行政院國家科學委員會補助專題研究計畫成果報告

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※ **共價鍵材料場效發射顯示技術之研究**(III) (Study on Field Emission Display Technology of Covalent Bond Materials(II)) ※

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行政院國家科學委員會專題研究計畫成果報告

共價鍵材料場效發射顯示技術之研究(III)
(Study on Field Emission Display Technology of Covalent Bond Materials(III))
計畫編號: NSC89-2216-E009-020
執行期限:89 年 8 月 1 日至 90 年 10 月 31 日
主持人:郭正次　交通大學材料工程系

一、中文摘要

本研究整合三元 Si-C-N**，　二元** C-N, **及鑽石材料於場效發射顯示技術之應用**:

在 Si-C-N **的薄膜研究中，使用微波電漿化學氣相沉積法，使用甲烷，氫氣與氮氣為前驅物，並利用鈷矽棒環繞為試片四周作為鈷與矽源。為了得到不同基材粗度的試片使用機械拋光與化學蝕刻** ($HF-KIO_3-H_2O$) **來改變。基材前處理與觸媒應用於表面形貌，鍵結，組成，與場效發射將予以分析。奈米碳管與碳線在使用鐵鈷與鉑被觀察到。使用目前的製程，場效發射的起始電壓可低至** 1.3 V/μm **而電場在** 20 V/μm **超過了** 2000 μA/cm^2**。**

在 C-N **研究中成功的利用有機化合物取代傳統的石墨來作為合成二元** C-N **之前驅物靶材。所使用的前驅物靶材經成份分析** C/N **之比例趨近** 3/4, **經由螢光發發光譜儀的分析顯示其波鋒位於** 418.2nm**，為藍光發光材料。**

在鑽石的薄膜研究中, **準直性與具方向性與高高寬比的奈米針成功的製作於三極的場效發射陣列。奈米針快速的成核於** 4μm **無外加觸媒的矽晶片。此外，擇區沉積的奈米針亦成功的沉積在有外加鉑的情況下於外加偏壓下。場效發射的電流為** 154 μA. **此項結果歸諸於**(I) **短閘極到針尖的距離**(II) **小的閘極孔徑與**(III) **高的高寬比的奈米針。**

關鍵字：矽碳氮、碳氮、 鑽石、場效發射

Abstract

This work integrates the novel material of Si-C-N, C-N and diamond for field emission materials application. With regard to the study of Si-C-N films, the Si-C-N films were synthesized on Si substrates by a microwave plasma chemical vapor deposition (MPCVD) system with CH_4, H_2 and N_2 as the source gases. Metal coating on Si columns were placed around the specimen and acted as catalyst and additional source of Si. Some of the Si substrates were mechanically polished or chemically etched with $HF-KIO_3-H_2O$ solutions to obtain different surface roughness before film depositions. Effects of the substrate pretreatment and the action of catalysts on surface morphologies, compositions, band structure, field emission of the films were examined. Nanotubes or nanowires structures were found for films deposited on no-treatment substrate using Fe,Co and Pt catalysts. Under the present deposition conditions and by using Fe catalyst, the lowest turn-on voltage of the films can be as low as 1.3 V/μm, while the corresponding emission current density at field strength of 20 V/μm can go beyond 2000 μA/cm^2.

With regard to the study of C-N films, to reduce the activation energy barrier for the formation of carbon nitride during ion beam sputtering, a novel material, instead of the conventional graphite target, is attempted to deposit the crystalline carbon nitride film. The melamine target consists of a high N/C ratio as well as a 6-fold carbonitro-ring structure similar to that in the hypothetical C_3N_4. White the deposited films via melamine targets have the highest N/C ratio of 1.57, these film retain the bonding characters and crystal structure of melamine. However, a blue light emission at 418.2 nm is observed on the CL spectrum of the deposited film via melamine targets. An obvious red light shift occurs in the deposited film after Ar ion bombardment of melamine targets.

With regard to the study of diamond film, the vertically well-aligned, high aspect ratio carbon nano-tips have been directly grown upward on the triode-type field emission arrays (FEAs).

