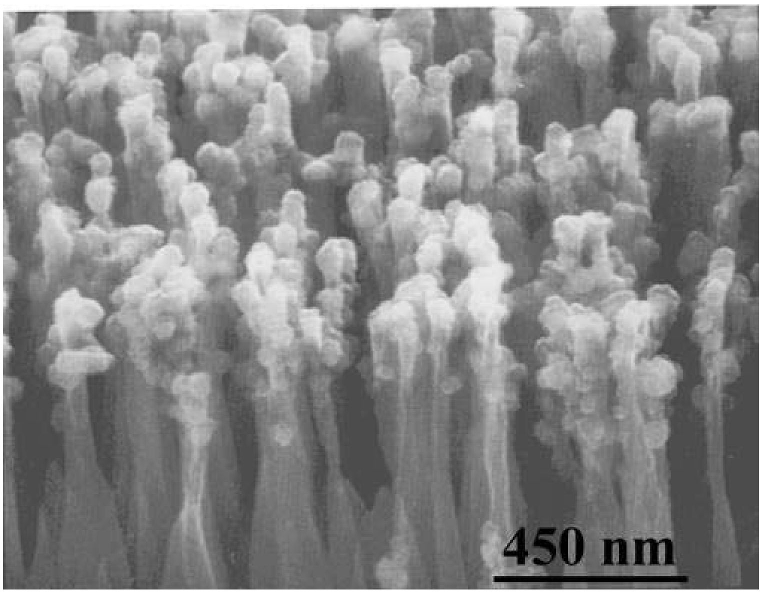


Fig. 4.2 TEM of (a) Si tips and (b) high-resolution images of individual Si tip.

(a)



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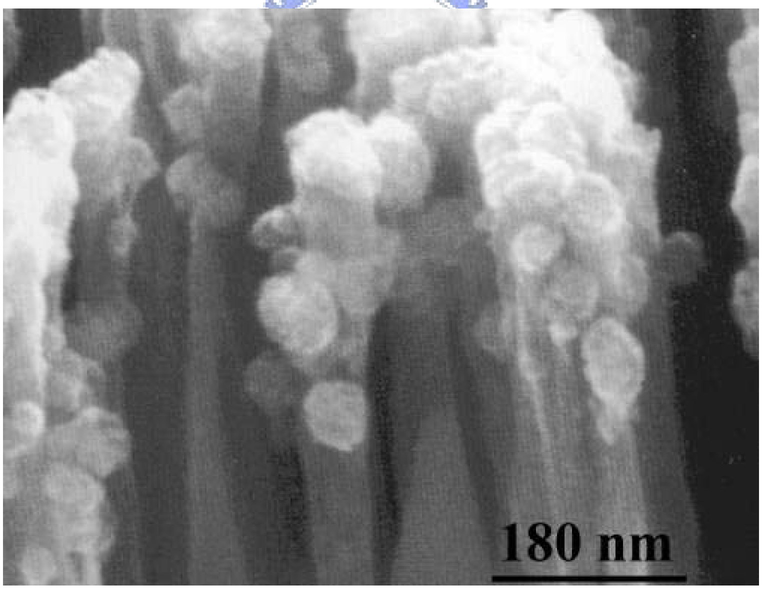


Fig. 4.3 (a) High and (b) low magnification of SEM photographs of DLC-clad Si nanotips

coated on the sharp Si tips may be attributed to the inherently higher field-enhanced effect near the sharp Si tips as a strong negative bias (-120V) is applied on the Si substrate. The high field near the tip surface leads to a higher concentration of reactive hydrocarbon radicals and carbon ions. This consists with negative bias effect on the diamond growth [5-7]. There are some advantages in applying negative bias on DLC-clad process by using MWCVD. For instance, a high vacuum environment is not required for thin film deposition; and this process is preferentially deposited on the surface of the cone-shaped structure. The diameter of tips can be reduced as a result of applying negative bias. Besides, the needle-like shaped of Si tips becomes blunt after DLC deposition. This is due to the competition between deposition and etching rate simultaneously occurred in the plasma.

