Technology and Characterization of Diamond Field Emitter Structures

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***Abstract*—In an effort to develop diamond field emitters with high current densities, diamond film technology compatible with Si integrated circuits is used to design new experiments for a systematic study of field emission as a function of sp^3/sp^2 ratio, grain size, doping level, patterning, field enhancement at the grain tips, and anode to emitter separation. Boron-doped polycrystalline diamond films with low sp^3/sp^2 ratios, high density of small grains and grain boundaries, and patterned structures result in high current densities and low emission fields. Electric fields to initiate emission, measured at $J = 0.01$ mAcm^{-2}, are in the range of 0.1–0.4 MV/cm depending upon diamond growth conditions. The results of this study have important consequences for diamond triode field emitter displays.**

***Index Terms*— CVD, diamond materials, electron emission, finite element methods.**

I. Introduction

DIAMOND is rapidly becoming a material of choice for field emission devices due mainly to its chemical immunity and negative electron affinity (NEA) [1], [2]. Recent advances in diamond film technology compatible with Si integrated circuit technology have led to inexpensive p-type polycrystalline diamond films [3] which can be used for field emission displays (FED) if high current densities can be achieved. Although field emission has been demonstrated from doped, undoped, polycrystalline, or crystalline diamond [4]–[9], it is not clear which type of diamond is best for field emission.

One important aspect of field emission from chemical vapor deposited (CVD) polycrystalline diamond is its dependence on processing parameters and patterning. In this study, in an effort to achieve high current densities, we design new experiments for a systematic study of field emission as a function of diamond quality measured by the sp^3/sp^2 ratio, grain size, doping level, patterning, field enhancement at the grain tips, and anode to emitter separation. The diamond films with low sp^3/sp^2 ratios, high density of small grains and grain boundaries, and patterned structures are found to be the best for high current densities and low emission fields.

II. Experimental

Encouraged by our earlier results [6], we developed a diamond field emitter testchip, using a 4-in wafer technology compatible with integrated circuit fabrication as shown in Fig. 1(a). The field emitter chip area, shown in Fig. 1(b), contains triode and diode display cells, diamond field emitter pressure sensors and a number of other diamond field emitter structures. Two different types of field emitter structures were fabricated. For the type A, targeted for pressure sensor applications, p-type diamond film was grown directly on p-type Si. For the type B, targeted for display applications, the diamond film was grown on oxidized Si and chromium was used as the contact to the diamond film.

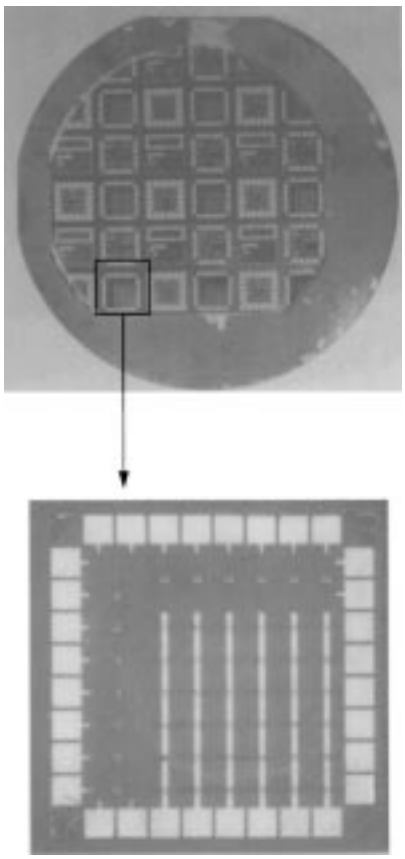

Fig. 1. (a) Test chips on a 4-in Si wafer and (b) a view of diamond field emitter test chip.

The fabrication process for the types A and B is depicted in Figs. 2 and 3, respectively. A 3-μm thick layer of SiO_2, deposited at 400 °C on p-type (100) Si, is annealed in N_2 at 1000 °C for 30 min to improve its insulating properties. For the type A structure, the oxide is patterned using buffered oxide etch and is used as a mask for Si etching [Fig. 2(a)]. Before the diamond growth, the seeding and patterning is accomplished using photoresist mixed with diamond powder

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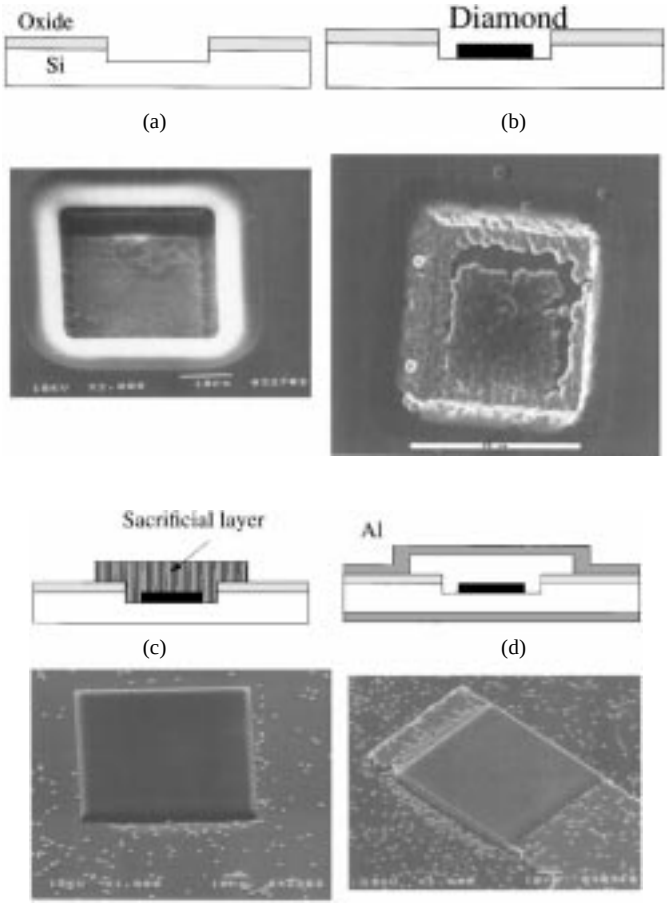

