

Enhanced Electron Emission from Phosphorus-Doped Diamond-Clad Silicon Field Emitter Arrays

T. K. Ku, S. H. Chen, C. D. Yang, N. J. She, C. C. Wang, C. F. Chen, I. J. Hsieh, and H. C. Cheng

Abstract—Undoped and phosphorus (P)-doped diamond-clad Si field emitter arrays have been successfully fabricated using microwave plasma chemical vapor deposition (MPCVD) technology. The electron emission from the blunt diamond-clad microtips are much higher than those for the pure Si tips with sharp curvature due to a lower work function. Furthermore, the characteristics of emission current against applied voltage for the P-doped diamond-clad tips show superior emission at lower field to the undoped ones. After the examination of Auger electron spectroscopy (AES) and electrical characteristics of as-grown diamond, such a significant enhancement of the electron emission from the P-doped diamond-clad tips is attributed to a higher electron conductivity and defect densities.

I. INTRODUCTION

DIAMOND has recently been considered as the most appropriate and promising cold-cathode material for vacuum microelectronic devices due to its several important advantages. (1) The (111) diamond has a negative or at least very small electron affinity [1]. (2) Diamond is well known to be one of the most chemically and physically stable material and simultaneously has the highest thermal conductivity [2]. (3) High breakdown threshold and large high-field electron velocity of diamond enhance the maximum emission current limited by current saturation [2]. Recently, several papers reported the electron emission from CVD-grown diamond films and Si tips coated with diamond particles at their apex end regions [3]–[7]. Our previous work further indicated that the diamond-clad tips show a much better electron emission capability as compared with pure Si and Cr-clad microtips and diamond films coated on plain substrates [8]. However, the doping of diamond is necessary since diamond itself is an excellent insulator. Generally, n-type doping is preferred over p-type for electron emission. However, the implementation of effective and reliable n-type dopants is still difficult. Up to date, only Okano *et al.* reported the electron emission from phosphorus (P)-doped diamond films on plain Si substrates, showing low-field emission as compared to boron (B)-doped films [9]. In this letter, P-doped diamond films on Si microtips have been successfully fabricated by the microwave plasma chemical vapor deposition (MPCVD) technique and

characterized. This is the first report on the electron emission characteristics of P-doped diamond-clad Si tips.

II. EXPERIMENTAL PROCEDURES

A 1 μm -thick oxide layer was grown and was photolithographically patterned to form arrays of 50×50 circular discs 3 μm in diameter on 2 ~ 4 $\Omega\text{-cm}$, (100)-oriented n-type Si substrates. Employing the previously patterned oxide layer as the mask, the cone-shaped Si microtip arrays were subsequently formed using SF_6/Cl_2 reactive ion etching [10]. An oxidation-and-stripping process was applied to further sharpen the etched tip to about 250 \AA in radius [11]. The aspect ratio of the resultant sharp silicon microtips is about 3 $\mu\text{m}/3 \mu\text{m}$. Before the deposition of diamond, the as-fabricated sharply curved Si microtips were first cleaned by H_2 plasma pretreatment and followed by diamond powder (particle size, 0.1 μm) scratching. In order to grow a continuous diamond film, diamond powder scratching process is necessary to create nucleation sites on the surface of Si substrates. Then, the undoped diamond films were deposited on the $2 \times 2 \text{ mm}^2$ Si substrates with a 50×50 tips array using microwave plasma enhanced CVD at 850°C using a gaseous mixture of CH_4 in CO_2 . The microwave power was set at 450 W and the reaction time was 2 h. The pressure during deposition was 25 Torr. For the P-doped diamond, the deposition conditions were the same as the undoped ones except that trimethyl phosphite ($\text{P}(\text{OCH}_3)_3$) was introduced as the doping reactant during diamond deposition [12].

III. RESULTS AND DISCUSSION

In general, high-quality diamond films can be obtained by reducing the flow rate ratio of CH_4/CO_2 . However, perfect diamond is an excellent insulator which makes stable electron field emission impossible. According to our previous work and other works by Zhu *et al.* and Xu *et al.*, the higher defect densities in CVD-grown diamond films are responsible for the enhanced electron emission [6], [7]. Besides, the low flow rate ratio leads to a rough and nonuniform coating morphology on the high curvature tip region. Hence, the defective diamond crystallites deposited by a higher flow rate ratio of CH_4/CO_2 are preferred. The flow rate ratio of CH_4/CO_2 consequently chosen was 68.4% (20.5/30) with 0.2 sccm $\text{P}(\text{OCH}_3)_3$ dopant (or a P/C ratio of 3960 ppm) to achieve the defective P-doped diamond films. The SEM images shown in Fig. 1(a) and (b) demonstrate the surface morphology of undoped and P-doped diamond-clad Si tips deposited by 68.4% CH_4 in CO_2 gaseous mixture with a P/C ratio of 3960 ppm. To form a continuous

