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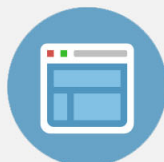
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Characterization of phosphorus-doped and boron-doped diamond-like carbon emitter arrays

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We synthesized phosphorus-doped and boron-doped emitters by using trimethylphosphite $P(OCH_3)_3$ and trimethylborate $B(OCH_3)_3$ as doping sources in a microwave plasma chemical vapor deposition system. Based on our experimental results from scanning electron microscopy and Raman spectra, there is much difference among undoped, phosphorus-doped, and boron-doped diamondlike material. In addition, doping both phosphorus and boron can enhance electric properties by reducing the turn-on voltage and can increase the emission current density. The turn-on voltages of undoped, boron-doped, and phosphorus-doped emitters in triode-type field emitter arrays are 15, 8, and 5 V, respectively. The emission currents of boron-doped and phosphorus-doped emitters are about 20 and 80 times larger than the undoped. © 2001 American Institute of Physics.
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I. INTRODUCTION

Diamond and diamond-like carbon (DLC) are presently being investigated and applied for use in field emission devices because diamond has negative electron affinity and robust mechanical and chemical properties. The diamond growth process used by researchers to make the devices also varies greatly. Observations of electron emission from chemical vapor deposition (CVD) diamond under relative low electric fields (3–40 V/ μm) have been reported.^{1–3} Fabrication of diamond field emitter arrays has also been attempted⁴ and a diode-structured prototype field emission display based on a diamond-like carbon cathode has been demonstrated.⁵ However, it is not entirely clear how the electron emission from these seemingly undoped or *p*-typedoped CVD diamonds can occur at such low fields.

Usually, for a semiconductor field emitter, the emitter electrons can originate from either the conduction band, the valence band, and/or surface states. Diamond has a wide band gap with $E_g = 5.5$ eV. In order to induce stable electron field emission from diamond, either the bulk or the surface must first be made conductive. It is believed that the impurities such as nitrogen, boron or phosphorus can enhance diamond's electron property by offering holes or electrons.

II. EXPERIMENT

A similar fabrication process for this metal-insulator-semiconductor (MIS) diode and diamond deposition procedure has been previously presented.⁶ In this work, first we designed the MIS diode structure and fabricated the MIS diode by semiconductor process technologies. Figure 1 displays the procedure of the MIS diode and Fig. 2 shows the photographs of MIS diode structure. After fabricating the MIS diode, we put it in the bias assisted microwave plasma chemical vapor deposition system to deposit diamond-like

emitters. The reactive gases used in deposition were the conventional mixture of CH_4-H_2 with trimethylphosphite $P(OCH_3)_3$ and trimethylborate $B(OCH_3)_3$ as the doping sources. All the experiments of the diamond deposition used two-step depositions. The first step is employed as a nucleation process: the flow rates of CH_4/H_2 and deposition time remain constant at 10/200 sccm and 30 min, respectively. The second step is the growth process and the total deposition normally lasts for 60 min. While processing, the specimens were subjected to a negative bias voltage of 130 V. Table I lists the experimental conditions. After processing, the CVD material was to characterize the quality of the diamond material.

III. RESULTS AND DISCUSSION

A. SEM analysis

For the undoped emitters, the diamond nuclei are not observed when the negative bias voltage is below 80 V. Furthermore, the bias voltage of 90–100 V only grows tiny tips inside the hole. The higher bias voltage we apply, the more emitters we can obtain. This implies that the higher bias voltage enhances the growth of the emitters. Once we increase the bias voltage over 150 V, diamond was not only inside the hole but also on the Pt gate. Indeed, the diamond may replace the Pt to form the diamond-gated field emissions arrays (FEAs). In the worst case scenario, this phenomenon will taint the $I-V$ measurement because the field emission current may be inexact because of the influence from both the diamond-like nano emitters and diamond-like-gated surface. In this article, the negative bias voltage = 130 V is used. Figures 3 and 4 display scanning electron microscopy (SEM) photographs of the undoped diamond emitters. Undoped diamond emitters have several branches on their lateral or top directions. But from Figs. 5 and 6, the doping ones only have tiny tips around them. The most significant phenomenon is the quantity of diamond emitters. Undoped diamond emitters

