行政院國家科學委員會專題研究計畫成果報告

Study on Low-Work-Function Materials and Processess for Field Emission Devices

場發射元件用之低工作函數之材料及製程研究

計畫編號：NSC 87-2215-E-009-052

執行期限：86 年 8 月 1 日至 87 年 7 月 30 日

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中文摘要:

近年來,由於場發射顯示器(Field Emission Display)的優越性能與快速發展，使得更多的研究人員進入真空微電子的領域。其中，降低元件的操作電壓與提高可靠度是場發射顯示器技術最重要之課題。最有效的方式之一是採用具有較低工作函數且性質穩定的材料來製作場發射元件。而鑽石(111)或(100)面特有的負電子親和力與其極穩定之物理與化學特性，使其成為最佳的場發射陰極材料。因此，為了增進場發射冷陰極低電壓場發射的能力與穩定性，我們利用微波電漿化學氣相沉積法(MPCVD)，來合成不同的鑽石或類鑽膜，並將其塗佈在矽尖錐場發射陣列上，以比較不同結構鑽石場發射陰極之性能。此外，並建立反應氣體甲烷/二氧化碳(CH_4/CO_2) 的流量比與場發射電流特性之關連性，進而求得最佳化的沉積條件。

Abstract:

Field emission display (FED) has recently attracted more attention because of their superior performance and rapid progress. The key point of field emission display is the fabrication of low-voltage operated and highly reliable cold cathode. These requirements can be implemented using lower work function and highly reliable emitter materials. Hence, diamond has been considered as the most appropriate and promising emitter material for field emission devices due to the presence of a negative electron affinity (NEA) provided by diamond {111} or {100} planes, and simultaneously has the most stable physical and chemical properties. In order to further enhance the low-voltage field emission capability and stability of field emitter arrays, various diamond and diamond-like films have been synthesized and coated on the sharp Si tips using microwave plasma chemical vapor deposition (MPCVD) to investigate the field emission characteristics. Correlation of diamond films deposited under various flow rate ratio of CH_4/CO_2 is also studied to optimize the deposition conditions.

KEYWORDS: field-emission array, diamond-clad, DLC, low workfunction, flat-panel display

INTRODUCTION

Although microsized field emitter arrays (FEAs) fabricated with advanced micromachining technology has been intensively progressed as the promising electron sources for vacuum microelectronic devices, there has still been no "superior" material discovered desirable for such emitters. in order to achieve low voltage and high efficiency for cold cathode operation, the surface work function of a field emitter should be made as small as possible. In addition, emission stability is also a very important issue in practical applications. However, the drawbacks of high work function, low electron conductivity, and poor stability for practical application of the Si micro-tip emitters are needed to be improved. Recently, there has been an increasing interest in the application of CVD diamond films as the material of electron emitters or cold cathodes due to the unique electronical properties of diamond, for example, the so-called "negative electron affinity" (NEA) on the hydrogen-terminated {111} planes [1], the outstanding chemical inertness and stability as well as the highest thermal conductivity [2]. Fabrication of low-field diamond field emitter arrays has also been attemped [3]-[5], and a diode-structured prototype field emission display based on a diamond-like carbon has been demonstrated [6].

Our study pointed out that an uniform polycrystalline diamond films coated on Si tips by microwave plasma chemical vapor deposition (MPCVD) exhibited better emission characteristics than those coated on plain Si substrate.

EXPERIMENTAL

An 1-μm-thick oxide layer was thermally

grown and was then photo-lithographically patterned to form arrays of 50×50 circular discs 3 μm in diameter. The patterns of photoresist were then transferred into underlying oxide using dry etching. Employing the previously patterned oxide layer as the mask, cone-shaped Si microtip arrays were subsequently formed using SF_6/Cl_2 reactive ion etching. An oxidation-and-stripping process was used to further sharpen the etched tip. The as-fabricated sharply curved Si microtip surfaces were first cleaned employing H_2 plasma pretreatment and carbon films were then deposited on the Si tips by microwave plasma chemical vapor deposition with CH_4-CO_2 gas mixtures. Carbon films in different phases were obtained by varying the flow rate ratios of CH_4/CO_2 from 18/30 to 40/30. The microwave power was set at 450 W, and the reaction time was 2 h at 850 °C. The chamber pressure was kept at 25 Torr. In order to grow continuous diamond films, some Si substrates were scratched using diamond powders (particle size, 0.1 μm) before the deposition process exception for deposition conditions under CH_4/CO_2 gas mixtures of 30/30 and 40/30. The experimental conditions are listed in Table I.

RESULTS and DISCUSSION

The silicon microtips with tip radius about 200 Å were used to be a coating precursor. Figures. 1 (a)-(e) exhibit the surface morphologies of carbon films coated Si microtips with the deposition conditions A-E listed in Table I. It can be seen that the higher flow rate ratios of CH_4/CO_2, the smaller grains and the smoother surface morphologies of carbon films are deposited. Exception for Si tips coated under condition A, other ones that coated under conditions B-E exhibit proper deposition uniformity, as can be seen from Figs. 1. Moreover, the deposition rate increases with the increasing CH_4 concentration in the CH_4-CO_2 mixture.