Fig. 2. Top and cross-sectional views of type A device in different process steps.

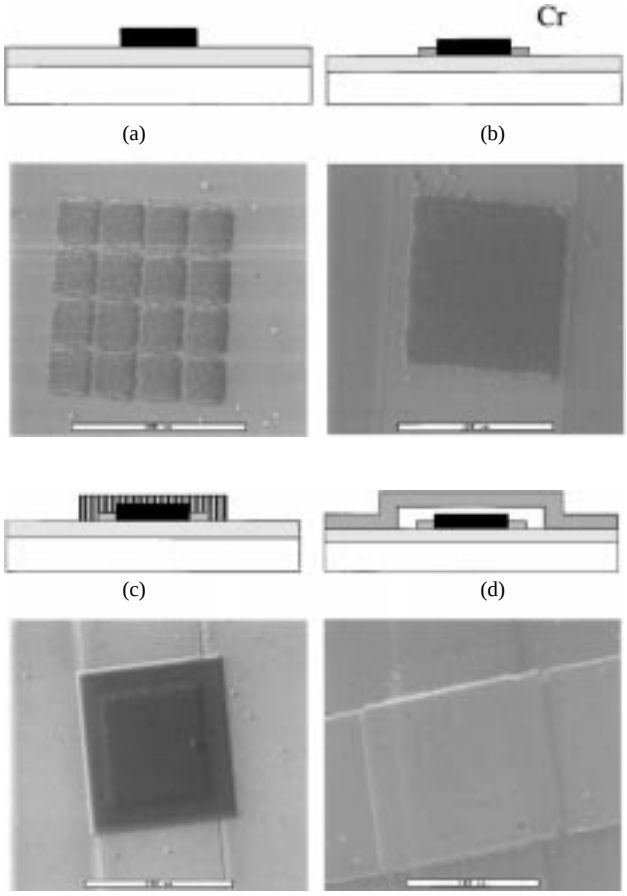

Fig. 3. Top and cross-sectional views of type B device in different process steps.

with an average particle size of 0.1 μm. The mixture is spin-coated and patterned using a standard lithographic process. As the diamond is typically deposited at 900 °C, the photoresist evaporates leaving behind the diamond particles which act as seeds for diamond growth by the CVD process [10]. Using hot filament CVD (HFCVD) reactor, p-type polycrystalline diamond is grown on Si for type A devices [Fig. 2(b)] and on SiO_2 for type B devices [Fig. 3(a)].

For the type B devices, approximately 2000 Å thick Cr is thermally evaporated on diamond and patterned. Using wet etching, the thickness of the Cr layer on diamond is reduced. As the diamond surface is rough [Fig. 3(b)], part of its surface is exposed after etching. Since some diamond emitters consist of a continuous film while others consist of patterned dots, we show SEM micrographs of a dot patterned film in Fig. 3(a) and a continuous film in Fig. 3(b). Photoresist, serving as a sacrificial layer, is spin coated at a speed of $\sim$1000 rpm and is patterned [Figs. 2(c) and 3(c)]. Al, thermally evaporated on top of the photoresist layer, is patterned and part of the sacrificial photoresist is now exposed to remove it. After removing the sacrificial layer, the separation between Al and diamond, computed by taking into account the thicknesses of sacrificial photoresist, oxide, etched Si and diamond film, is in the range of 9–10 μm for type A devices and 2–3 μm for type B devices. Al is also evaporated on the backside of the wafer to provide an ohmic contact for type A devices [Fig. 2(d)]. For type B devices [Fig. 3(d)], Cr is the cathode contact. Completed samples are annealed at 400 °C in N_2 ambient for 30 min using a rapid thermal processor.