The nano-tips rapidly nucleate and grow on a 4μm patterned silicon substrate without any catalyst. In addition, selected area deposition (SAD) of nano-tips was successfully achieved by using the Pt layer as inhibitor in the bias assisted microwave plasma chemical vapor deposition (BAMPCVD). The field emission current of nano tips on FEAs is 154 μA. This is resulted from the following reasons. (I) short gate-tips spacing, (II) small gate aperture and (III) the high aspect ratio of nano-tips.

keyword：Si-C-N、C-N、Diamond、Field emission

2.Experimental details

The Si-C-N films were deposited on Si wafer using a microwave plasma chemical vapor deposition (MPCVD) system. Table 1 lists detailed parameters of each sample. In addition to the Si in the wafer itself, the additional Si sources of Si columns were inserted into the specimen holder around the specimen in symmetrical positions (sample 1, 2 and 9). Metal films of Fe, Co and Pt were coated by physical vapor deposition (PVD) method on one side of the Si columns to act as catalysts (sample 3 to 8). Before film deposition, all substrates were cleaned with a few solvents, and some of the substrates were chemically etched in an HF-KIO_3-H_2O solution using magnetic stirring. One substrate was mechanically polished for comparison. The film deposition conditions were microwave power of 800 watt, deposition pressure of 12 Torr and flow ratio of $CH_4/N_2/H_2$ = 10/100/50 sccm/sccm/sccm. The deposition was carried out at temperature ranging from 1000 ~ 1200℃ and it took 4 hours.

According to diamond tip synthesis, at the beginning, the fabrication of the Pt-gated triode-type field emission arrays (FEAs) with 50X50 circles was made by semiconductor process technology. The width and the depth of each circle are 4μm and 7000Å, respectively. After fabricating the triode-type diode, specimens were put in the bias assisted microwave plasma chemical vapor deposition (BAMPCVD) system to deposit carbon nano-tips. The reactive gases used in deposition were the mixtures of CH_4-CO_2. The flow rates of CH_4/CO_2 and deposition time remained constant at 30/30 sccm and 15 minutes, respectively. While processing the deposition, the specimen was subjected to a negative bias voltage.

3. Results and Discussion

The field emission properties of the Si-C-N films fabricated using different process conditions are listed in Table 1. The emission current densities at applied electric field of 20 V/μm have been measured. The turn-on electric field is defined as the electric field required for the emission current density to reach 2 $\mu A/cm^2$, i.e., emission current = 1 μA under the anode area = 0.5 cm^2.

For the turn-on voltage, the films of samples 2 and 7 show the highest values (>10.6 V/μm). This is in agreement with the morphological features of blunt facets in Fig. 2 and preferred orientation in Fig. 6. The lowest turn-on voltages (< 2.1 V/μm) are found with the nanotube morphologies of Samples 3 and 5, where the effective emitting area and the field enhancement factor are much larger, and the corresponding current densities are the highest and beyond our measurement range. The higher emission current density may also relate to higher carbon content in the nanotubes or nanowires.

According to diamond tip results, Fig. 1 shows SEM photographs of carbon nano-tips grown under different bias. Each picture is only one of the 50 x 50 circles on the FEAs. Every picture in the right side is an enlarged image of the left one. The SEM images indicate that carbon nano-tips can be uniformly grown only inside the Pt-gated FEAs without the presence of amorphous carbon (a-C) on the Pt-gated surface. The selective area deposition of nano-tips is attributed to the following two reasons. First, it is easier to grow carbon materials on silicon than the Pt-gated layer because Pt is a highly chemically inert material that does not nucleate carbon materials on an unscratched Pt surface [5,6]. Second, the bias current concentrated on the silicon substrate surface occurs because the n-type silicon conducts electrons, but electrons can not pass through silicon dioxide (dielectric layer) within a Pt-gated layer. Therefore, the local deposition biased effects are all within the silicon substrate. However, increasing the

deposition time will cause some a-C on the Pt-gated surface.