Scanned Auger electron microscopy (SAM) was used to confirm which phases were formed on the surface of the carbon-clad Si emitters. The obtained Auger electron spectra (AES) are shown in Figs. 2. These result indicate that there are less probability in forming SiC and SiO_2 at the surface of these carbon-clad emitters. Furthermore, the AES spectra corresponding to the specimens in Figs. 1 (a)-1 (e) are also shown in Fig. 2. The low-energy shoulder around 258~260 eV (peak a) and 248~250 eV (peak b) existed in spectra of tips coated with carbon films under conditions A and B indicated that the surface structure were polycrystalline diamond rather than graphitic or amorphous carbon [7]-[8]. However, AES spectra of sample deposited under condition C and D exhibits only a small peak a implying a diamondlike carbon nature containing a large amount of graphitic, amorphous carbon and/or other defects. Moreover, the spectra of sample deposited under condition E exhibit no obvious peaks a, which suggest their graphitelike or amorphous carbon natures.

Field emission properties of the diamond-clad samples were characterized in high-vacuum environment with a base pressure of about 2×10^{-7} Torr. The spacing between a unit emitter array and the graphite collector was controlled at a constant ~ 30 μm and a unit array contains 50×50 tips. Six sets of emission current versus applied voltage (Ie-Va) characteristic curves, from five arrays of carbon-clad Si tips under various deposition conditions A-E and one μc-SiC-clad Si tips, are shown in Fig. 3. Moreover, it can be seen from Figs.3 that the emission currents of 42, 45, 460, 1175, 728 and 8 μA were observed when the voltage Va of 1100 V was applied on the carbon-clad tip arrays deposited with gas mixture of 18/30, 20.5/30, 22/30, 30/30, 40/30 (conditions A-E) and the 500 Å-thick μc-SiC-clad tip array, respectively. The turn-on voltages V_{on}, defined as those for which the emission current Ie reaches 1 μA, for carbon-clad tips formed under conditions D, C, E, A, B and μc-SiC-clad tips are about 580 V, 680 V, 728 V, 757 V, 769 V and 843 V, respectively. The best emission capability was then observed from carbon-clad samples coated with gas mixture of 30/30, followed by 22/30, 40/30, 20.5/30 and 18/30. All the carbon-clad Si tip arrays exhibit much superior I-V performance to μc-SiC-clad one. This result suggests that the field emission mechanism of silicon carbide is very different from the carbon-based materials and exhibits a lower emission capability.

It is clear that the flow rate ratio of CH_4/CO_2 plays a very significant effect on emission current, since the reactive gases mixture is the most dominant factor on determining carbon phases during CVD deposition. Amorphization and defects of deposited carbon films were increased with higher concentrations in CO_2 plasmas (i.e. higher CH_4/CO_2 ratios), in accordance of SEM images and AES spectra mentioned above. Besides, Ie is also rapidly increased with increasing CH_4/CO_2 ratio when $20/30 \leq CH_4/CO_2$ ratio $\leq 30/30$. Since the better characteristics were achieved from samples deposited under higher CH_4/CO_2 ratios (= 22/30, 30/30), it seems to reveal that the diamondlike carbons containing higher defects and/or graphitic inclusions perform much better electron emission capability compared to polycrystalline diamonds. It is believed that defect densities will increase the energy state densities within the band gap of the diamond film and subsequently cause a higher conductivity and/or a lower work function in diamondlike carbon. [9]. If these bands are wide enough or closely spaced, the

electron within the band(s) or excitation from the valence band could easily provide a steady flow of electrons to the surface or surface states to sustain stable emission of electrons into vacuum [10]. On the other hand, higher proportion of conductive graphite inclusions also contribute more emission electrons and/or enhanced conductivity along grain boundaries [3]. Both phenomena suggest that electron emission can be significantly enhanced by applying diamondlike carbon instead of the polycrystalline diamond.

CONCLUSIONS

In summary, uniform and continuous diamond and other carbon films have been successfully coated on Si microtips using the MPCVD technology. According to SEM, AES and TEM examinations, various carbon-based surface coating materials including polycrystalline diamond, diamondlike carbon (DLC), and graphitielike carbon were achieved. The characteristics of emission current against applied voltage for the blunt undoped diamond-clad tips show superior emission at lower field to those of both Cr-clad and pure Si microtips. Such great improvement of the emission properties should be at least partially attributed to the lowering of the work function due to the negative electron affinity of the hydrogen terminated (111) and (100) diamond surfaces and/or the much larger effective emission area of the diamond coating. It is concluded that the interaction effects of the defect induced surface states, conductive graphitic impurities and embedded fine diamond particles are responsible for the enhanced electron emission

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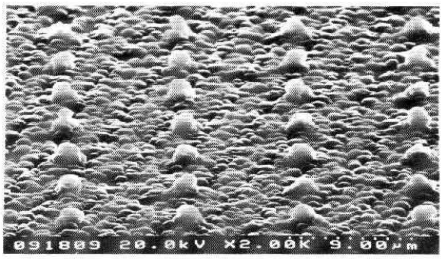
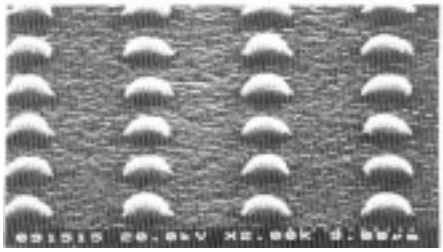
Samples shown in Figs. 1 (a)-(e)					
Conditions	A	B	C	D	E
$[CH_4]$ (sccm)	18	20.5	22	30	40

a) $[CO_2]$= 30 sccm; microwave power= 450 W; pressure= 25 Torr; deposition temperature = 850 °C; reaction time = 2 hr.

