

Enhanced electron emission from phosphorus- and boron-doped diamond-clad Si field emitter arrays

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Abstract

A new fabrication technology of polycrystalline diamond-clad Si microtips using microwave plasma chemical vapor deposition (MPCVD) has been developed to improve the characteristics of electron field emission from the pure Si tips. A uniform and smooth coating morphology for the diamond-clad Si tips have been achieved. Electron emission currents of diamond-clad tips are much higher than those of pure Si tips. Such great improvement is attributed to the lowering of the effective work function in the diamond-clad tips. The effects of phosphorus- and boron-doped diamond-clad Si tips have been also studied in comparison with the undoped ones. The current-voltage characteristics of the undoped diamond-clad tips were further enhanced by the in-situ doping of phosphorus or boron due to a higher electron supplement. Moreover, the P-doped diamond-clad tips show a better field emission performance as compared to the B-doped ones. This difference is surmised to be associated with the higher electron conductivity and defect densities of P-doped diamond films.

Keywords: Diamond-clad Silicon tips; Field emission; Field emitter arrays; Effective work function

1. Introduction

Microsized field emitter arrays (FEAs) fabricated with advanced micromachining technology has been intensively progressed as the promising electron sources for vacuum microelectronic devices especially for the ultra-thin flat panel displays [1]. Other potential applications include microwave devices [2], ultra-speed switches, microsensors, [3] and microsized intense electron sources. In order to achieve low voltage and high efficiency for cold cathode operation, the tip radius and surface work function of a field emitter should be made as small as possible [4]. Moreover, emission stability is also a very important issue [5]. Among the various types of FEAs, silicon microtips have become a very attractive candidate because of two notable advantages. First, they are easy to fabricate using modern IC technology, and second, their tip radius can be easily sharpened to the nanometer range [6]. On the other hand, their high work function, low electron conductivity, and poor stability are the major drawbacks of Si FEAs. These drawbacks, however, can be minimized using surface coating. Coating of the surface of Si microtips with various materials to enhance their emission efficiency and stability has been reported [7,8]. Most of these reports

focused on metals. 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 electrical properties of diamond: first, hydrogenated-(111) diamond has a negative or at least very small electron affinity, i.e. a very low effective work function; and second, diamond is well known to be one of the most chemically and physically stable materials and has the highest thermal conductivity ($20 \text{ W cm}^{-1} \text{ } ^\circ\text{C}^{-1}$) [9,10]. Hence, fabrication of low-field diamond field emitter arrays has been attempted [11-14], and a diode-structured prototype field emission display based on a diamond-like carbon has been demonstrated [15].

In order to take the advantage of the diamond negative electron affinity (NEA) property, there must exist a source of electrons either in the conduction band or in a subband with energies near or above the vacuum level. In addition, the conductive channels of electrons are also necessary to induce stable electron emission from the insulating diamond. Zhu et al. [13] reported that the defects created additional energy subbands within the band gap of diamond and thus contributed electrons for emission at low electric fields. Xu et al. [14] suggested that the graphite inclusions embedded in the diamond film might play an important role for the

contribution of electron conduction channels. However, the mechanism of electron emission from diamond or other carbon films is still not entirely clear. Recently, Okano and Gleason [16] reported the electron emission from phosphorus-doped diamond films on plain Si substrates, showing low-field emission as compared to boron-doped films. However, the implementation of effective and reliable n-type dopants is still difficult.

In this report, the microsized silicon field emission tips coated with polycrystalline diamond film has been successfully fabricated and characterized. This study has pointed out that uniform polycrystalline diamond films coated on Si tips by microwave plasma chemical vapor deposition (MPCVD) exhibited better emission characteristics than those merely coated on plain Si substrate. The P-doped and B-doped diamond films on Si microtips have also been formed employing in-situ doping technology. Hence, effects of diamond doped with phosphorus and boron on emission properties were evaluated.

2. 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 $2 \sim 4 \Omega \text{ cm}$, (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. An oxidation-and-stripping process was applied to further sharpen the etched tip to about 25 nm in radius [17]. 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. Next, the scratched Si substrates were dipped into a solution of $\text{HF}:\text{H}_2\text{O} = 1:100$ for a few seconds to remove the native oxide on the silicon. Then diamond films were deposited on the $2 \times 2 \text{ mm}^2$ Si substrates with a 50×50 tips array using microwave plasma-enhanced chemical vapor deposition (MPCVD) at 850°C using a $\text{CH}_4\text{-CO}_2$ gas mixture. For the P-doped and B-doped diamond, vapor dopant sources of trimethyl phosphite ($\text{P}(\text{OCH}_3)_3$) and trimethyl borate ($\text{B}(\text{OCH}_3)_3$) were introduced in the diamond deposition [18–20]. The flow rate of $\text{P}(\text{OCH}_3)_3$ and $\text{B}(\text{OCH}_3)_3$ was varied from 0 (undoped) to 0.5 sccm when they were introduced to the flow ratios of CH_4/CO_2 of $18/30 \sim 20.5/30$. The microwave power was set at 450 W and the reaction time was 2 h. The pressure during deposition was 25 Torr. The fabrication procedures are shown in Fig. 1.