Observing Fig. 1(a) ~ (c), the applied bias could enhance the growth of carbon nano-tips in CH_4/CO_2 gas mixtures. These imply that the higher bias drastically enhances the growth of carbon nano-tips. The bias-assisted effect is also valid for the hydrocarbon diluted in hydrogen [7]. However, samples grown under bias over 130V will cause the height of the tips to exceed the Pt-gate. In this situation, the triode-type FEAs becomes the diode structure. By contrast, bias below 130V only leads to tiny tips inside the hole. In addition, all the tips grow upward under bias condition. We also find that the tip angle of the nano-tips decreases with increasing bias. In other words, under higher bias will generate high density and sharper as well as high aspect ratio nano-tips. Compared with conventional gas mixtures (hydrocarbons diluted in hydrogen, e.g. CH_4/H_2), using CH_4/CO_2 can promote the growth rate [8]. This is due to the nano-tips grown with a high carbon concentration gas source in the CH_4/CO_2 gas mixtures.

Fig. 2 (a) displays the TEM images of an end section of an individual nano-tip. The main feature of note is the tip has a somewhat irregular shape, with one primary protrusion. The Fourier filtering transformation (FFT) indicates the end section is amorphous carbon. Moreover, Fig. 2 (b) displays the lateral section of the same tip. It shows microcrystalline graphite on the lateral section. The FFT of Fig 2 (b) also proves the existence of the microcrystalline graphite.

Fig. 3 is Raman spectra of tips grown under applied various biases. We find there is no obvious difference among these spectra. All of them have two sharp peaks located on about 1355 cm^{-1} and 1582 cm^{-1}, respectively. These imply that the nano-tips are characteristic of microcrystalline graphite. The Raman spectra of amorphous carbon can be decomposed into two features located approximately at 1550cm^{-1} (corresponding to the G-line associated with the optically allowed E_{2g} zone center mode of crystalline graphite) and 1350 cm^{-1} (roughly corresponding to the D-line associated with disorder-allowed zone-edge modes of graphite). The positions, widths, and relative intensities of these two peaks are found to vary systematically with deposition conditions and tips' properties [9, 10]. The intensity of these two peaks are the same. This indicates that there is much amount of amorphous carbon in the samples.

Fig. 4 displays the electron-emitting characteristic of the nano-tips on FEAs. The field emission properties of the FEAs are measured by using a triode technique. An anode plate, an ITO Glass, is placed at 100 μm above the Pt gate and is biased to +800 V. The anode current (I_A) is then measured as a function of gate-to-cathode bias voltage in a vacuum of 1×10^{-6} Torr. The gate-to-cathode voltage (Vgc) is biased from 0 to 50 V. The field emission current (I_a) of nano-tips on FEAs is about 154 μA (at gate-to -cathode voltage ,V_{gc}= 50V). Therefore, the higher emission current of the nano-tips on FEAs is resulted from the following reasons. (I) short gate-tips spacing, (II) small gate aperture, and (III) the high aspect ratio of nano-tips.

4. Conclusions

S-C-N film and diamond tip have been successfully synthesized and demonstrated high emission current and low turn on voltage. Suitable catalysts applications such as Fe, Co and Pt also indicate can adjust SiCN film structures, properties. In additions, elected area deposition (SAD) of nano-tips was successfully achieved by using the Pt layer as inhibitor in the bias assisted microwave plasma chemical vapor deposition (BAMPCVD).

