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# Emission current influence of gated structure and diamond emitter morphologies in triode-type field emission arrays

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#### Abstract

Field emission display is evolving as a promising technique for the future generation of flat panel displays. Characteristics affecting the power of field emitter arrays include the shape and work function of emission materials, distance between tip and gate, and the environmental vacuum condition.

In this work, we present a novel scheme that involves a new fabrication process of gate structure metal-insulator-semiconductor (MIS) diode using IC technology. Deposition of the diamond film in this MIS diode forms a column-like diamond with gated field emission arrays (FEAs). This process is completed using a bias-assisted microwave plasma chemical vapor deposition system.

Our results indicate that the threshold voltage of column-like diamond FEAs is about 10 V, and the field emission current density is about 139 mA cm<sup>-2</sup> (at  $V_{\rm gc}$ =20 V). The diamond field emitter array devices with the new gate structure and tip morphology significantly influence the electron field emission characteristics. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Emission current; Field emission arrays; Flat panel displays

### 1. Introduction

Field emission devices (FEDs) with a high emission current density have been developed in metal tip [1] and silicon tip arrays [2]. Having great potential as electron emitters in flat panel displays, the devices have attracted much attention. However, the electrical field required to trigger field emission is rather high and the FED's performance declines rapidly as a result of thermal effects, resulting in serious contamination of, and damage to, the emission material.

Diamond films possess negative electron affinity, and useful properties such as high electron mobility  $(2.2 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ , high thermal conductivity  $(20 \text{ W cm}^{-1} {}^{\circ}\text{C}^{-1})$  at room temperature, high breakdown threshold voltage  $(10^7 \text{ V cm}^{-1})$ , and chemical inertness. It also exhibits a rather high field electron velocity  $(2.7 \times 10^7 \text{ cm s}^{-1})$  which increases the maximum emission current that can be attained before saturation.

Therefore, diamond films are considered to be very useful in electron FEDs and their related emission properties have been widely investigated [3–5]. Accordingly, this work fabricates field emission array (FEA) devices in diamond by bias-assisted microwave

\* Corresponding author. Fax: +886-3-5723811. E-mail address: cfchen@cc.nctu.edu.tw (Chia-Fu Chen) plasma chemical vapor deposition, in which the process is successfully completed.

#### 2. Experimental

Fig. 1 illustrates the detailed process sequence for forming of a triode diamond tip array with a Pt gate. First, we designed the metal–insulator–semiconductor (MIS) diode structure and fabricated the MIS diode using semiconductor process technologies. Starting substrates were mirror-polished n-type, (100)-oriented wafers with a resistivity of 4–6  $\Omega$  cm. The silicone wafer was first cleaned by an RCA cleaning process. It was then covered with FH-6400 positive photoresist, using a spin coater. Next, a set of arrays of circle-shaped patterns was UV exposed and developed in the resist layer.

After formation of photoresist patterns, an RIE system (model Samco RIE-10, Japan) was used to etch the silicon layer at a depth of 300 nm. When the RIE system produced a hole with a depth of 300 nm depth, a dual e-gun evaporator (model ULVAC EBX-10C, Japan) deposited silicon dioxide (SiO<sub>2</sub>) to a thickness of 500 nm. Next, the adhesion between the Pt layer and the SiO<sub>2</sub> layer was increased by sequential deposition of the Ti (titanium) and Pt (platinum) layers, with thick-

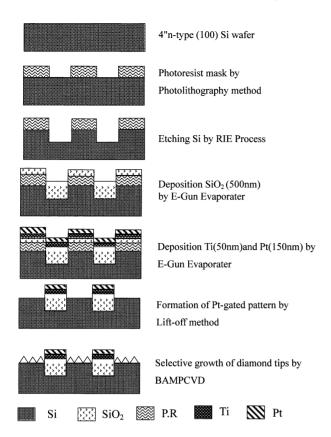


Fig. 1. Fabrication procedure of a triode diamond tip array.

nesses of 50 and 150 nm, respectively, as gated layers using the evaporator. After the gated layers (Ti and Pt) were formed, the photoresist mask was removed with an acetone solution in an ultrasonic agitator. The Pt-gated circles, have diameters of 4  $\mu$ m, were formed by a lift-off process. The sample was then placed into the chamber of the bias-assisted microwave plasma chemical vapor deposition (BAMPCVD) system to obtain the diamond tips. The BAMPCVD chamber was then evacuated to a pressure of  $\sim 0.01$  Torr with a