Auger electron spectrum can be utilized to investigate the surface properties of the bonding structure of carbon. The value of the main transition is located at 265 eV for diamond and at 270 eV for graphite. The Auger peak for DLC is between these values. Besides, graphite and DLC have a single peak around 249 eV, while diamond has two peaks located at 255 and 246 eV [8-9]. Fig. 4.4 shows a transition located about at 270 eV, implying the film is DLC one. Fig. 4.5 illustrates the AES surface survey of silicon and carbon element. It depicts the high carbon concentration on the top of the DLC-clad Si tips, revealing the existence of C-C bonds structure.

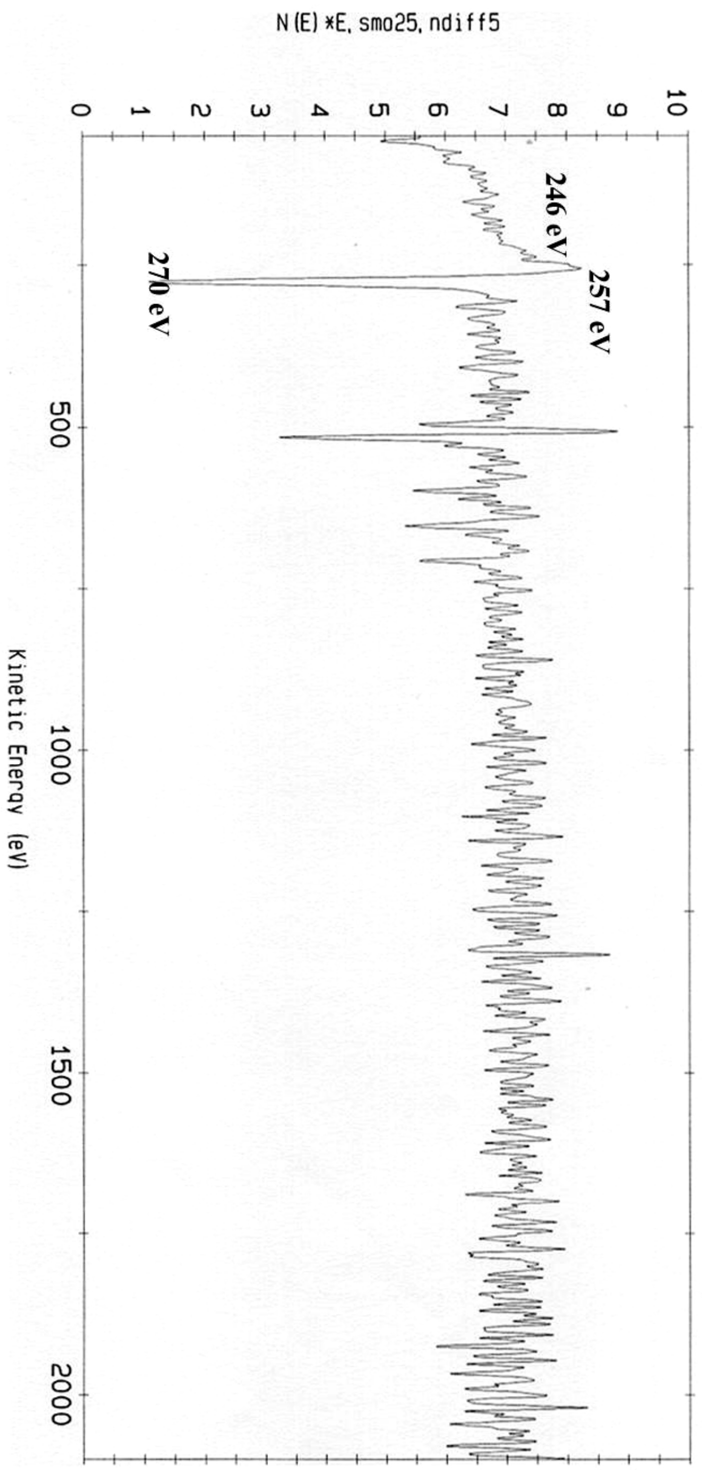


Fig. 4.4 AES profile of DLC-clad Si tips.