3. Results and discussion

After semi-anisotropic RIE etching and oxidation sharpening, the result of forming sharp silicon microtips with tip

radius about 25 nm are shown in Fig. 2. The aspect ratio of the resultant sharp silicon microtips is about $3 \mu\text{m}/3 \mu\text{m}$. According to our previous work and other works by Zhu et al. [13] and Xu et al. [14], the higher defect densities in CVD-grown diamond films are responsible for the enhanced electron emission. Hence, the defective diamond crystallites deposited by a higher flow ratio of CH_4/CO_2 ($> 20/30$) is preferred. Besides, the low flow ratio also leads to a rough and non-uniform coating morphology on the high curvature tip region. The SEM images shown in Fig. 3(a), 3(b) and 3(c) show the surface morphology of undoped, P-doped and B-doped diamond-clad Si tips deposited by a flow ratio of $20.5/30$ in a $\text{CH}_4\text{-CO}_2$ gas mixture with no dopant source, a

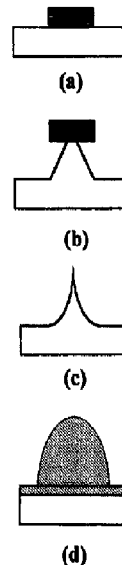


Fig. 1. Fabrication procedures of diamond-clad Si tips: (a) defining oxide mask; (b) Si tips etched by SF_6/Cl_2 RIE; (c) sharpening the etched tips employing an oxidation-and-stripping treatment; and (d) diamond film deposited on the Si tips.

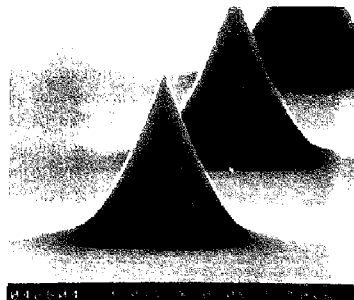


Fig. 2. The results of forming sharp Si microtips with an aspect ratio of $3 \mu\text{m}/3 \mu\text{m}$.

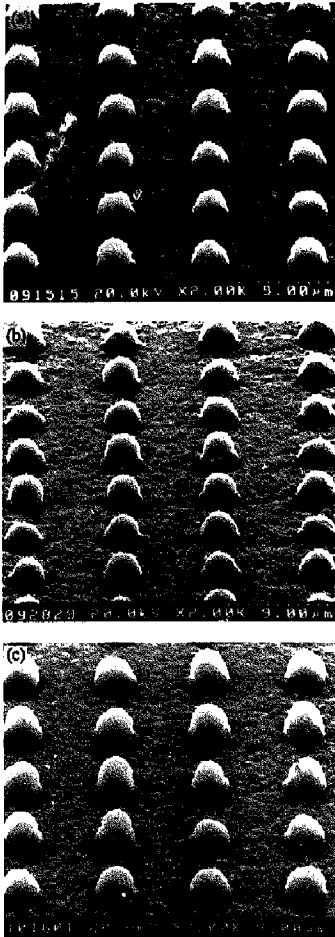


Fig. 3. Surface morphologies of diamond-clad Si tips deposited by a flow ratio of 20.5/30 in $\text{CH}_4\text{-CO}_2$ gas mixtures: (a) undoped ones; (b) P-doped ones with $\text{P}(\text{OCH}_3)_3=0.2$ sccm; and (c) B-doped ones with $\text{B}(\text{OCH}_3)_3=0.2$ sccm.

