# Field emission properties of diamond films of different qualities

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Field emission properties of diamond films were studied by macroscopic $I-V$ measurement. A lower turn-on field and a higher emission current were observed for diamond films produced by higher methane concentration, or with higher density of defects, introduced by ion implantation. However, diamond films of poorer quality experience a severe reliability problem. Cold implantation followed by rapid thermal or laser annealing produced diamond emitters with a turn-on field as low as 5 V/$\mu$m and the desired reliability. © *1997 American Institute of Physics.* [S0003-6951(97)04242-3]

As most results of low field emission are from chemical vapor deposited (CVD) diamond of both $n$ and $p$ type, with poorly characterized surfaces, it now seems clear that negative electron affinity (NEA) is not fully responsible for the process. In fact, there is a wide range of models such as the defect model,[1] the conducting channels in insulating diamond,[2] dielectric breakdown,[3–5] tip emission,[6] tunneling,[7] and hot electron injection,[8] that attempt to explain low field emission. In this work, we report on the effect of defects and activated dopants on the field emission properties of diamond films of various qualities and the related reliability problems of these diamond emitters under high applied electric field.

Diamond films studied in this report were deposited on (100) silicon substrates utilizing a 5 kW AsTex 5400 microwave plasma CVD system. The general biased nucleation and nonbiased growth conditions were reported elsewhere.[7] Detailed growth parameters of the samples tested are listed in Table I. The schedule of ion-implantation experiments is detailed in Table II. All of the implantation experiments were performed at liquid nitrogen temperature to try to minimize the ion damage to the diamond film samples. The samples were subsequently subjected to a RTA in a tube furnace at 1000 °C, for 10 min in a forming gas atmosphere. Some samples were not given RTA treatment in order to assess and to contrast their electrical properties with those that were treated. Laser annealing was undertaken at an excimer laser wavelength of 193 nm using a Lambda Physik Compex system, which delivered an average fluence of 100 mJ/cm$^2$ to the sample film per pulse. A pulse repetition rate of 1 Hz was used in this study to irradiate a given sample for periods up to 200 s.

Surface analysis was carried out using a Renishaw 2000 Ramanscope system (He–Ne laser), and a JEOL 6400 scanning electron microscope (SEM).

Figure 1 shows the $I-V$ curves of diamond films produced by 6%, 10%, and 12% methane concentration. The microstructures of these diamond films were reported elsewhere.[7] Clearly a lower turn-on field and higher emission current can be achieved by diamond films with a higher graphite content or defects, which were estimated by the $D$ and $G$ bands in Raman spectra. Similar results were also observed in ion-implanted samples (Table III). However, serious reliability problems occurred in these diamond emitters. For thin diamond films (about 2 $\mu$m) of poor quality, the graphite channels used to conduct currents have experienced a serious surface reconstruction in the high applied field. Figures 2(a) and 2(b) show the melting and recrystallization of low quality, graphitic, diamond grains in diamond films (randomly oriented crystallites) deposited on $p$- and $n$-type silicon substrates, respectively, by an applied field of 60 V/$\mu$m. The distinctively different morphology of the reconstructed surface suggests that either a different microstructure exists in diamond films deposited on $n$- and $p$-type silicon, or a different emission mechanism is involved due to the different majority carriers on $n$- and $p$-type silicon substrates.

For thicker diamond films (thickness larger than 5 $\mu$m) of better quality (methane concentration less than 6%), the large hysteresis loop was observed during the initial voltage running up and down. Reproducible $I-V$ curves can only be obtained after a high field ($>$120 V/$\mu$m) surface conditioning, which are accompanied by vacuum arc discharges. Diamond surfaces are covered by evenly distributed craters with diameters of a few microns and depth down to the silicon substrate (Fig. 3). The sharp facets of diamond crystals became much more smoother near the vicinity of emission sites. This SEM image is very similar to that observed where dielectric breakdown occurred.[9]

Table III lists the voltage threshold and the line width of Raman diamond peak at 1332 cm$^{-1}$ for implanted diamond

TABLE I. CVD diamond film growth parameters.

| Sample number | Growth | | |
|---|---|---|---|
| | Microwave power (kW) | $CH_4/H_2$ (sccm) | Substrate temp. (°C) |
| W-1 | 2 | 4/200 | 700 |
| TW-3, TW-4 | 2.5 | 24/200 | 925 |
| TW-2 | 2.5 | 24/200 | 700 |
| TW-6 | 2 | 20/200 | 700 |
| TW-12, TW-17 | 2 | 12/200 | 700 |

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TABLE II. Ion-implantation parameters.