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T. K. Ku, S. H. Chen, C. D. Yang, N. J. She, C. C. Wang, C. F. Chen, and H. C. Cheng are with National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

I. J. Hsieh is with Chung-Hua Polytechnic Institute, Hsinchu, Taiwan, R.O.C.

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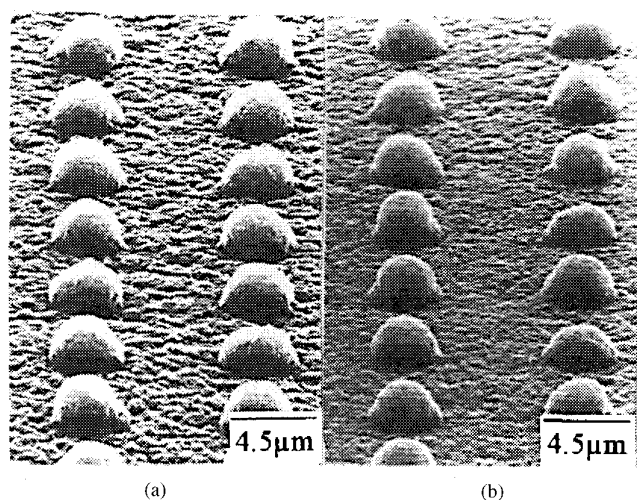


Fig. 1. The SEM images of diamond-clad Si tips deposited by 68.4% CH_4 in CO_2 gas mixture (a) the undoped diamond-clad Si tips (b) the P-doped diamond-clad Si tips deposited with the 0.2 sccm $\text{P}(\text{OCH}_3)_3$ dopant (or a P/C ratio of 3960 ppm).

and uniform coating, a thicker film ($\sim 3 \mu\text{m}$) was grown and therefore resulted in a much more blunt shape than the original un-coated Si tip. Moreover, the P-doped diamond-clad tips shown in Fig. 1 are slightly less in size uniformity compared to the undoped ones. This is due to the significantly decreased nucleation density for the P-doped diamond.

Auger electron spectroscopy (AES) was used to identify the surface compositions of the diamond-clad Si microtips. The AES spectra corresponding to the specimens in Fig. 1(a) and (b) are shown in Fig. 2. In these spectra, the carbon peak at 272 eV was detected and neither Si nor O peaks were detected. The low-energy shoulder around 260 eV in the positive peak of the carbon main peak existed in the undoped sample indicated that the surface structure was diamond rather than graphitic components [13]. However, the AES spectrum of P-doped sample did not exhibit an obvious shoulder, implying a diamond-like carbon nature containing a large amount of graphitic, amorphous carbon and/or other defects. Moreover, the small insert in Fig. 2 indicates a successful P doping by detecting a phosphorus peak at around 120 eV. According to the detectable sensitivity of AES spectrum, the P concentration is high, in the order of 10^{19} cm^{-3} .

Field emission properties of the diamond-clad samples were characterized in high-vacuum environment with a base pressure of 2.5×10^{-7} Torr. The spacing between the emitter and the graphite collector was controlled at a constant $\sim 30 \mu\text{m}$ and the tip number in an array was 50×50 . When a copper plate instead of the tip array was put on the cathode, a current of less than 1 nA was measured. As shown in Fig. 3, the emission current (I_e) versus applied voltage (V_a) characteristics of the P-doped and undoped diamond-clad microtips are both superior to that of pure Si microtips, in spite of their relatively blunt curvatures. This may be attributed to the lowering of the work function due to the negative electron affinity of (111) diamond films and/or the much larger effective emission area of the diamond coating. At $V_a = 1100 \text{ V}$, a much higher emission current (I_e) of 1.69 mA for the P-

