Abstract:

Field emission display (FED) has recently attracted more attention because of its 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 CH₄/CO₂ is also studied to optimize the deposition conditions.

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 electronic 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 attempted [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
deposition conditions under CH$_4$ were scratched using diamond powders (particle size, grow continuous diamond films, some Si substrates chamber pressure was kept at 25 Torr. In order to sharply curved Si microtip surfaces were first cleaned 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, same Si substrates were scratched using diamond powders (particle size, 0.1 µm) before the deposition process except 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, AES spectra corresponding to the specimens in Figs. 1 (a)-(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 graphitlike or amorphous carbon nature.

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 (I$_e$-V$_a$) 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 V$_a$ 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 I$_e$ 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 IV 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, I$_e$ is also rapidly increased with increasing CH$_4$/CO$_2$ ratio when 20/30 ≤ CH$_4$/CO$_2$ ratio ≤ 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 graphitic 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.

REFERENCES


Table I

<table>
<thead>
<tr>
<th>Conditions</th>
<th>A</th>
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Table I Experimental conditions for diamond-based films deposition using MPCVD
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 (I-Va) characteristic curves, from five arrays of diamond-based Si tips under various deposition conditions in Fig. 1 and one µ-c-SiC-clad Si tips.