Electron field emission from ion-implanted diamond

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Diamond films and islands grown by chemical vapor deposition were implanted with boron, sodium, and carbon ions at doses of $10^{14}-10^{15}/\mathrm{cm}^2$. This structural modification at the subsurface resulted in a significant reduction of the electric field required for electron emission. The threshold field for producing a current density of 10 $\mathrm{mA/cm}^2$ can be as low as 42 V/μm for the as-implanted diamond compared to 164 V/μm for the high quality *p*-type diamond. When the ion-implanted samples were annealed at high temperatures in order to anneal out the implantation-induced defects, the low-field electron emission capability of diamond disappeared. These results further confirm our earlier findings about the role of defects in the electron emission from undoped or *p*-type doped diamond and indicate that the improved emission characteristics of as-implanted diamond is due to the defects created by the ion implantation process. © *1995 American Institute of Physics.*

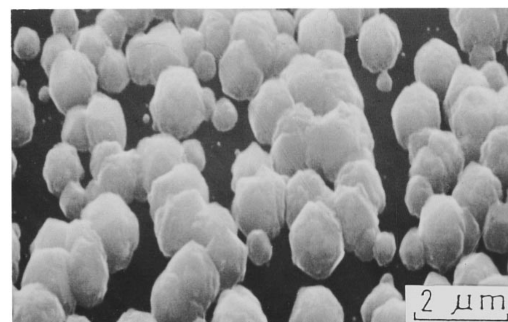
Field emission displays (FEDs) have the potential to be a low cost, high performance alternative to the currently dominant cathode ray tube and liquid crystal display technologies for flat panel displays. One of the key issues in FEDs has been the development of a reliable and efficient cold cathode material for electron field emitters. Earlier field emitters typically employed metals (such as Mo) or semiconductors (such as Si) with nanometer-sized sharp tips.[1] These emitters typically require complicated fabrication steps and need high control voltages for emission (~100 V) because of the high work functions associated with these materials.

Diamond has recently emerged as a desirable material for field emitters.[2–6] However, little is known about the mechanisms responsible for the electron emission, especially from the undoped or *p*-type doped diamond. Undoped diamond is known to be highly insulating which makes stable electron field emission impossible, while in *p*-type semiconducting diamond, the Fermi level is at least 5 eV below the vacuum level which is not helpful for low-voltage electron emission. Although surface states existing in the band gap, there are no obvious electron transport mechanisms to these surface states which can sustain the emission from undoped or *p*-type doped diamond.

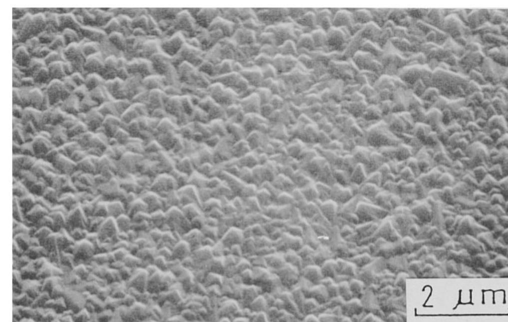
We have recently carried out an experimental and analytical study of field emission from both undoped and *p*-type doped diamond produced by chemical vapor deposition (CVD).[7] The study demonstrated a strong correlation between the emission properties and the defect densities in diamond. This letter further confirms the role of defects by reporting the effects of ion bombardment on the field emission characteristics of CVD diamond.

The diamond samples were prepared by microwave plasma enhanced CVD at 900–950 °C on *n*-type Si substrates using a gaseous mixture of 0.3%–0.8% methane in hydrogen. As shown in Fig. 1, diamond with both the island-type and continuous film-type surface morphologies were grown. Both types of samples present crystallographically defined sharp tips or edges which naturally become effective field emitters due to the effect of field concentration at sharp features. The island-type morphology potentially has the additional advantage for stable emission that the conductive path could be directly established between the substrate and the emitting surface rather than through the bulk of diamond as in the case of a continuous film.

The as-grown diamond samples were subjected to room-temperature implantation of 30 keV boron ions at doses of $10^{14}/\mathrm{cm}^2$ and $10^{15}/\mathrm{cm}^2$, 550 keV sodium ions at a dose of $10^{14}/\mathrm{cm}^2$, and 60 keV carbon ions at doses of $10^{14}/\mathrm{cm}^2$ and $10^{15}/\mathrm{cm}^2$, respectively. Under such conditions, the concentration of implanted atoms can be calculated to be peaked in a depth ranging from ~50 nm for boron, ~90 nm for carbon, to ~500 nm for sodium beneath the surface of diamond.[8] The energetic ion implantation, even at the moderate doses used here, is known to cause structural damage and defect



(a)



(b)

FIG. 1. SEM micrographs of CVD diamond samples showing (a) an island-type emitter and (b) a continuous film-type emitter.