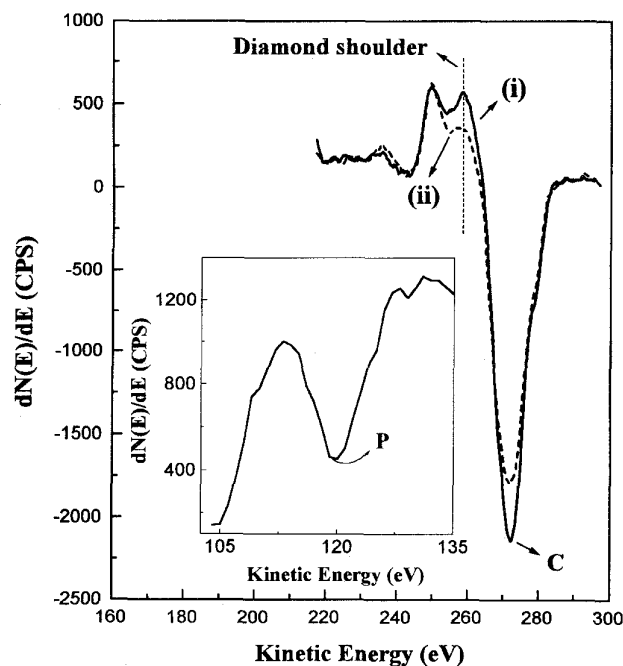


Fig. 2. Auger electron spectra (AES) of (i) undoped diamond-clad Si tips and (ii) P-doped diamond-clad Si tips. The main carbon peak at 272 eV was detected and neither Si nor O peaks were detected. Moreover, the small insert indicates a successful phosphorus doping by detecting a phosphorus peak at around 120 eV.

doped diamond-clad emitters with 3960 ppm P/C ratio was achieved, compared to only $45 \mu\text{A}$ from the undoped ones. Hence, the electron emission from the diamond-clad tips was greatly enhanced by introducing the P dopants. Defining F_T as the threshold values of the applied field needed to generate a current of $20 \mu\text{A}$ in our array size with about 0.2 mm^2 (i.e., a typical current density of 10 mA/cm^2 required for effectively exciting a phosphor pixel in a field emission display), the F_T value was reduced from $33.6 \text{ V}/\mu\text{m}$ for the undoped diamond-clad tips to $22.3 \text{ V}/\mu\text{m}$ for the P-doped ones. The resistivities of the P-doped diamond films were measured by the four-point probe method and were found at least one-order of magnitude lower than those of undoped films. It is believed that the P-dopants and their associated defect densities increase the energy state densities within the band gap of the diamond film [14]. Subsequently, it causes both a higher conductivity and the remarkable enhancement of the electron emission from the P-doped diamond-clad tips. To confirm that the emission was indeed field emission, the currents emitted from plain substrates coated with P-doped and undoped diamond layer were also investigated. The emission currents measured at $V_a = 1100 \text{ V}$ were only about $17 \mu\text{A}$ for the former and 760 nA for the latter. This indicates that most of the emission currents are contributed from the diamond-clad tips.

IV. CONCLUSIONS

In summary, uniform and continuous diamond films have been successfully coated on Si microtips using the MPCVD technology. The characteristics of emission current against applied voltage for the blunt P-doped diamond-clad tips show

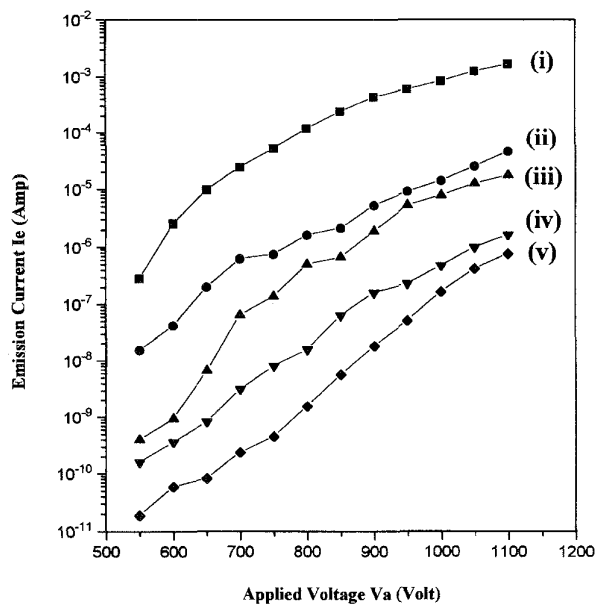


Fig. 3. Emission current (I_e) versus applied voltage (V_a) characteristics of (i) the P-doped diamond-clad tips; (ii) undoped diamond-clad tips; (iii) the P-doped diamond-clad plain Si substrate; (iv) the sharp Si tips; (v) the undoped diamond-clad plain Si substrate. The spacing between the emitter and collector was a constant about $30 \mu\text{m}$ and the tip number in an array is 50×50 .

superior emission at lower field to both the un-doped ones and sharp Si tips. By examining with Auger electron spectroscopy and by electrically characterizing the as-grown diamond, the significant enhancement of the electron emission from the P-doped diamond-clad tips can be attributed to a higher electron conductivity and higher defect densities.

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