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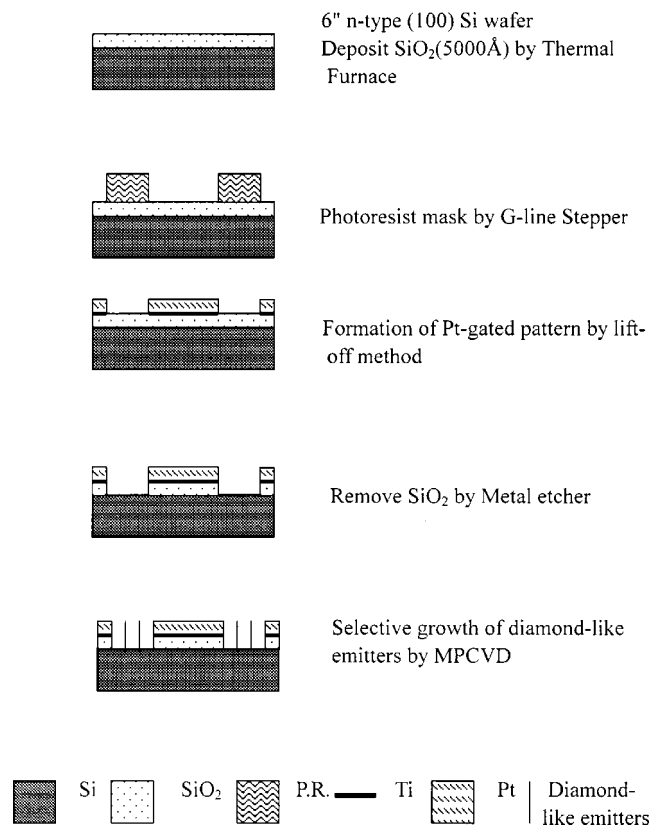


FIG. 1. Fabricated procedure of diamond emitters on the FEAs with gated diode pattern.

TABLE I. Deposition conditions.

Sample	First step flow rate CH ₄ /H ₂ +doping source (sccm)	Second step flow rate CH ₄ /H ₂ +doping source (sccm)
A (undoped)	10/200	7.5/200
B (undoped)	10/200	5/200
C (undoped)	10/200	2/200
D (phosphorus doped)	10/200+2	2/200+2
E (phosphorus doped)	10/200+1	2/200+1
F (phosphorus doped)	10/200+0.5	2/200+0.5
G (Boron doped)	10/200+2	2/200+2
H (Boron doped)	10/200+1	2/200+1
I (Boron doped)	10/200+0.5	2/200+0.5

First step deposition time=30 min Second step deposition time=30 min
 Bias voltage=-130 V Total pressure=2 KPa
 MW power=300 W Substrate temp.(°C)~660
 Doping source: P(OCH₃)₃ and B(OCH₃)₃

have higher growth rate than doping ones. The lower growth rate of the doped emitters could be explained by the following points. (I) P(OCH₃)₃ or B(OCH₃)₃ is a CH₃-rich compound that decomposes in plasma to produce an equal quantity of CH₃ radicals to balance the carbon source in the gas phase, thus the deposition rate will be reduced due to the increase of etching rate. (II) The lower growth rate of the doped samples is most likely due to the oxygen content contained in the P(OCH₃)₃ or B(OCH₃)₃. There were more oxygen atoms than phosphorus atoms in the doping source, which may be related to the etching of nondiamond carbon from the growing surface resulting in a lower growth rate.

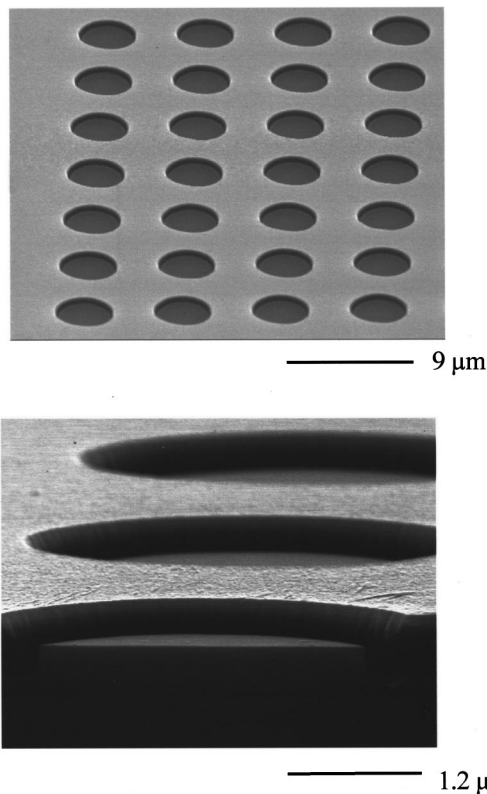


FIG. 2. The SEM photograph of MIS diode structure with 50×50 circles.