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TABLE I. Field emission properties of various diamond samples.

Sample No.	Growth conditions	Post-growth treatment	Morphology	FWHM of Raman peak (cm^{-1})	Turn-on field (V/μm)[a]	Threshold field (V/μm)[b]	Comments
1	0.4% CH_4/H_2 7 h	⋯	Island	3.8	⋯	⋯	No emission
2	0.8% CH_4/H_2 45 h	⋯	Continuous film	4.2	⋯	⋯	No emission
3	0.3% CH_4/H_2 30 h	B doped during growth	Continuous film	3.7	111	164	B content 10^{20} cm^{-3}
4	0.4% CH_4/H_2 7 h	B implanted (10^{14} cm^{-2})	Island	7.9	47	75	⋯
5	0.4% CH_4/H_2 7 h	B implanted (10^{15} cm^{-2})	Island	7.5	37	62	⋯
6	0.8% CH_4/H_2 7 h	B implanted (10^{15} cm^{-2})	Continuous film	7.2	87	117	⋯
7	0.8% CH_4/H_2 7 h	Na implanted (10^{14} cm^{-2})	Continuous film	8.3	15	58	⋯
8	0.5% CH_4/H_2 7 h	C implanted (10^{14} cm^{-2})	Continuous film	8.9	47	80	⋯
9	0.5% CH_4/H_2 7 h	C implanted (10^{15} cm^{-2})	Continuous film	9.4	23	42	⋯
10	0.4% CH_4/H_2 7h	B implanted (10^{14} cm^{-2}) and annealed at 1000 °C/2 h	Island	5.0	⋯	⋯	No emission
11	0.8% CH_4/H_2 7 h	Na implanted (10^{14} cm^{-2}) and annealed at 975 °C/1 h	Continuous film	8.1	⋯	⋯	No emission

[a]Turn-on field is defined as the electric field required to produce a current density of 0.01 mA/cm^2.
[b]Threshold field is defined as the electric field required to produce a current density of 10 mA/cm^2.

generation in the surface region of various materials, including diamond.[9,10] Raman spectroscopy indicated that the full width at half-maximum (FWHM) of the diamond peak at 1332 cm^{-1} increased after the ion implantation, suggesting that defects were generated in diamond. Table I lists the diamond samples, their Raman characteristics, and the electric fields (voltage per micron distance between the anode and cathode) required to produce an emission current density of 0.01 and 10 mA/cm^2, respectively.

Details of the experimental setup and procedures for field emission measurements have been given earlier.[7] Briefly, a voltage up to +2 kV was applied to a tungsten probe to collect emitted electrons from the diamond samples. A precision step controller (3.3 μm step size) was used to control the movement of the probe toward the sample surface, and the emission current–voltage (I–V) characteristics was measured as a function of the distance between the anode probe and the cathode diamond surface. The obtained I–V data were analyzed using the classic Fowler–Nordheim theory[11] by taking into account variations of the geometric (field enhancement factor β) and electronic (work function ϕ) properties among the active diamond emitting tips under the probe. Details of the numerical curve fitting analysis and extrapolation for the emission data have been published earlier.[7] Although it is found to be difficult to determine the individual values of β, ϕ, and the emitting area parameter α, from the data analysis, the electric fields needed to generate current densities of 0.01 mA/cm^2 (defined as the turn-on field) and 10 mA/ cm^2 (defined as the threshold field which is typically required for effectively exciting a phosphor pixel in a flat panel display) were calculated and used as a figure of merit to rank the various diamond samples.