III. Results and Discussions

Using the setups shown in Fig. 4(a) for type A and in Fig. 4(b) for type B, the current–voltage (I–V) measurements are taken by placing the samples inside a vacuum chamber with a pressure of 10^{-6} Torr. The current density J measured as function of field strength F for the diode structure is shown in Fig. 5 for type A and B devices. The current density measured at 0.2 MV/cm is approximately 0.5 A/cm^2 for type A device and 0.1 A/cm^2 for type B device. A number of factors may have contributed to the difference in the current densities for devices A and B. First, the diamond film is partly covered with Cr for type B devices, reducing the effective emission area. Secondly, the emitter contact resistance might have affected the emission at high emission current values, as the emitter with smaller contact resistance was found to exhibit higher current density [11]. It may be noted that for the type A device, the metal semiconductor contact is ohmic. Lastly, the different anode-to-emitter spacing for type A and B may affect the field at the emitting surface. The diamond surface consists of tiny tips of diamond due to the surface roughness. It was

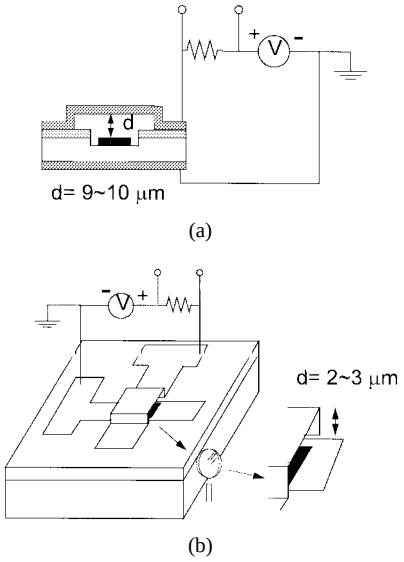

Fig. 4. Measurement setup for (a) type A and (b) type B device.

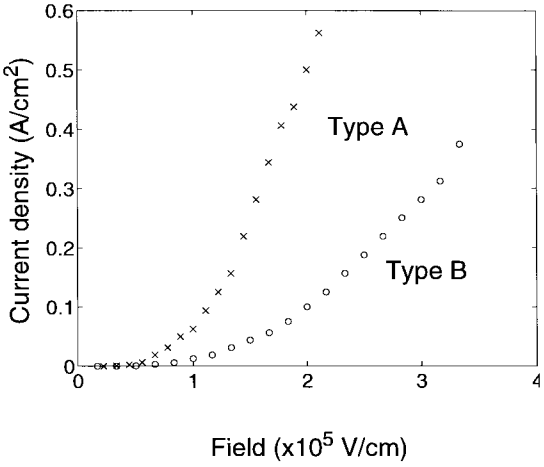

Fig. 5. I–V curve of diamond field emitter for type A and B device.

found [12] that, for the same field, a larger anode-to-emitter spacing results in a higher current. It is argued that as the anode is moved away from the emitter, the area of relatively uniform electric field under the probe expands, and more emitters can contribute to the measured current. Our simulation studies and measurements, which will be discussed later in detail, support this argument.

The testchip contains a number of type A and B device structures consisting of a continuous or patterned diamond film as the emitter. As shown in Fig. 6, for both types of emitters, the current density for an array of dots is higher than that of a continuous film for equal areas of the emitters. As the continuous and patterned films are prepared under similar deposition conditions, their doping level, surface morphology, sp^3/sp^2 ratio and surface termination are expected to be similar. Using a phosphor-coated glass plate as an anode, it was found that the emission from doped diamond films is nonuniform [6]. In another study [13], the emission from isolated diamond particles showed a higher current density than that from a continuous film. Although our results seem

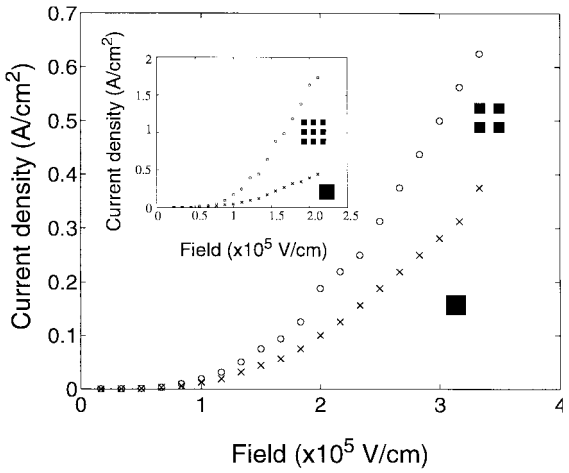

Fig. 6. I–V curves of type A (inset) and type B devices for continuous and array type emitters with the same total area.

to suggest a larger number of emission sites for the patterned emitter, it is not clear whether the enhanced emission takes place at edges. However, these findings raise an important question: What is the best emitter structure for achieving high current densities needed for FED?

To study the role of film deposition parameters on the field emission current density, three different sets of diamond films were prepared on p-type Si. Using different CH_4 concentrations in hydrogen, the samples with different sp^3/sp^2 ratios were produced in the first set. The sp^3/sp^2 ratio is calculated by subtracting the base line value from Raman spectrum and comparing count numbers at 1332 and 1550 cm^{-1}. In the second set, the boron doping concentration of films was varied using solid or powder sources for *in situ* doping of diamond [3]. The resistivity was measured by the four-point probe method. Depending upon the relative position from either solid source or boron powder crucible, the resistivity varies. The solid or powder sources were used to prepare samples in the high or low resistivity ranges, respectively. For the third set, diamond films with grain sizes in the range of $\sim$0.3 to $\sim$1.5 μm and film thicknesses in the ranges of $\sim$0.5 to 2.5$\sim\mu$m were prepared using initial nucleation densities in the ranges of 10^{11} and 10^8 cm^{-2} [14], respectively. Table I summarizes the deposition conditions of all the films used in this study.