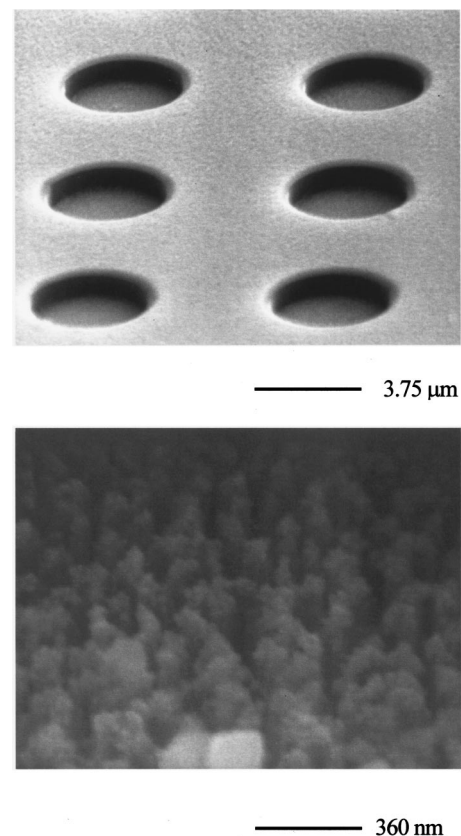


FIG. 3. The SEM photograph of undoped diamond emitters.

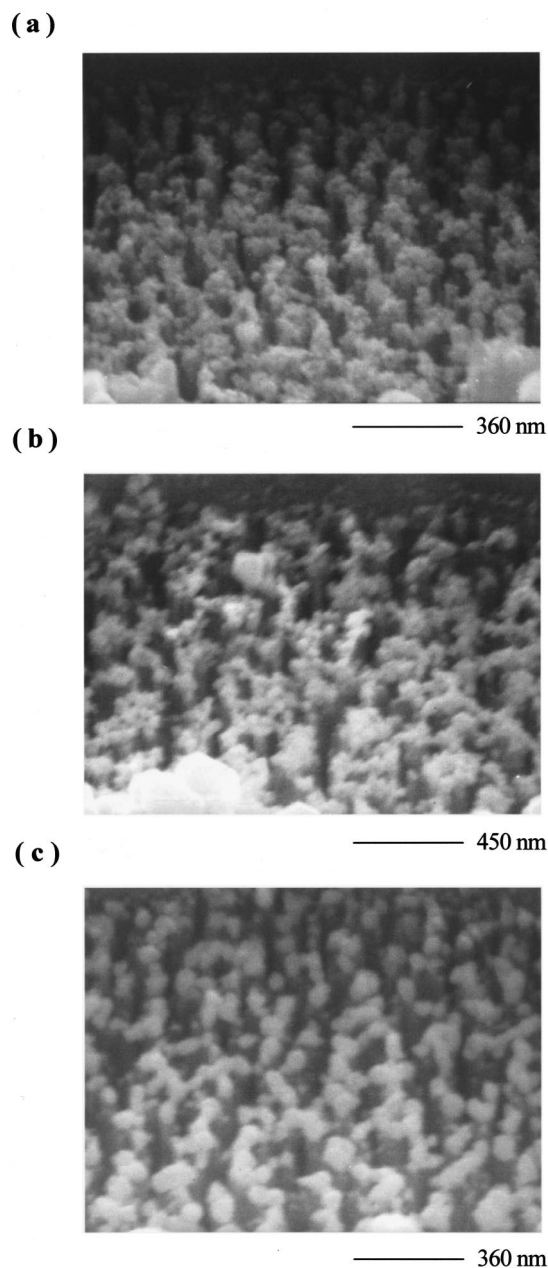


FIG. 4. The SEM photograph of undoped diamond emitters with various methane concentration (a) sample A, (b) sample B, and (c) sample C.