Typical emission I–V curves are shown in Fig. 2. In the figure, the voltage was raised from zero to the maximum (+2 kV) and then decreased to zero. As the probe moved one step closer (3.3 μm) to the sample surface, the above voltage cycle was repeated. The maximum current was limited by a protective circuit to 3 μA. The as-deposited, high quality diamond films or islands (samples No. 1 and No. 2 in Table I) showed no electron emission except an arc that formed when the anode probe was moved very close to the diamond surface [Fig. 2(a)]. This is indicative of an electrical breakdown of the surface under the intense field from the probe,

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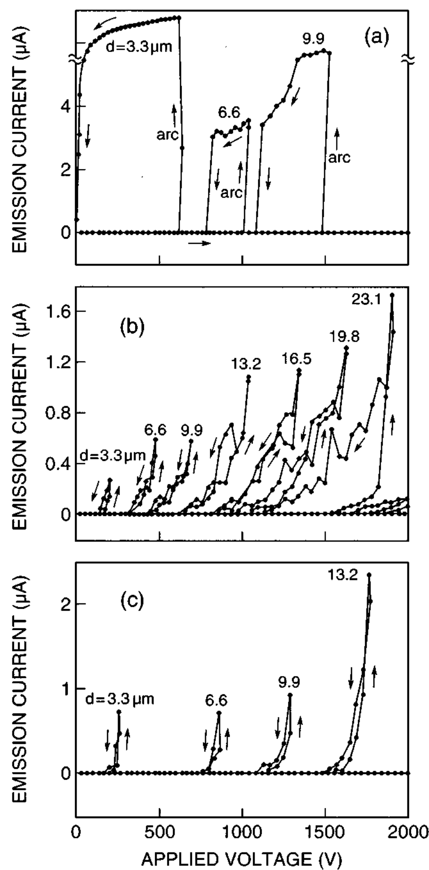

FIG. 2. Typical *I–V* emission curves from diamond measured as a function of the distance (d) between the anode probe and the cathode diamond surface. (a) sample No. 1, (b) sample No. 5, and (c) sample No. 3.

which is believed to be associated with the highly insulating nature of the diamond.

However, when the diamond samples were subjected to ion implantation (samples No. 4–No. 9 in Table I), characteristic Fowler–Nordheim emission curves were obtained as shown in Fig. 2(b). The current varied smoothly and consistently with the voltage and in an approximately history-independent manner, indicating sufficient conductivity of the samples which was mostly likely along the ion-implanted surface region. Calculations of both the turn-on field and threshold field based on curve fitting of the Fowler–Nordheim equation gave a value of 37 and 62 V/μm, respectively, for this particular sample (sample No. 5). This represents a significant reduction from the field required for the high quality, *p*-type semiconducting diamond [111 V/μm for the turn-on field and 164 V/μm for the threshold field for sample No. 3 as shown in Fig. 2(c)]. Reproducibility tests of the emission behavior from different locations of the same sample and from other similarly treated samples consistently yielded fields which were much below that required for the high quality, *p*-type diamond sample (see Table I).

The emission characteristics of the as-implanted samples were further found to be insensitive to atmospheric exposure. When a sample was exposed to air for weeks and even months after the implantation, it exhibited the same emission behavior as the freshly implanted sample. This suggests that the modified surface structure produced by the implantation process is very stable and chemically inert.

However, when the implanted samples were annealed in a hydrogen atmosphere at a high temperature of 975–1000 °C for 1–2 h (samples No. 10 and No. 11 in Table I), a similar arcing phenomenon as shown in Fig. 2(a) occurred. The possible reason is that the defects near the surface region were annealed-out, while the dopants (boron or sodium) were still not effectively activated, resulting in relatively insulating films.

These results suggest that the defects introduced in the surface regions by ion implantation increased the conductivity and altered the work function of as-grown diamond samples, thus directly affecting their field emission properties. While the exact nature of the responsible defects is yet to be identified, the types of defects formed can include vacancies, dislocations, stacking faults, and second phases such as graphite and amorphous carbon components. When the number of these defects is significant, the electronic states of defects could form a band or bands within the bulk diamond band gap.[12,13] Electrons can be emitted directly into vacuum from these band(s) or be transported to the surface states for emission. This is consistent with our earlier findings about the roles of defects in a field emission process from diamond.[7] In essence, the formation of these defects and their associated electronic structures elevates the Fermi level, and consequently, the energy barrier that the electrons must tunnel through is reduced.

In summary, the field required for emission from CVD diamond can be significantly reduced when the diamond is implanted by energetic ions. The as-implanted samples typically demonstrate a turn-on field (for a current density of 0.01 mA/cm^2) of 15–45 V/μm and a threshold field (for a current density of 10 mA/cm^2) of 40–80 V/μm. These field values were significantly lower than those required for high quality, *p*-type semiconducting diamond. The results suggest that the broad types of defects created by the ion implantation are responsible for electron emission at low electric fields.

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