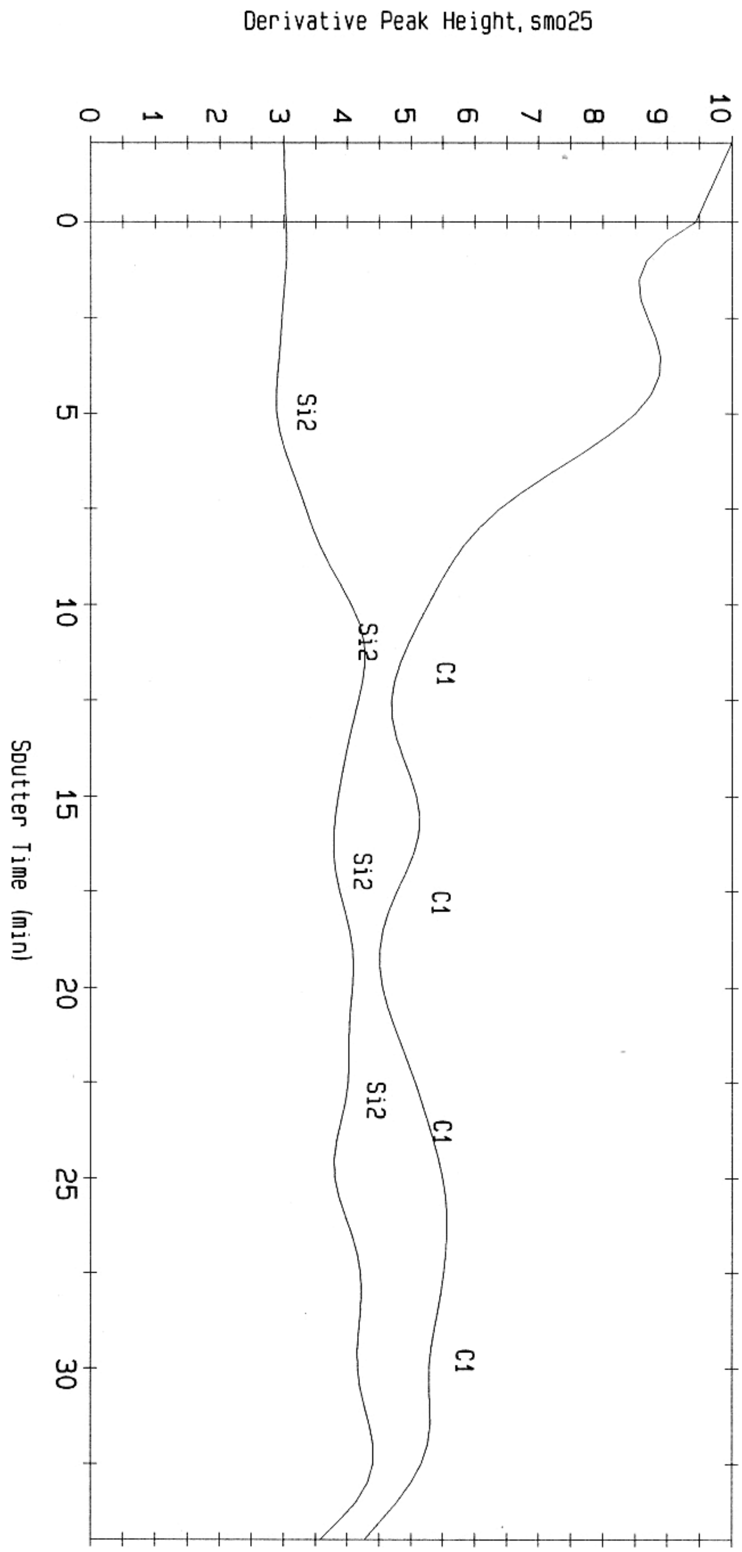
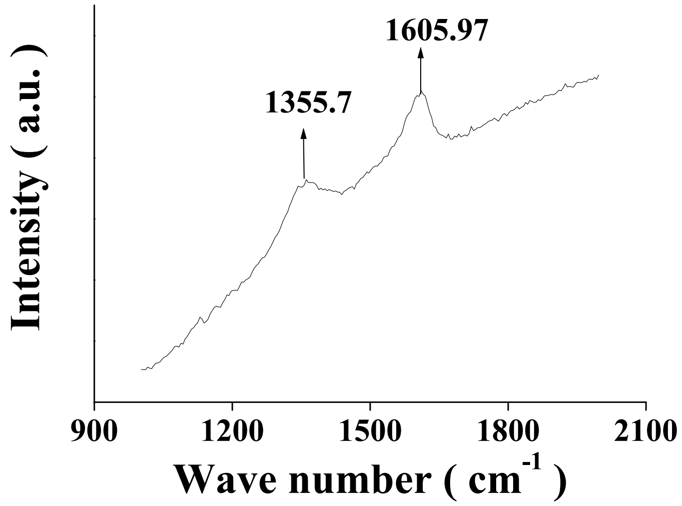