The same effects may also occur when adding O_2 to the CH_4-CO_2 gas mixture.⁷ Additionally, many investigations have confirmed that phosphorus will lower the diamond growth rate in H_2-CH_4 mixtures.^{7,8}

B. Raman spectra

The microstructure and quality of the amorphous diamond-like carbon films were determined by Raman spectra. Raman measurements were performed at 514.5 nm at 1 cm^{-1} resolution, integration times were 1 min at 30 mW Ar ion laser power. Figure 7 gives the Raman spectrum of undoped diamond emitters. We can see there are two obvious peaks located around 1350 cm^{-1} (*D* band) and 1580 cm^{-1} (*G* band). Normally a sharp peak at 1332 cm^{-1} corresponding to the diamond zone center phonon line would be the principle

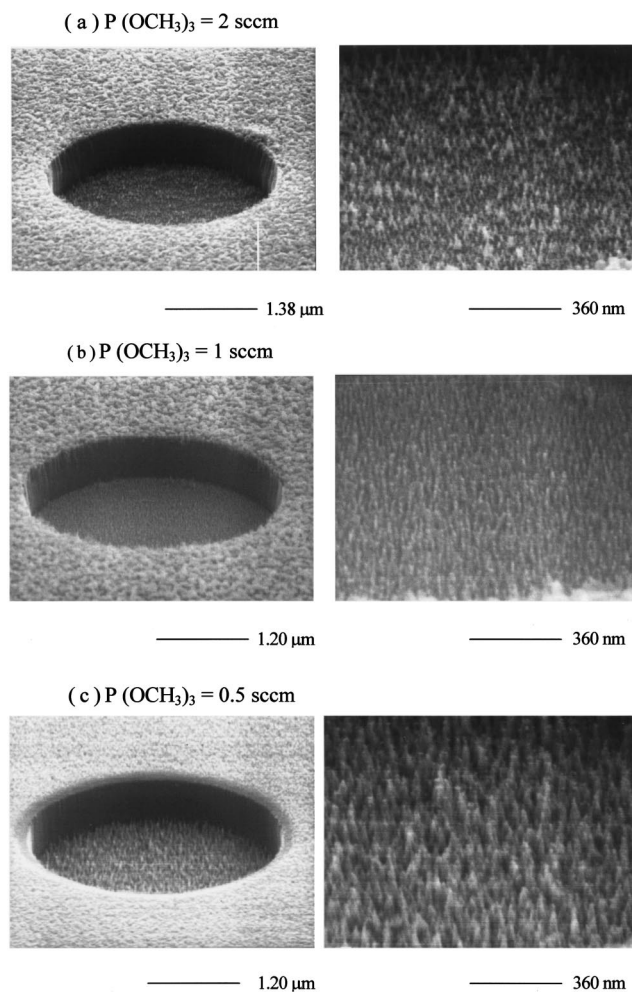


FIG. 5. The SEM photograph of phosphorus-doped diamond emitters with various doping concentration (a) 2 sccm, (b) 1 sccm and (c) 0.5 sccm, respectively.

Raman active feature in high quality crystalline CVD material. In this work, the spectral feature is diminished by stronger phonon bands attributable to diamond-like carbon (*D* band) and crystalline graphite (*G* band). This implies that the undoped emitters contain more graphitic material than diamond, and should strictly be classified as a diamond-like carbon (DLC) material. Figures 8 and 9 indicate that the graphitic content becomes even more dominant in the emitter material as the doping level of boron or phosphorus is increased. This observation is borne out by the fact that both doping gases are methyl-rich compounds. Thus, the etching rate declined while the quantity of amorphous carbon or graphite increased in the resultant films. A Raman shift occurs because of the internal stress in the diamond. This stress could be attributed to the following reasons: (I) the lattice mismatch between the diamond and phosphorus during growth; and (II) the thermal expansion coefficients of the diamond and substrate as well as the nanocrystalline nature of the diamond.

C. *I-V* measurement

Although diamond and DLC films have stable electron emissions at the low field, the nature of electron emission