$\text{P}(\text{OCH}_3)_3$ flow rate of 0.2 sccm and $\text{B}(\text{OCH}_3)_3$ flow rate of 0.2 sccm, respectively. To form a continuous and uniform coating, a thicker film ($2\sim 3\ \mu\text{m}$) was grown and therefore resulted in a much more blunt shape than the original uncoated Si tip. Both the P-doped and B-doped diamond-clad tips are slightly less in size uniformity compared to the undoped ones, as shown in Fig. 3(a)–3(c). This result indicates that the doping process has no significant effect on the surface morphology of deposited 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. 3(a) and 3(b) are shown in Fig. 4. In the spectra, the carbon peak

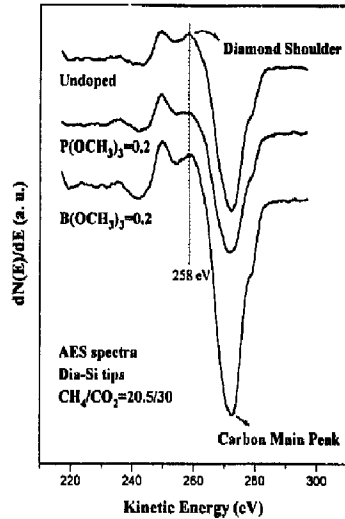


Fig. 4. Auger electron spectra (AES) of undoped, P-doped and B-doped diamond-clad Si tips. The main carbon peak at 272 eV was detected and neither Si nor O peaks were detected. A detectable phosphorus peak at around 120 eV was not shown.

at 272 eV was detected and neither Si nor O peaks were detected. The low-energy shoulder around 258 eV in the positive peak of the carbon main peak in the undoped sample, shown in Fig. 3(a), indicated that the surface structure was diamond rather than graphitic or amorphous carbon components [21]. As for B-doped samples, their AES spectra were similar to those of undoped samples. It reveals that diamond films deposited with a dopant source of $\text{B}(\text{OCH}_3)_3$ do not significantly change their film property. However, the AES spectrum of the P-doped sample shown in Fig. 3(b) did not exhibit an obvious shoulder, implying a diamond-like carbon (DLC) nature containing a large amount of graphitic, amorphous carbon and/or other defects. To simplify the description, the Si tips coated with diamond films under CH_4/CO_2 flow ratio of 20.5/30 were represented as "Dia-Si tips" in the following description. Moreover, a small phosphorus peak at around 120 eV was detected. It indicates that P dopants are successfully doped into diamond. According to the detectable sensitivity of AES spectrum, concentration of P dopant is high, in the order of $10^{19}\ \text{cm}^{-3}$.

Field emission properties of the diamond-clad samples were characterized in high-vacuum environment with a base pressure of about 2.6×10^{-10} Pa. A schematic diagram of the test configuration is shown in Fig. 5. The spacing between a unit emitter array and the graphite collector was controlled at a constant $\sim 30\ \mu\text{m}$ and a unit array contains 50×50 tips. When a copper plate instead of the tip array was put on the cathode, a current of less than 1 nA was measured. Prior to the electrical measurement, a high constant voltage of about 1100 V was applied to the emitters to exhaust the adsorbed

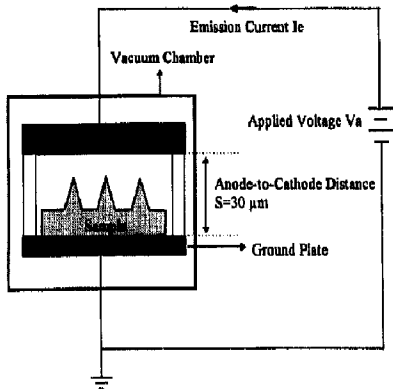


Fig. 5. Schematic diagram of a high-vacuum field emission characterization system.

molecules and evaporate the native oxide. As shown in Fig. 6, the emission current (I_e) versus applied voltage (V_a) characteristics of the P-doped, B-doped and undoped diamond-clad microtips are all superior to that of pure Si microtips, in spite of their relatively blunt curvatures. It is 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. Besides, the secondary electric field enhancement due to the nano-protrusion on the rough diamond-clad tip surface may also be partially

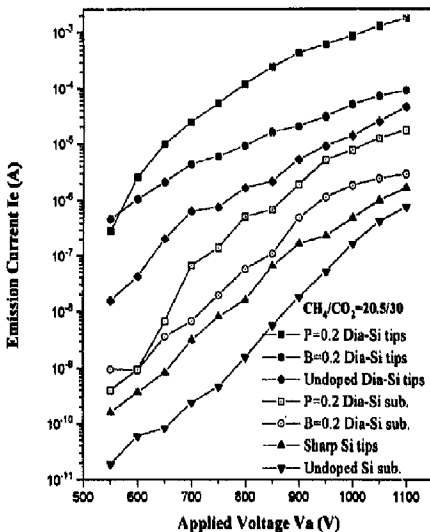


Fig. 6. Emission current (I_e) versus applied voltage (V_a) characteristics of the P-doped, B-doped and undoped diamond-clad tips; the P-doped, B-doped and undoped diamond deposited on Si plain substrates; and the pure Si tips. The spacing between the emitter and collector was a constant about 30 μ m and the tip number was 2500.