Fig. 4.5 AES surface survey of DLC-clad Si tips.

Furthermore, two single peaks at 257 and 246 eV are also found in our Auger spectrum. It is speculated that the DLC-clad Si tips maybe possess more sp^3 bonding.

Raman spectrum of amorphous-carbon indicates a broad band around 1550 cm^{-1} (G band) and a shoulder around 1360 cm^{-1} (D band) [10-12]. If the maximum peak is around 1560 cm^{-1}, it is DLC characteristic peak [13]. Beeman et al. [14] suggest that when D band shifts to lower wave number it suggests that sp^3 bonding increases. If G band, which stands for the signal of sp^2 bonding, shifts to lower wave number, it means that the properties of DLC increase. In Raman spectra, the peak of β-SiC signal located approximately 980 cm^{-1} is also found. It suggests β-SiC (1 1 1) is incorporated in the tips. However, the β-SiC signal is possible induced by the intermediate layer between substrate and tips. The intermediate layer, formed due to the chemical interactions of activated gas species with the substrate surface, may consist of diamond-like amorphous carbon (DLC, a-C, or a-C:H), metal carbides, or graphite, depending on substrate materials, pretreatment methods and deposition parameters. The AES and Raman spectrum analysis give little evidence of the existence of DLC on the top of the Si tips. Hence, it is difficult to definitely distinguish whether the presence of C-C bonds showing a carbon-rich SiC layer, or whether the a-C and/or diamond nuclei are covered by SiC which prevents their detection by AES. Despite this doubt, negative bias effect is proved to significantly enhance the growth of carbon

(a)



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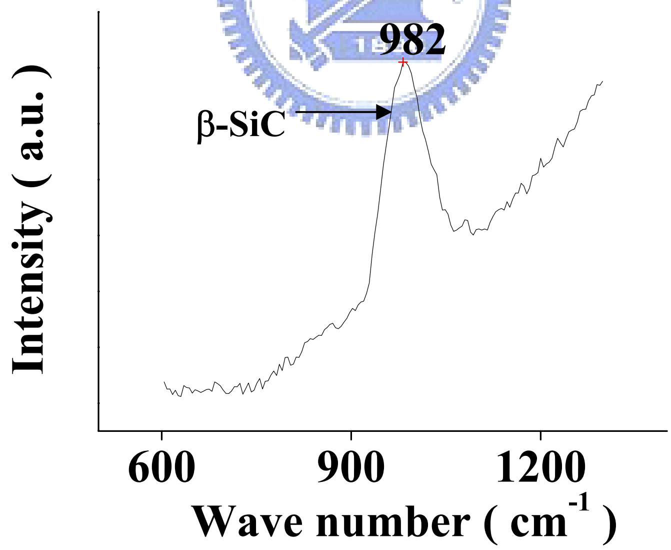

Fig. 4.6 Raman spectrum of DLC-clad Si nanotips.

materials.