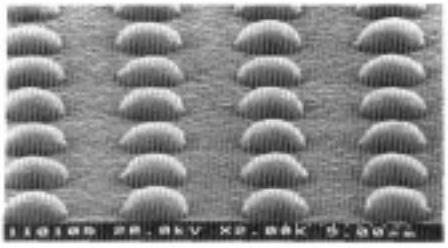
Table I Experimental conditions[a] for diamond-based films deposition using MPCVD



(a)



(b)



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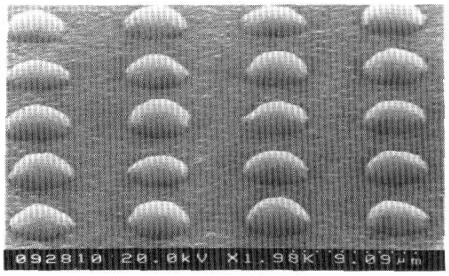
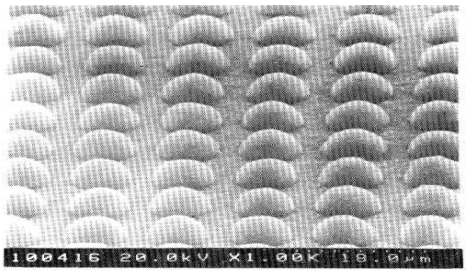


(d)



(e)

Fig. 1 (a)-(e) exhibit the corresponding surface morphologies of diamond-based films coated Si microtips with the deposition conditions CH4/CO2 flow ratio(a)18/30 (b)20.5/30 (c) 22/30 (d) 30/30 (e) 40/40

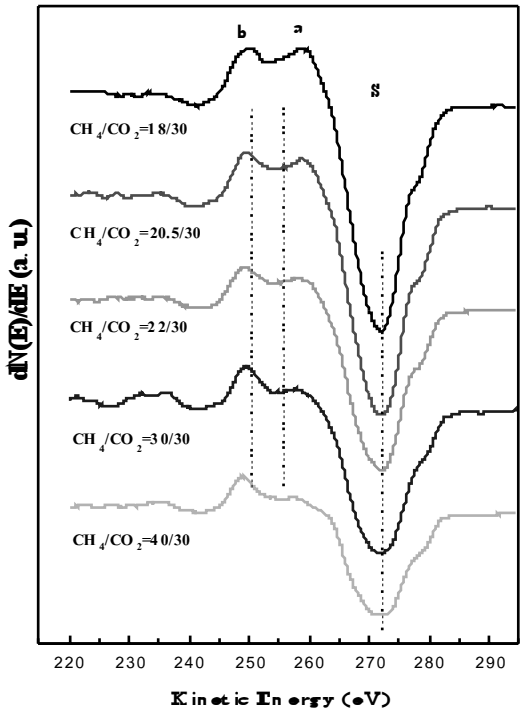


Fig. 2 The AES spectra with respect to the specimens in Fig.1. The low-energy shoulders around 258~260 eV (peak a) and 248~250 eV (peak b) are indicated

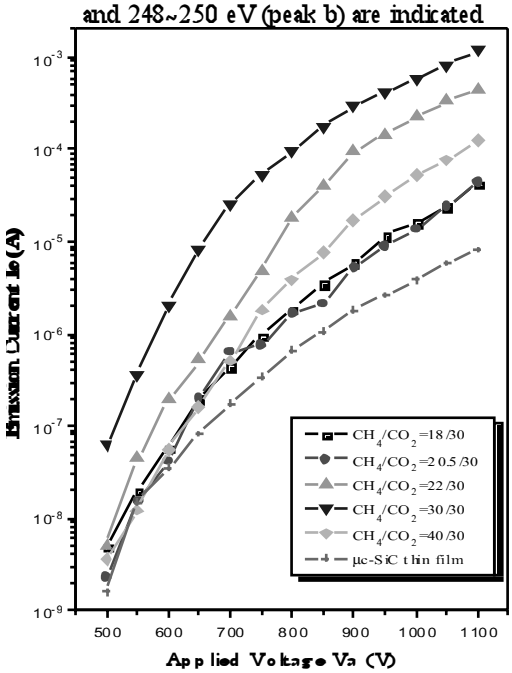


Fig. 3 Six sets of emission current versus applied voltage (Ie-Va) characteristic curves, from five arrays of diamond-based Si tips under varios deposition condition in Fig.1 and one μc-SiC-clad Si tips