responsible for the emission current enhancement [12]. At $V_a = 1100$ V, a much higher emission current (I_e) of 1.69 mA for the P-doped Dia-Si tips with $P(OCH_3)_3 = 0.2$ sccm was achieved, as compared to the 91 μ A for B-doped one with $B(OCH_3)_3 = 0.2$ sccm and only 45 μ A for the undoped one. Hence, electron emission from the Dia-Si tips was greatly enhanced by introducing dopants. P-doped emitters exhibited higher emission currents than B-doped samples for $V_a > 600$ V. In order to evaluate the effects of flow rate of P and B dopant sources on emission current enhancement, one may introduce the "enhancement ratio" defined as

$$R_{en} = (I_d/I_u)$$

where I_d and I_u are emission current of doped and undoped Dia-Si tips at a maximum V_a of 1100 V. The value of R_{en} represents the degree of electron emission enhanced by introducing various dopant concentrations. Fig. 7 shows that the R_{en} of Dia-Si tips is significantly dependent on the flow rate of dopant sources. For dopant flow rates beyond 0.05 sccm, the value of R_{en} is rapidly increased with increasing $P(OCH_3)_3$ flow rate until R_{en} reaches a maximum value of 38 at $P(OCH_3)_3 = 0.2$ sccm, and R_{en} is then rapidly dropped to be 3.5 at $P(OCH_3)_3 = 0.5$ sccm, as shown in Fig. 7. The resistivities of the diamond films doped with $P(OCH_3)_3 = 0.2$ sccm were measured by the four-point probe method and were found to be 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 bandgap of the diamond film [22]. Subsequently, it causes both a higher conductivity and the remarkable enhancement of the electron emission from the P-doped Dia-Si tips. This suggests that the flow rate of $P(OCH_3)_3 \leq 0.05$ sccm is not sufficient to activate the doping P impurities and the associated defect densities in the as-deposited diamond films to significantly increase their con-

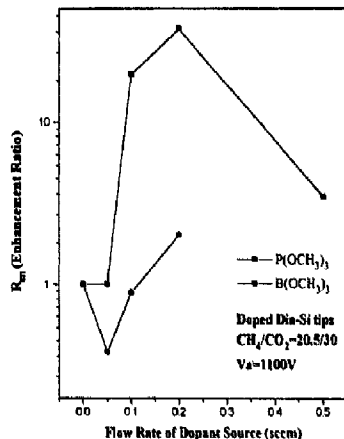


Fig. 7. Enhancement ratio (R_{en}) versus dopant source flow rate characteristics of doped diamond-clad Si tips.

ductivity. However, as a result of the AES analysis shown in Fig. 5, the quality of diamond film is degraded by introducing P dopants. Although the defective diamond coating is preferred, the as-deposited diamond is degraded to be a fully amorphous sp^2 carbon (a-C) film losing the NEA property of diamond, if too much P dopant is introduced. The rapidly decreased R_{en} of Dia-Si tips doped under $P(OCH_3)_3 = 0.5$ sccm was then attributed to the above phenomenon. Therefore, the dopant concentration of $P(OCH_3)_3$ should be optimized to achieve the maximum field emission enhancement.

As for the B-doped Dia-Si tips, the flow rate of $B(OCH_3)_3$ exhibits little effect on the value of R_{en} compared to those of the P-doped ones. The R_{en} of B-doped Dia-Si tips were smaller, apart from one exception for doped $B(OCH_3)_3 = 0.2$ sccm. It suggests that for the B-doped Dia-Si tips it was necessary to introduce a higher $B(OCH_3)_3$ concentration for making a significant effect on electron emission. This result is expected since electron emission from n-type semiconducting diamond is generally preferred. As a result of characterization, the P-doped diamond-clad tips show a better field emission performance as compared to the B-doped ones. This difference is surmised to be associated with the higher electron conductivity and defect densities of P-doped diamond films. Besides, defining F_T as the threshold value of the applied field needed to generate a current of 20 μA 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 $V\ \mu m^{-1}$ for the undoped diamond-clad tips to 22.3 $V\ \mu m^{-1}$ for the P-doped ones and 30 $V\ \mu m^{-1}$ for the B-doped ones. It indicated the electron emission from P-doped Dia-Si tips shows low-field emission as compared to B-doped ones. However, it can be seen from Fig. 6, that when the applied voltage V_a is $< 600\ V$, the I_e values of P-doped and B-doped are very close, which suggests that their effective work function are similar. Hence, the I_e difference between P-doped and B-doped diamond films seem to be dominated by the variation of the electron conductivity.