For the field emission measurement, a 50-μm thick quartz plate was used as a spacer between the anode and the diamond emitter. A polished brass column was used as an anode. The details of the measurement setup are described elsewhere [6].

Fig. 7 shows I–V curves, Raman spectra, and SEM pictures for samples with CH_4/H_2 ratios of 0.5, 1, and 2%. With increasing CH_4 concentration, a deterioration of sp^3/sp^2 ratio and thus the diamond quality is indicated by the decreasing height of the diamond peak in the Raman spectra. The diamond with low sp^3/sp^2 ratio exhibits low emission fields and high current densities. It is particularly interesting to note from the SEM micrographs that with an increasing CH_4 concentration the number of small grains on the diamond surface increases, resulting in a higher density of grain boundaries. A similar trend is also observed in films grown in microwave CVD [15].

TABLE I
SUMMARY OF SAMPLE PREPARATION AND CHARACTERIZATION

Sample ID	CH_4/H_2	sp^3/sp^2 ratio	Growth time (hours) undoped+ doped	Doping source	Resistivity (Ωcm)	Emission field ($MVcm^{-1}$) at	
						0.01 $mAcm^{-2}$	1$mAcm^{-2}$
#1	0.5%	~5.4	6 + 2	B powder	~35	~0.36	~0.49
#2	1%	~4.1	6 + 2	B powder	~27	~0.23	~0.41
#3	2%	~1.3	6 + 2	B powder	~10	~0.15	~0.29
#4	1%	~6.3	8 + 0			~0.4	~0.68
#5	1%	~5.8	4 + 0		~189	~0.27	~0.39
#6	1%	~3.7	0 + 8	B_2O_3 wafer	~52	~0.3	~0.45
#7	1%	~4.8	6 + 2	B_2O_3 wafer	~110	~0.33	~0.38
#8	1%	~3.3	0 + 8	B powder	~3	~0.18	~0.29
#9	1%	~2.8	0 + 2	B powder	~1.7	~0.1	~0.18

A higher CH_4 concentration results in lower resistivity as measured by 4-point probe method. As the density of grain boundaries is enhanced through high CH_4 concentration, their contribution to the conduction may be responsible for the observed low resistivity. This may suggest that the presence of graphitic phase may be related the enhanced conduction.

As the high doping levels affect sp^3/sp^2 ratio, grain boundaries and grain sizes [16], we studied the effect of doping on the field emission current. As seen in Fig. 8, the doped film shows enhanced emitter current. Again, the low sp^3/sp^2 ratio and high density of grain boundaries seems to result in a low field and high current density. Although during the preparation of the undoped sample no dopant source was used, the early stage of noncontinuous film shows some conductivity with resistivity larger than 1 kΩcm as evident from the 4-point probe measurement. When it is grown longer and becomes continuous, this conducting behavior disappears probably indicating that B source, presumably from p-type Si wafer, is now completely covered by diamond film and diamond film is becoming nonconducting. During the measurements on some undoped films, arc was observed before the start of the emission, the origin of which is not well understood.

To produce samples with large differences in doping levels, boron powder or B_2O_3 wafer was used as a dopant source. As shown in Fig. 9, although CH_4 concentration is the same, sp^3/sp^2 ratio tends to decrease with increasing B concentration. Highly doped film shows low field and high current density emission. In our earlier experiments [17], it was found that a diamond film deposited directly on Si results in a lower sp^3/sp^2 ratio than the one deposited on top of an undoped diamond film. As shown in Fig. 10, the emission current from a doped film deposited directly on Si was higher than that of a film deposited on top of undoped diamond. In all the above results, the relationship between the low emission field and i) low sp^3/sp^2 ratio and ii) high grain density is consistently obvious. Another interesting feature of the results is the presence of both small and large grains. Lower quality diamond films were found to results in enhanced emission in earlier studies [12], [13].

It would be interesting now to compare the emission behavior of small and large grain films. As shown in Fig. 11, the small grain film results in the lowest emission field (Table I). In an earlier study, current densities in the range of 10 Acm^{-2}, the highest reported for diamond, were reported for nanocrystalline diamond [5].

The data in the present study provides an experimental evidence for the enhancement of current density and reduction in the emission field for diamond films with low sp^3/sp^2 ratios, high doping densities, and large densities of grain boundaries (i.e., high densities of small grains). Field enhancement at the grain tips, surface termination, defects, number of emission sites and grain orientation may have played a role in the field emission. These considerations lead to a number of questions: Does the fine grain film result in a higher density of emission sites than a film with a combination of small and large grains? Are these emission sites related to field enhancement at the tips? Is the presence of defects in diamond necessary for field emission from p-type or undoped diamond? Is the field emission from single crystal diamond with a smooth surface [18] also related to defect densities?