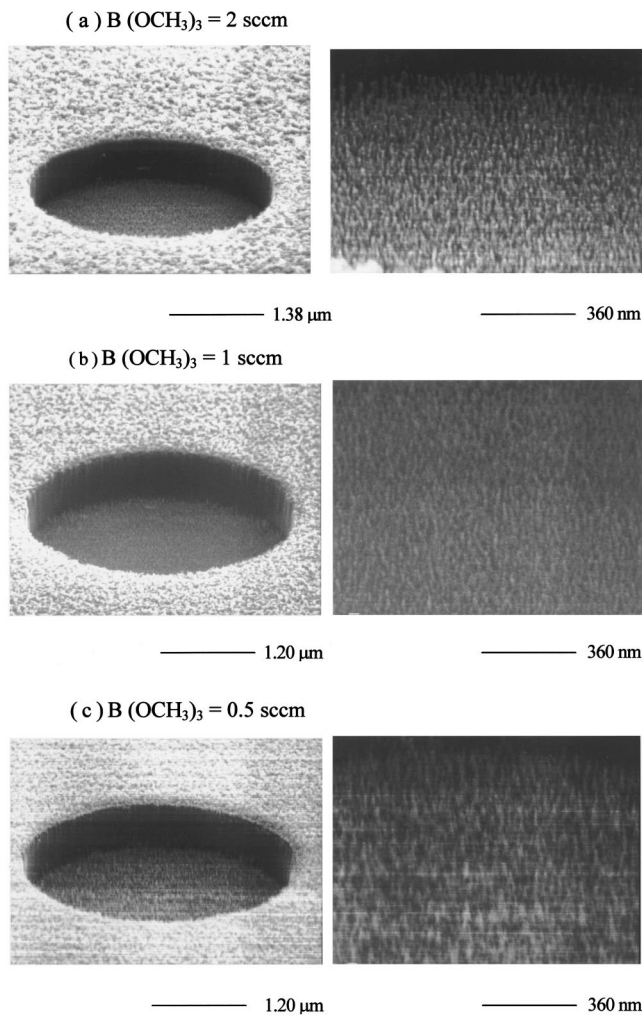


FIG. 6. The SEM photograph of boron-doped diamond emitters with various doping concentration (a) 2 sccm, (b) 1 sccm, and (c) 0.5 sccm, respectively.

from these materials remains unclear.⁹ We are currently employing different approaches to explain the ultralow emission fields. Many factors affect the field emission characterization of diamond including impurity, and defect levels¹⁰ in the diamond band gap; hot electron transport in interfaced

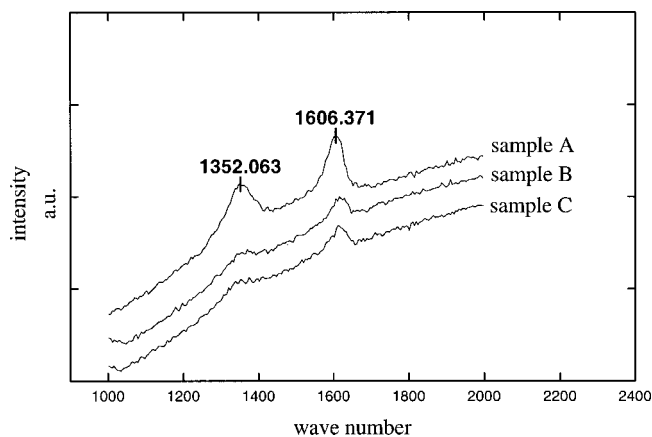


FIG. 7. The Raman spectrum of samples A, B, C grown at different methane concentration.

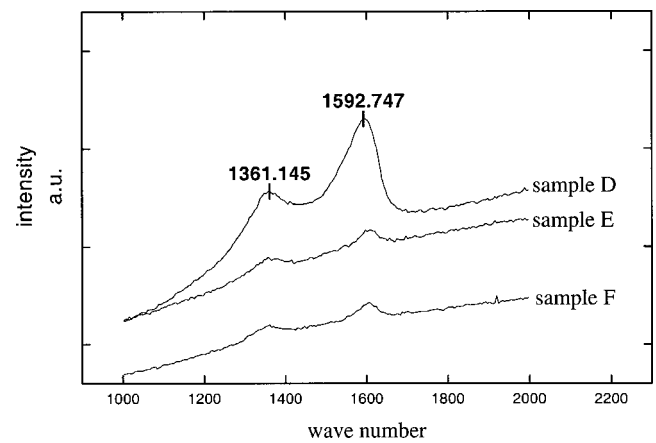


FIG. 8. The Raman spectrum of samples D, E, F grown at different phosphorus concentration.

structures;¹¹ grain boundary effects;¹² and geometric field enhancement (β) by morphology protrusions or narrow conductive grain boundaries between insulating grains. In this article, there are significant differences between phosphorus and boron doping. Figure 10 shows the field emission current density (J_e) of undoped; boron-doped, and phosphorus-doped diamond-like emitters with 0.013, 0.24, and 1.03 A/cm². The currents of boron-doped and phosphorus-doped emitters are 20 and 80 times larger than the undoped one. The electron emitting properties were further evaluated by the Fowler–Nordheim plot shown as an inset to Fig. 10.