The field emission tests are performed on a diode structure, in which CNTs are separated from the anode, indium-tin-oxide glass, using 500 μm glass as spacers. The emission current (I) is then measured as a function of anode-to-cathode voltage in a vacuum of 1×10^{-6} torr. A useful parameter for comparison with other field emitters is E_{to} (turn-on field), which is the field V/d (applied voltage/ distance between cathode and anode) required to produce a current of 10 $\mu A/cm^2$. The turn-on field of Si tips and DLC-clad ones are 1.44 and 1.38 V/μm, respectively. The improvement of I-V characteristic on DLC-clad Si tips are expected to be due to the negative electron affinity (NEA) property of DLC. In addition, the current density at 2 V/μm is increased from 240 to 340 $\mu A/cm^2$ of pure and DLC-clad Si tips. Obviously, DLC-clad Si tips significantly enhance the field emission property of pure Si tips. It is worth noting that the carbon nanoparticles on the tips observed in SEM images maybe also play an important role in field emission enhancement. In spite of the origin and materials of this carbon nanoparticles, which is possible coming from DLC; graphite; β-SiC and α-C, the carbon nanoparticles are thought to be increased the electron conductivity and stability under high field because of nanosize effect. Besides, carbon nanoparticles could emit electrons under high field due to possessing more emitting surfaces. How to determine the structure and effect of carbon nanoparticles is the main course in feature.

4.4. Conclusion

According to the mentioned results, the major findings are summarized as follows:

1. The application of hydrogen plasma to induce Si tips is an easy method to produce high aspect ratio field emitters in many systems.
2. The average diameter and height of needle-like Si tips are approximately 70 and 350 nm, respectively.
3. Due to the competition between deposition and etching rate simultaneously occurred in the plasma, the needle-like shaped of Si tips becomes blunt after DLC deposition.
4. Negative-bias effect is expected to enhance the growth rate of DLC during deposition.
5. Improvement on I-V characteristic of DLC-clad Si tips is due to the negative electron affinity (NEA) property and carbon nanoparticles.

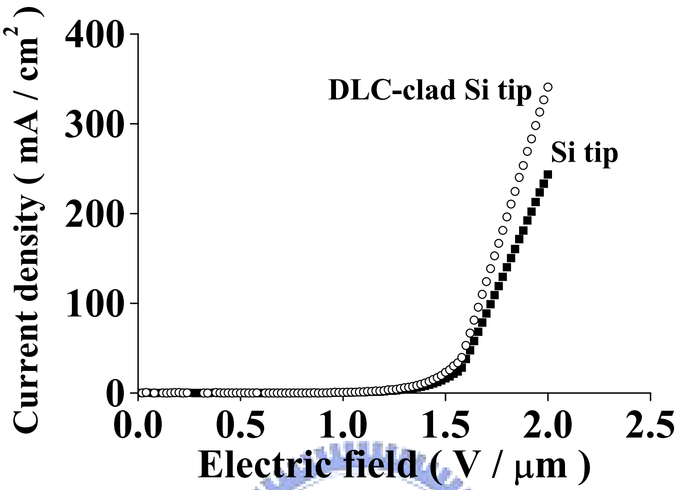

Fig. 4.7 Electric field (E) versus current density (J) of Si and DLC-clad Si tips, repsectively.

4.5 Reference

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