Electron emission has been reported [18] from flat surface of boron-doped natural diamond. In this case, defects, orientation, and surface passivation of the diamond may be among the critical factors. However, in the case of polycrystalline diamond, additional factors such as grain boundaries, grain

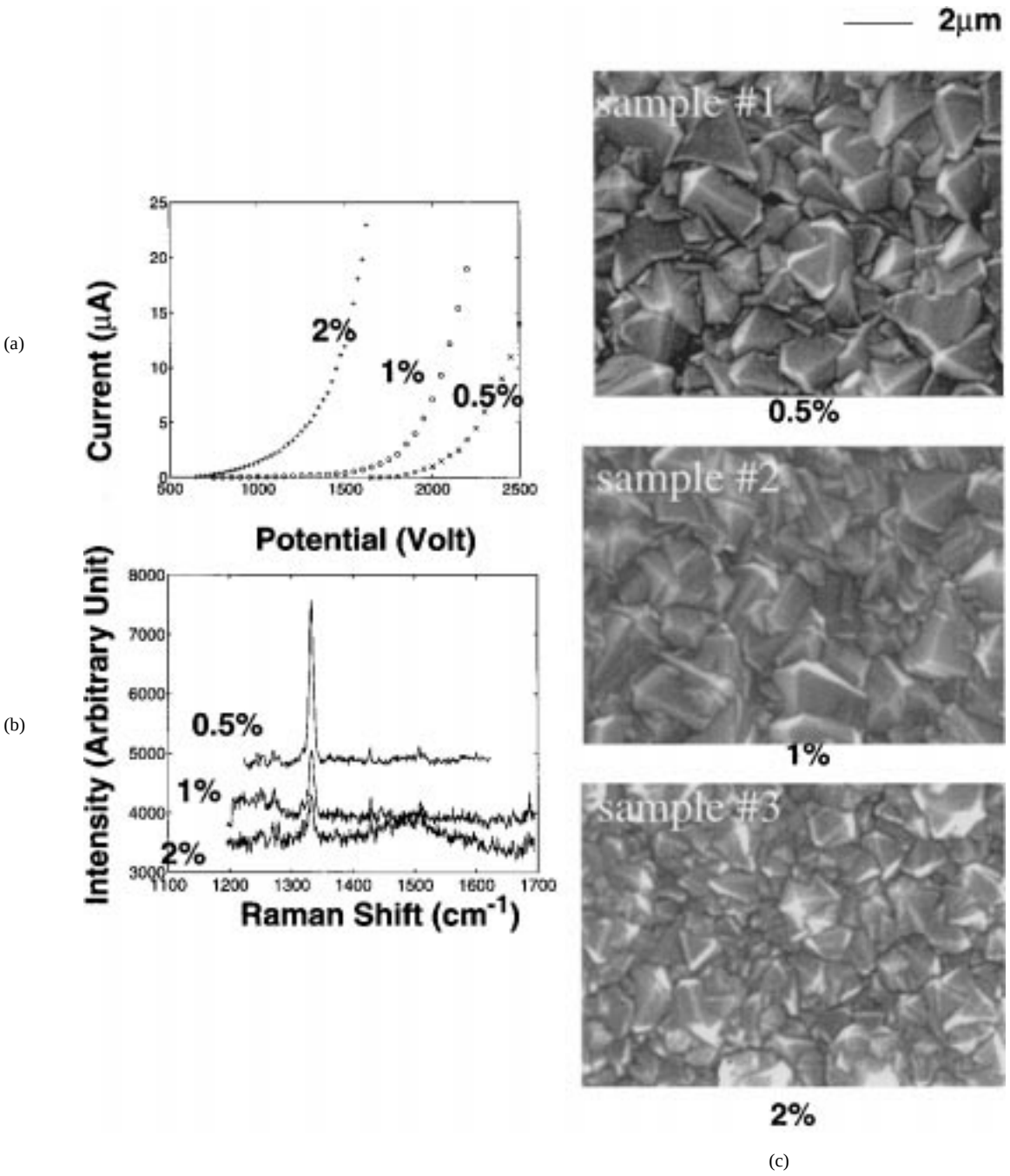

Fig. 7. (a) I–V curves, (b) Raman spectra, and (c) SEM pictures of samples for samples with different CH_4 concentrations.

size differences, high densities of surface defects and the field enhancement at grain tips, should be taken into account. The lower threshold fields and higher current densities for polycrystalline than those of single crystal diamond have been attributed to lower sp^3/sp^2 ratios and the related defects found in polycrystalline films [12], [13]. The role of field enhancement at the grain tips may vary for small and large grain films, and for films containing both the small and large grains. The density of emission sites in a particular film may depend on field enhancement, grain size, surface termination, and defect densities. We simulated the effect of field enhancement at the grain tips on the field emission using films with small and large grains.

When both the small and large grains are present on the diamond surface, the height of large grains can lead to a larger field at their tips and, therefore, the emission may be initiated at these sites first when a field is applied. The small grains present between the large grains will have a lower field at their tips and the field emission will primarily take place from the highest tips. However, when the number of small grains between the large grains increases, the density of emission sites in the small grains area increases. Thus, for a film consisting of small grains only, a larger density of the emission sites may be observed due to similar fields at the emitting tips.