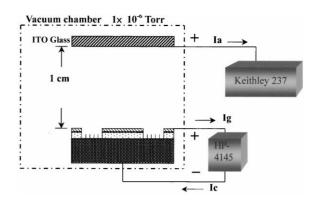


Fig. 2. The scheme of the instrument for the I-V measurement.

rotary pump. Initially, the reactant gas, hydrogen, was introduced into the chamber at a rate of 200 sccm to clean the substrate by the following hydrogen plasma. The reactant gas pressure was set at 15 Torr. Microwaves were introduced at a power of 300 W and, in doing so, a bright plasma was obtained. Next, a negative bias voltages of 80, 120 or 170 V was applied. Under these conditions, a substrate temperature of 650–680°C was obtained. At this stage, the reactive gases were introduced into the system. The reactive gases used in deposition were the conventional mixture of CH<sub>4</sub> and H<sub>2</sub>.

All the experiments involving the diamond deposition used two-step depositions. The flow rate CH<sub>4</sub>/H<sub>2</sub> and the deposition time of the first step remained constant at 10/200 sccm and 30 min, respectively. Deposition typically lasted for 30-60 min. Table 1 summarizes the experimental conditions. Scanning electron microscopy (SEM) was used to observe the morphology of columnlike diamond FEAs with a gated structure. A Hitachi S-4000 scanning electron microscope was used in our experiments. The column-like diamond was qualitatively analyzed laser micro-Raman spectroscopy bv (Renishaw, Model 2000). Auger electron spectroscopy (AES) was used to identify the surface compositions of

Table 1 Diamond deposition conditions

	Negative bias voltage (V)	Deposition time (min)	Flow rate of CH <sub>4</sub> /H <sub>2</sub> (sccm)	Operating pressure (Torr)	Microwave power (W)	Substrate temperature (°C)
First step conditions						
A	80					
В	120					
C	170	30	10/200	15	300	~660
D	120					
E	120					
Second step conditions						
A	80		2/200			
В	120		2/200			
C	170	30	2/200	15	300	670-680
D	120		1.4/200			
E	120		4/200			

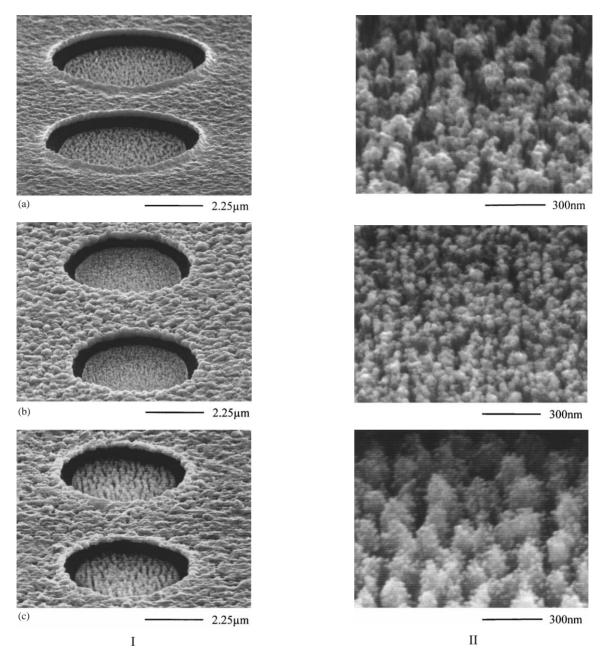


Fig. 3. (a) SEM photographs of triode diamond FEAs grown under conditions A at different magnitudes: (I) 8K; (II) 60K. (b) SEM photographs of triode diamond FEAs grown under condition B at different magnitudes: (I) 8K; (II) 60K. (c) SEM photographs of triode diamond FEAs grown under conditions C at different magnitudes: (I) 8K; (II) 60K.

the column-like diamond. Fig. 2 presents the field emission properties of the column-like diamond FEAs with a gated structure. These properties were measured using a triode technique. An anode plate (ITO Glass, MBC 6R1697) was placed 1 cm above the Pt gate and was biased to  $+1000 \, \text{V}$ . The anode current ( $I_a$ ) was then measured as a function of the gate-to-cathode bias voltage in a vacuum of  $1 \times 10^{-6} \, \text{Torr}$  using a Keithley SMU 237. Next, the gate-to-cathode voltage ( $V_{gc}$ ) was biased from 0 to 30 V using a HP-4145 system. During testing, the device was in a common emitter configuration with the grounded emitter. The anode and gate

were maintained at positive potentials to allow the device to be turned on.