5. References

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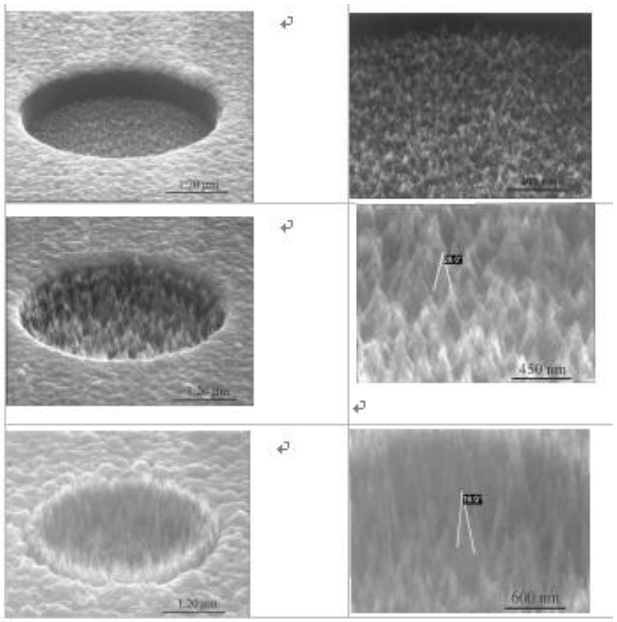

Fig. 1 SEM photographs of nano-tips grown under (a) 100V, (b) 130V and (c) 150V

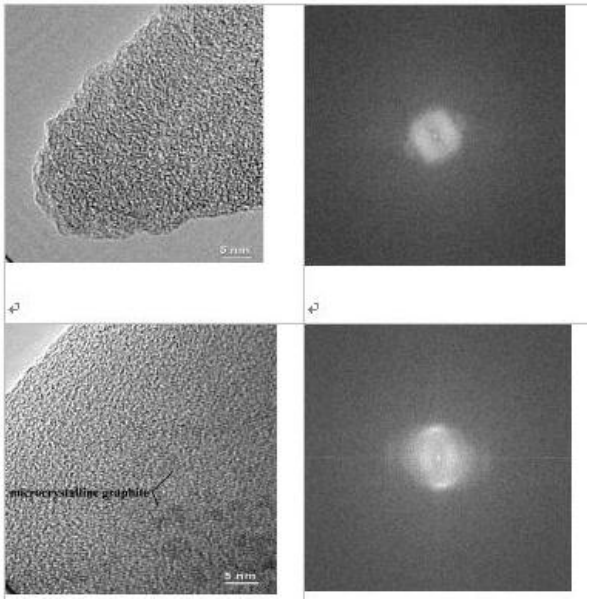

Fig. 2 TEM images of (a) the end section and (b) lateral section of an individual tip

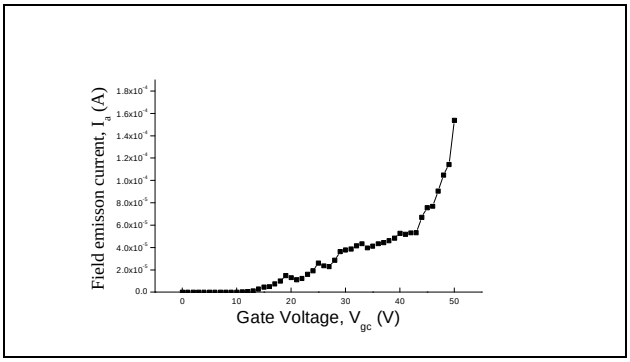

Fig. 4 The emission current (I_a) versus the gate voltage (V_{gc}) of nano-tips on FEAs

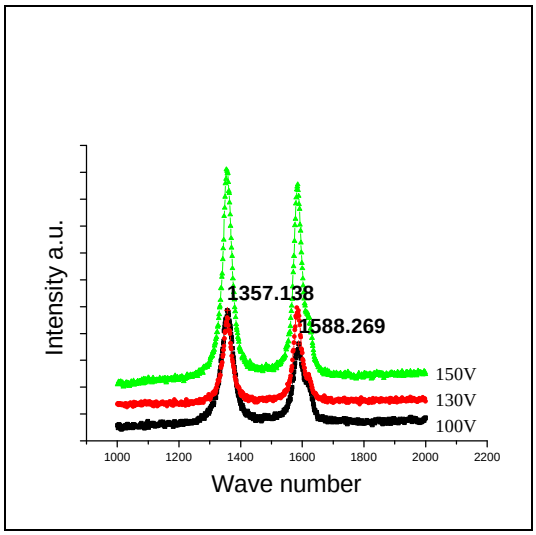

Fig. 3 Raman spectra of nano-tips growing under different applied bias