As shown in Fig. 12, films with small and large grains, categorized into types I, II, III, and IV, were simulated to

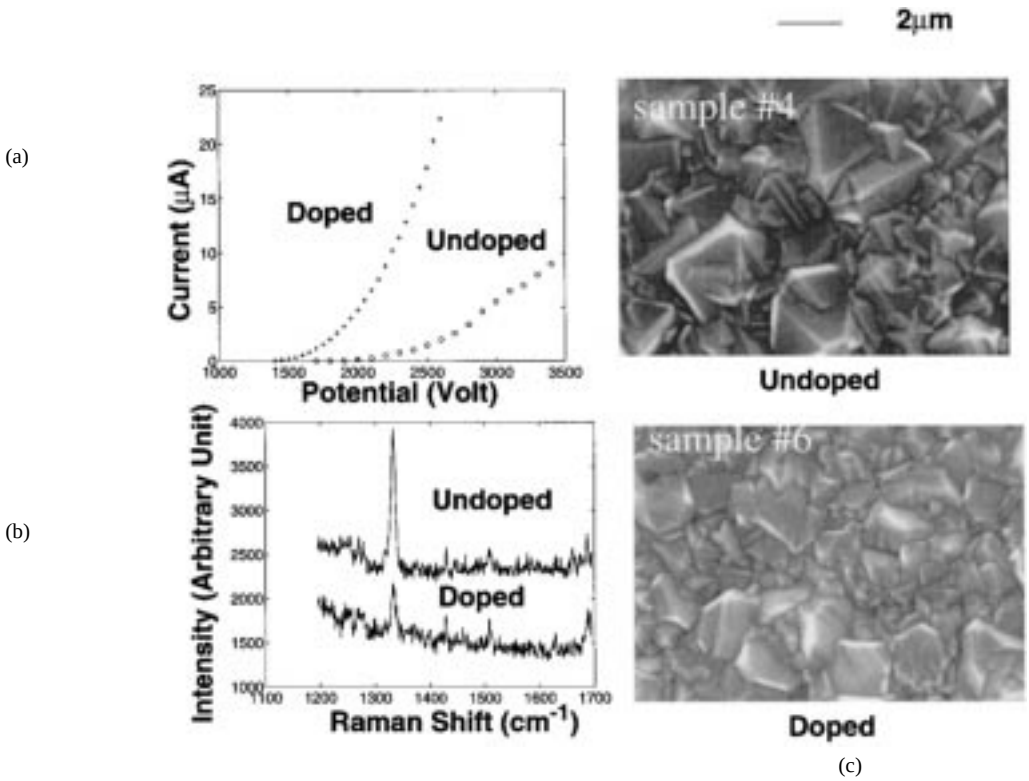

Fig. 8. (a) I–V curves, (b) Raman spectra, and (c) SEM pictures of samples for samples with doped and undoped film.

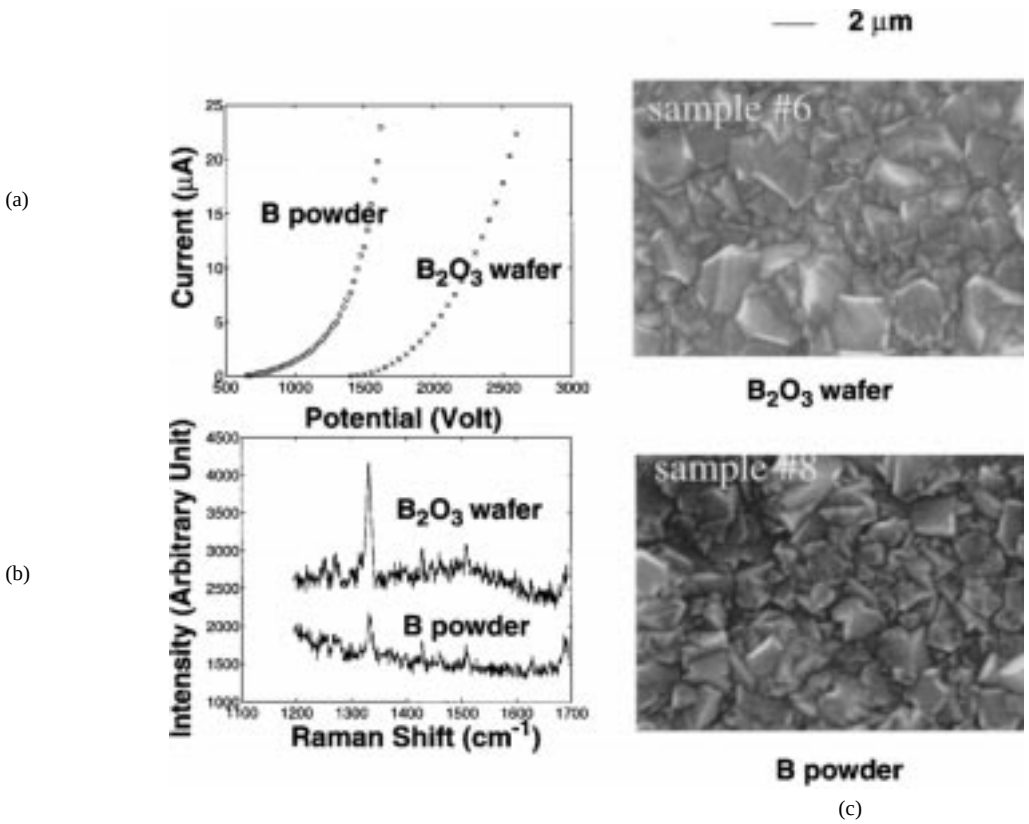

Fig. 9. (a) I–V curves, (b) Raman spectra, and (c) SEM pictures of samples for samples doped with two different doping methods.