## 3. Results and discussion

A previous investigation has indicated that, when the carbon active species in the plasma were accelerated to the silicon substrate by the high negative voltage to form sp<sup>2</sup>, non-crystalline clusters, some clusters transformed into sp<sup>3</sup> clusters through the collision of carbon species and subsequently formed diamond nuclei sites

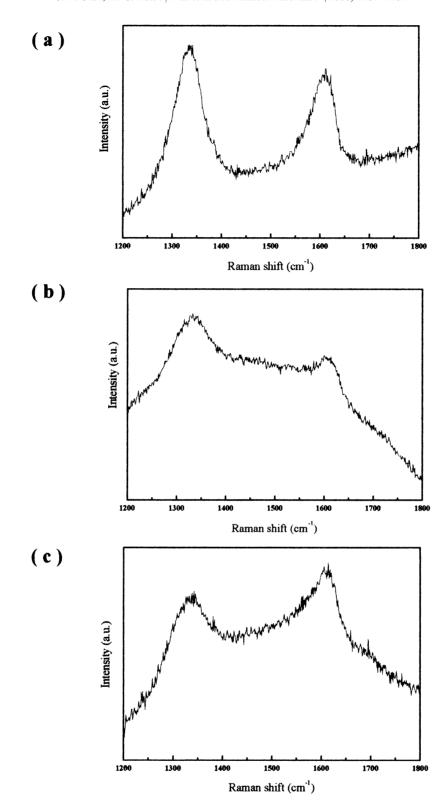


Fig. 4. Raman spectra of samples grown at different methane concentrations in the second step: (a) condition D, 0.7 vol.%; (b) condition B, 1 vol.%; (c) condition E, 2 vol.%.

[6]. The other sp<sup>2</sup> clusters could be found near these diamond nuclei sites, which have lower activation energy than other sites. Therefore, the active hydrogen radicals

in plasma were accelerated to the silicon substrate by the bias voltage to remove the lower energy sp<sup>2</sup> clusters and reserve the higher energy diamond nuclei sites. During this process, etching and deposition compete with each other for the diamond in favor of deposition, while sp<sup>2</sup> non-crystalline clusters are still being etched [7]. Besides, early growth on the Pt-gated surface underwent the following etching of surface graphite and formation of an adsorbed hydrocarbon deposit. Furthermore, removal of surface graphitic carbons goes essentially to completion without the nucleation or growth of a diamond on the Pt-gated surface [8].

Fig. 3 presents SEM photographs of the column-like diamond FEAs with a Pt-gated diode structure using 80, 120 and 170 V negative bias voltage, respectively. The diamonds' density, size and irregularity of shape increase with the bias absolute voltage. Also, biasenhanced nucleation and the plasma etching effect can be observed [9]. Moreover, the column-like feature is more obvious with an increased bias.

Fig. 4 displays the micro-Raman spectra for the column-shaped diamond on the Pt-gated FEAs: D, B and E deposition conditions grown at different methane concentrations in the second step of the deposition process. Both the significant peaks at 1332 and 1580 cm<sup>-1</sup> appeared in the Raman spectrum. Therefore, the full width at half-maximum (FWHM) of the diamond peak (near 1332 cm<sup>-1</sup>) increased with an increasing CH<sub>4</sub> concentration. This result is characteristic of an amorphous carbon phase with sp<sup>2</sup> bonds.

The AES fine structure taken from the conditions D, B, and E in Fig. 5 reveals the peak region of the intensity profile of the C KLL peak, indicating that the carbide is formed during the diamond deposition with a negative bias. Notably, low-energy shoulders around 258–260 eV (peak a) and 248–250 eV (peak b) appear in the spectra of the column-shaped diamond under conditions B and D. Their appearance suggests that the surface structure is a diamond structure with a few graphite, amorphous carbon and/or other defects [10]. However, AES spectra of the sample deposited under condition E exhibit no obvious peak a, implying a diamond-like carbon composition including a large amount of graphite, amorphous carbon and/or other defects.