The experimental results confirm that phosphorus-doped emitters have a better field emission property than boron doped for the following reasons. Doping with phosphorus has substantially more influence on conductivity than doping with boron. The other is due to the morphology of the emitters' structure. Phosphorus also provides its conduction electrons with more opportunity to be extracted because ionized donors form a space charge layer.¹³ Solid-state physics indicates that doping boron or phosphorus will instigate an energy band modification in the material by generating a donor or acceptor level that provides more electrons or holes for the

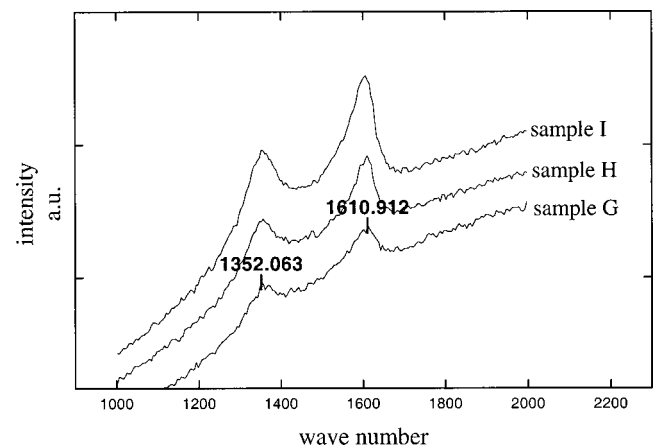


FIG. 9. The Raman spectrum of samples G, H, I grown at different boron concentration.

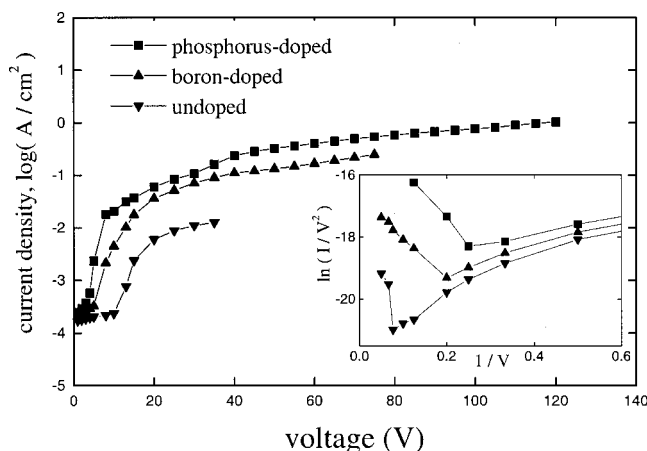


FIG. 10. The J_e - V curve of undoped, phosphorus-doped, and boron-doped diamond emitters and an inset of Fowler-Nordheim plot.

material. These increase the total conductivity and net flux of carriers.

The field emission property of diamond can be enhanced by increasing the sp^2 content because of the following reasons:

(I) The defect-induced band created by the sp^2 content.

The defect-induced energy band created by the sp^2 content is responsible for the field emission enhancement. A defect-induced energy band can be induced throughout the diamond energy gap in response to the presence of a wide variety of structural defects created as a consequence of the sp^2 particles. The formation of these defect bands raises the Fermi level toward the conduction band, and thus reduces the work function for enhancing field emission.

(II) The field enhancement factor is increased by the sp^2 -diamond- sp^2 microstructures.

Conducting sp^2 particles in isolated diamond form cascaded sp^2 -diamond- sp^2 metal-insulator-metal (MIM) microstructures which could enhance the field enhancement factor. The field enhancement factor β is affected by the following geometrical parameters of the device structure: the gate opening diameter, tip radius, emitter high, and tip position with respect to the center of the gate thickness and the emitter morphology. Adding phosphorus or boron changes their structures and also affects the field enhancement factor β .

IV. CONCLUSIONS

In this article, we synthesized phosphorus-doped and boron-doped emitters by using trimethylphosphite $P(OCH_3)_3$ and trimethylborate $B(OCH_3)_3$ as doping sources. Undoped emitters have higher growth rate than doping ones. The lower growth rate of the doped emitters could be explained by the following points. (I) $P(OCH_3)_3$ or $B(OCH_3)_3$ is a CH_3 -rich compound that decomposes in plasma to produce an equal quantity of CH_3 radicals to balance the carbon source in the gas phase, thus the deposition rate will be reduced due to the increase of etching rate. (II) The lower growth rate of the doped samples is most likely due to the oxygen content contained in the $P(OCH_3)_3$ or $B(OCH_3)_3$. Doping both phosphorus and boron can enhance electric properties by reducing the turn-on voltage and can increase the emission current density. The emission current densities of boron-doped and phosphorus-doped emitters are about 20 and 80 times larger than the undoped.

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