study the field enhancement using anode to emitter separations of 1 or 10 μm. Fig. 13 shows electric fields at the tips for the four emitter types. Data shows that field enhancement is larger when separation between the neighboring tips and anode to cathode is larger. This result is consistent with previous simulation studies of Si microtip emitters [19]. This may

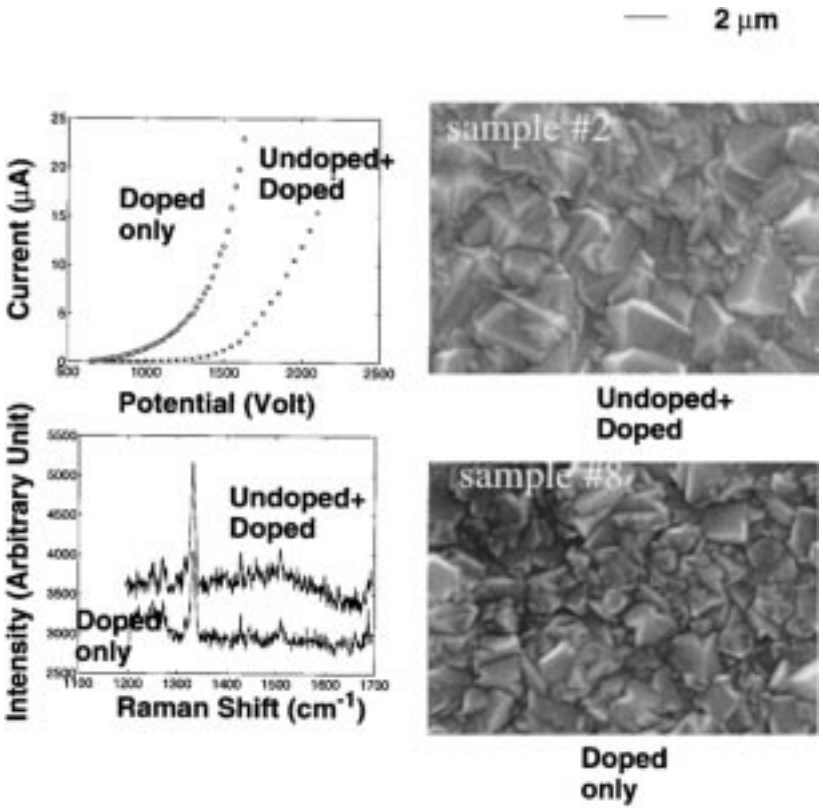

Fig. 10. (a) I–V curves, (b) Raman spectra, and (c) SEM pictures of samples for samples with doped only layer and doped layer over undoped layer.

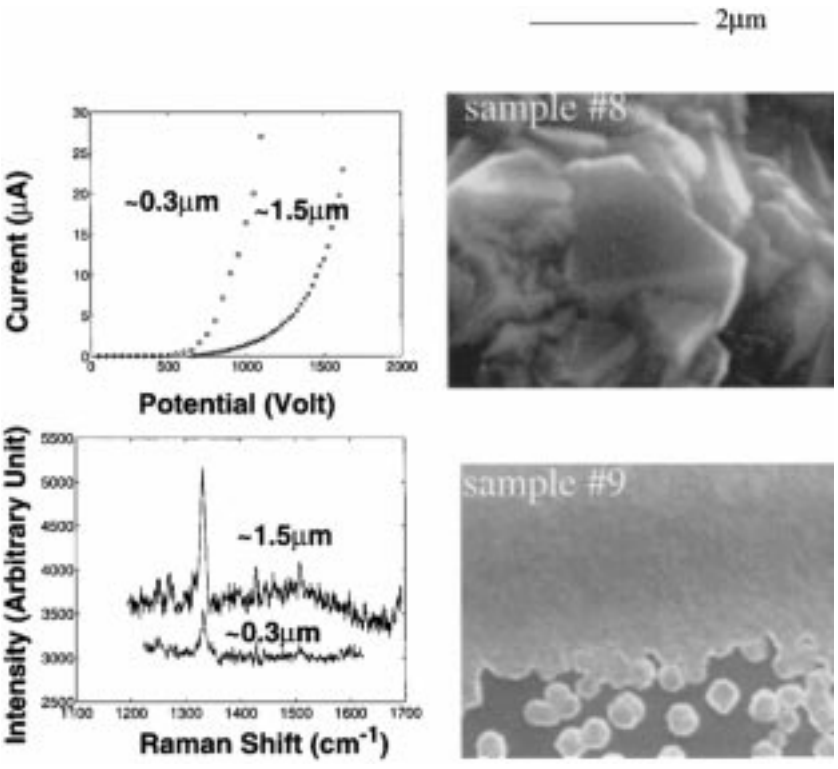

Fig. 11. (a) I–V curves, (b) Raman spectra, and (c) SEM pictures of samples for samples with different grain size.