CVD diamond and diamond-like carbon films show stable electron emission in a low field. Nevertheless, the nature of electron emission from these materials is still unclear. Related approaches have attempted to explain the ultralow emission fields: negative electron affinity effects available for diamond surfaces including n-doping and defect levels in the diamond band gap; hot electron transport in interfaced structures; grain boundary effects; and the effect of geometric field enhancement by morphology protrusions or narrow, conductive grain boundaries between insulating grains [11]. The field emission currents do not differ markedly from each other with respect to the change of methane contents for the second step of the diamond deposition process in column-like diamond FEAs. Fig. 6 shows the electron emitting characteristics of the column-like dia-

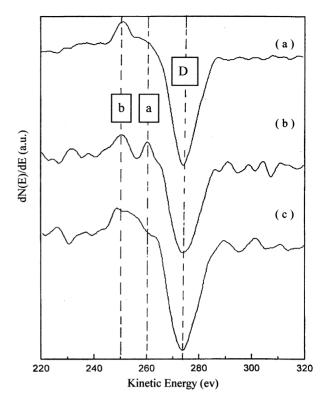


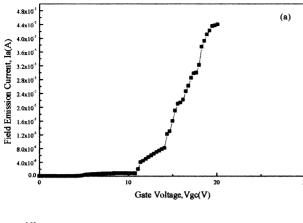
Fig. 5. The AES spectra of samples grown at different methane concentrations in the second step: (a) condition D, 0.7 vol.%; (b) condition B, 1 vol.%; (c) condition E, 2 vol.%.

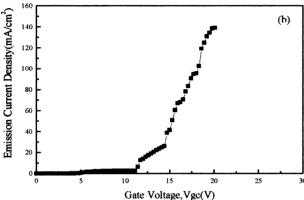
mond FEAs. The field emission current  $(I_a)$  of column-like diamond FEAs (condition B in Table 1) is about 44  $\mu$ A (at gate-to-cathode voltage,  $V_{\rm gc} = 20$  V), the emission current density  $(J_{\rm e})$  of column-like diamond FEAs is 139 mA cm<sup>-2</sup>. Therefore, the higher emission current density in the column-like diamond FEAs accounts for the gate structure (short gate-tip spacing and small gate aperture) or the diamond morphology. The threshold voltage  $(V_{\rm th})$  is defined as the intersection of the F-N plots with the abscissa. The threshold voltages  $(V_{\rm th})$  were around 10 V for column-like diamond FEAs.

Owing to the smaller gate aperture diameter and shallower gate aperture, a field emission current can be triggered at a lower threshold voltage. However, a saturated current occurs at  $V_{\rm gc} = 20~{\rm V}$  in column-like diamond FEAs. This current is attributed to the fact that the SiO<sub>2</sub> layer of the FEAs pattern is probably broken when the FEAs pattern in the BAMPCVD diamond process, thus increasing the leakage current from the SiO<sub>2</sub> layer. Therefore, the emission current decreases for the column-like diamond FEAs, when the SiO<sub>2</sub> layer has been broken during the BAMPCVD diamond process, particularly if the bias exceeds 120 V.

#### 4. Conclusion

In this work we fabricated a new structure MIS diode to triode diamond FEAs for decreasing the turn-on





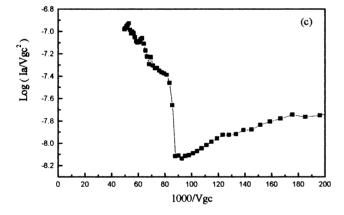


Fig. 6. The electron emitting characteristics of the column-like diamond FEAs (condition B in Table 1). (a) The field emission current  $(I_a)$  of column-like diamond FEAs; (b) the emission current density  $(J_e)$  of column-like diamond FEAs; (c) the threshold voltages  $(V_{th})$  of column-like diamond FEAs.

voltage and enhancing the emission current density. Results presented herein can be summarized as follows.

- The proposed scheme involving a new fabrication process of triode diamond FEAs is feasible. The new MIS diode has a small gate aperture and shallow field emission cells.
- 2. Selective area deposition (SAD) of diamond within

- the silicon substrates was successfully achieved using a patterned Pt-gated layer as a nucleation inhibitor in the new structure MIS diode. A diamond tip with a new column-like shape was obtained. Many particle-caps were placed on the top of the tip, using the BAMPCVD system. SAD column-like triode diamond FEAs possess field emission properties appropriate for application as electron emitters in a flat panel display.
- 3. Characterizing the electrical properties of the column-like triode diamond FEAs with a new gated structure reveals that the field emission current density is about 139 mA cm<sup>-2</sup>; the threshold voltage is about 10 V and lower than that of the metal tip. The results follow from the effect of a gate aperture, the distance between a diamond tip, and the tip morphology.
- 4. The field emission current of the column-like triode diamond FEAs might become higher when the diamond deposition bias is higher so that a bulkier diamond tip can be obtained. Future work must solve the problem of the quality of the SiO<sub>2</sub> in our new MIS diode process. Therefore, the SiO<sub>2</sub> can resist the high field in the BAMPCVD diamond process.

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