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 $V_a = 1100\ V$ were only about 17 μA for the former and 760 nA for the latter. This indicates that most of the emission currents are from the diamond-clad tips.

4. 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 undoped diamond-clad tips show superior emission at lower field compared to the pure Si tips. It is 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. The P-doped and B-doped diamond films on Si microtips have also been formed employing in situ doping technology. Effects of the phosphorus and boron dopants on the emission properties were evaluated. The P-doped diamond-clad tips show a better field emission performance as compared to the B-doped ones. This difference is surmised to be concerned with the higher electron conductivity and defect densities of P-doped diamond films.

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References

- [1] P. Vaudaine and R. Meyer, *IEEE IEDM Tech. Dig.*, (1991) 197.
- [2] C.A. Spindt, C.E. Holland, A. Rosengreen and I. Brodie, *J. Vac. Sci. Technol.*, B11 (1993) 468.
- [3] H.H. Busta, J.E. Pogemiller and B.J. Zimmerman, *J. Microchem. Microeng.*, 3 (1993) 45.
- [4] T. Usumi, *IEEE Trans. Electron Device*, 38 (1991) 2275.
- [5] H.H. Busta, D.W. Jenkins, B.J. Zimmerman and J.E. Pogeiller, *IEEE IEDM Tech. Dig.*, (1991) 213.
- [6] R.B. Marcus, T.S. Ravi, T. Gmitter, K. Chin, W.J. Orvis, D.R. Ciarlo, C.E. Hunt and J. Trujillo, *Appl. Phys. Lett.*, 56 (1990) 236.
- [7] H.H. Busta, R.R. Shaddock and W. Orvis, *IEEE Trans. Electron Device*, 36 (1989) 2679.
- [8] V.V. Zhirmov and E.I. Givargizov, *J. Vac. Sci. Technol.*, B12 (1994) 633.
- [9] F.J. Himpsel, J.A. Knapp, J.A. Van Vechten and D.E. Eastman, *Phys. Rev.*, B20 (1979) 624.
- [10] M.N. Yoder, in R.E. Clausing et al. (eds.), *Diamond and Diamond-Like Films and Coatings*, Plenum, New York, 1991, p. 11.
- [11] C. Wang, A. Garcia, D.C. Ingram, M. Lake and M.E. Kordesch, *Electron. Lett.*, 27 (1991) 1459.
- [12] E.I. Givargizov, V.V. Zhirmov, A.N. Stepanova, E.V. Rakova, A.N. Kiselev and P.S. Piekhanov, *Appl. Surf. Sci.*, 87/88 (1995) 24.
- [13] W. Zhu, G.P. Kochanski, S. Jin and L. Scibles, *J. Appl. Phys.*, 78 (1995) 2707.
- [14] N.S. Xu, R.V. Latham and Y. Tzeng, *Electron. Lett.*, 29 (1993) 1596.
- [15] J.E. Jaslike, *Mater. Res. Soc. Bull.*, (1996) 59.
- [16] K. Okano and K.K. Gleason, *Electron. Lett.*, 31 (1995) 74.
- [17] T.K. Ku, M.S. Chen, C.C. Wang, W.F. Loe, M.S. Feng, I.J. Hsieh, C.M. Huang and H.C. Cheng, *Proc. Int. Symp. Electron Device and Material*, Taiwan, 1994, pp. 11–34, 136.
- [18] S.H. Chen, S.L. Chen, S.F. Lo and C.F. Chen, *Diamond Related Mater.*, 5 (1996) 766.
- [19] S. Bohr, R. Haubner and B. Lux, *Diamond Related Mater.*, 4 (1995) 133.
- [20] S.H. Chen, S.L. Chen, M.H. Tsai, J.J. Shyu and C.F. Chen, *J. Electrochem. Soc.*, 142 (1995) L223.
- [21] P. Sauter, U. Kaiser, M. Altebockwinkel, L. Wiedmann, A. Benninghoven, R.E. Sah and P. Koidl, *J. Vac. Sci. Technol.*, A5 (1987) 1470.
- [22] G.B. Bachelet, G.A. Baraff and M. Schlüter, *Phys. Rev.*, B24 (1981) 4736.