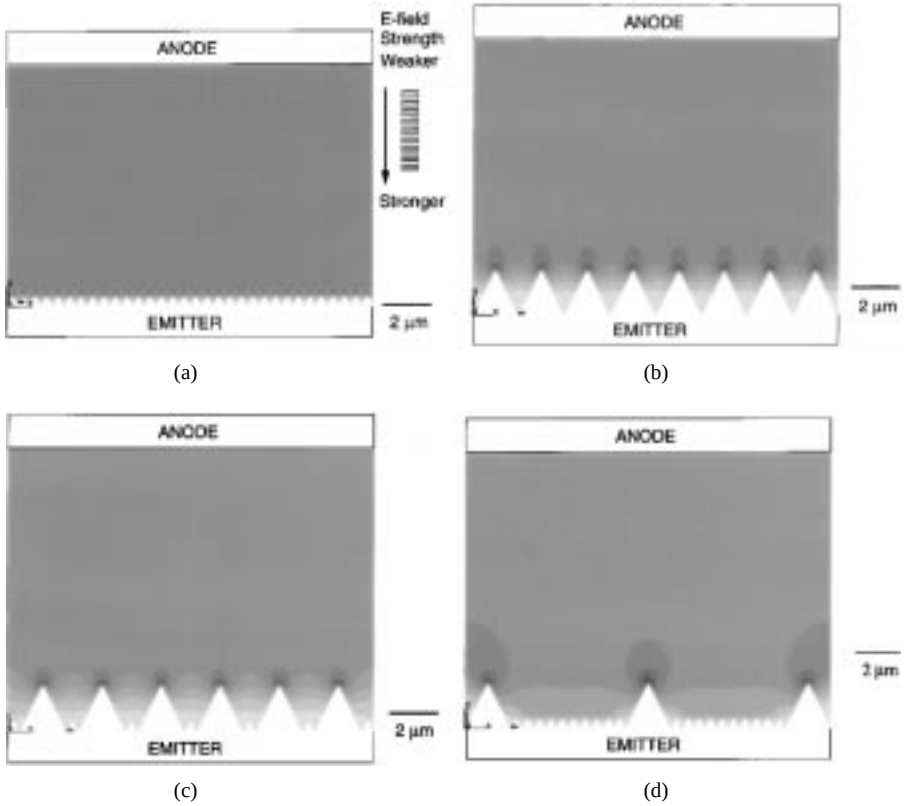

Fig. 12. Four different structures for ANSYS simulation: (a) Type I, (b) Type II, (c) Type III, and (d) Type IV.

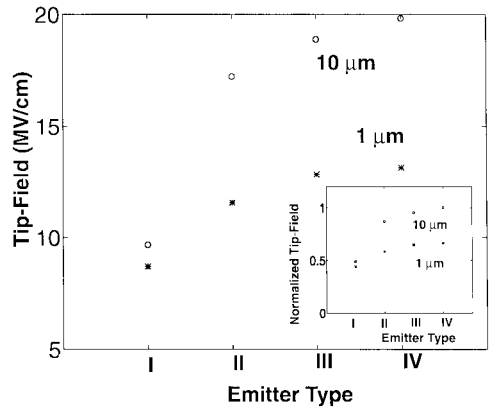

Fig. 13. Simulated electric fields at the tip for different types for anode to emitter distances of 1 and 10 μm.

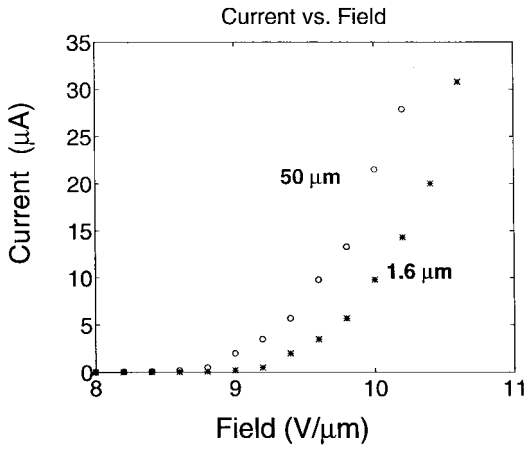

Fig. 14. Measured emission current as a function of field for anode to emitter distances of 1.6 and 50 μm.

suggest that the emission is enhanced when anode to emitter distance is larger at a given field strength and may indicate that emission is predominantly coming from grain tips. To verify this effect experimentally, the same film was measured for anode to emitter separations of 1.6 and 50 μm. As shown in Fig. 14, the larger separation results in higher current and lower threshold field.

The adsorption of H on the surface of diamond is known to lower its electron affinity [20]. As all our samples were treated in hydrogen plasma in the HFCVD system just after the diamond film deposition, it is believed that the film surface is passivated with hydrogen for all samples. It is conceivable that the surface termination with hydrogen is more pronounced for small grain films due to a larger density of grain boundaries. Consequently, the enhanced field emission behavior of small grain films may also be due to low electron affinity.

IV. Conclusions

Boron-doped polycrystalline diamond films with low sp^3/sp^2 ratios, high density of small grains and grain boundaries, and patterned structures result in high current densities and low emission fields. Electric fields to initiate emission, measured at $J = 0.01$ mAcm^{-2}, are in the range of 0.1–0.4 MV/cm depending upon diamond growth conditions. The results of this study have important consequences for diamond triode field emitter displays.

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