| Sample | Ion species | Energy, keV | Dosage, $cm^{-2}$ | Anneal | Comment |
|---|---|---|---|---|---|
| TW-3-B | *B* | 50 | $1.58\times10^{14}$ | No anneal | Flat profile |
| | | 40 | $6.35\times10^{13}$ | | $5\times10^{19}$ $cm^{-3}$ |
| | | 30 | $1.22\times10^{14}$ | | |
| | | 20 | $1.05\times10^{14}$ | | |
| TW-4/1-B | *B* | 2000 | $7.30\times10^{13}$ | Rapid thermal | Flat profile |
| | | 1900 | $7.45\times10^{13}$ | anneal (RTA), | $1\times10^{-19}$ $cm^{-3}$ |
| | | 1800 | $8.13\times10^{13}$ | 1000 °C for 10 | |
| | | 1700 | $8.09\times10^{13}$ | min | |
| TW-4/2-B | as 4/1 | as 4/1 | as 4/1 | No anneal | as 4/1 |
| W-1-NP | *N* | 30,24,18,12 | $3.3\times10^{14}$ | RTA (1000 °C for | |
| | *P* | 50,40,30,20 | $6.6\times10^{14}$ | 30 min) | |
| W-1-B | *B* | 18.75 | $1.05\times10^{14}$ | No anneal | $4.55\times10^{19}$ $cm^{-3}$ |

TABLE III. Field emission turn-on field and Raman ''diamond'' linewidths for implanted diamond films.

| | Voltage Threshold | | | Raman Diamond Linewidth | | |
|---|---|---|---|---|---|---|
| Samples | Untreated | RTA | Laser anneal | Untreated | RTA | Laser anneal |
| TW-3-B | 10 V/μm | | 20 V/μm | 3.66 $cm^{-1}$ | | 2.70 $cm^{-1}$ |
| W-1-B | 46 V/μm | | 22 V/μm | 4.18 $cm^{-1}$ | | 2.16 $cm^{-1}$ |
| TW-4/1-B (RTA) | | 22 V/μm | | | 2.13 $cm^{-1}$ | |
| TW-4/2-B | 13 V/μm | | 23 V/μm | 3.99 $cm^{-1}$ | | 2.19 $cm^{-1}$ |
| W-1-NP | | 5 V/μm | | | 2.03 $cm^{-1}$ | |

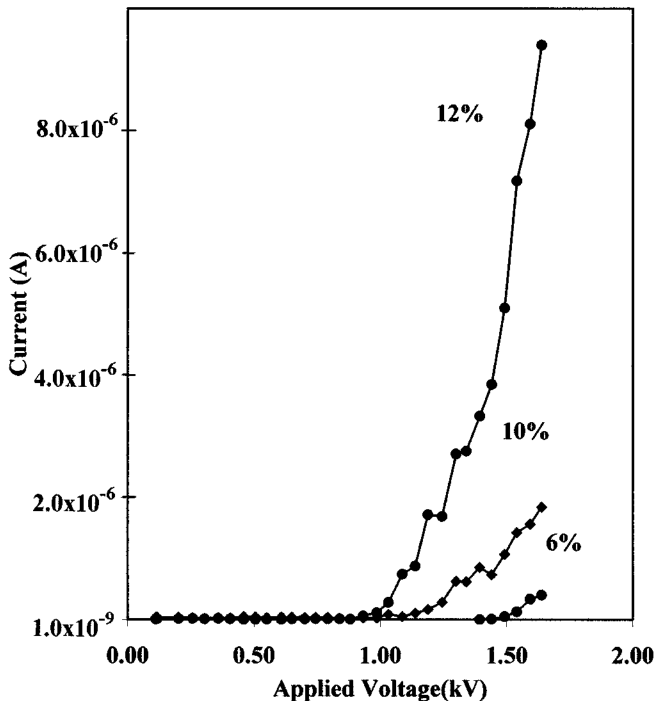


FIG. 1. $I-V$ curves of diamond films produced by 6%, 10%, and 12% methane concentration with 20 μm anode-cathode gap.

films. In general, it was noted from the narrowing of Raman peak, that the surface treatment by laser annealing was as effective as RTA at reducing the defects present within a given CVD film. However, this improvement in diamond quality was gained at the expense of an increase in the applied electric field required to initiate electron emission for low quality undoped and boron-doped diamond films. These observations are consistent with that reported by Zhu *et al.*[10,11] The field emission results are quite different for boron-, nitrogen-, and phosphorus-implanted, high quality diamond films defined by the full-width at half-maximum (FWHM) of 1332 $cm^{-1}$ diamond peak, being less than 2.2 $cm^{-1}$. Boron implantation on W-1 free-standing white diamond reduced the turn-on field from 80 V/μm to 46 V/$\mu m^{-1}$, further reduction of the turn-on field to 22 V/μm was achieved by laser annealing for 200 s. W-1 with multiple *N* and *P* implantation followed by RTA at 1000 °C for 30 min is found to provide the best field emission performance. The FWHM of this implanted and annealed W-1 was restored back to 2.03 $cm^{-1}$. Figure 4 shows the $I-V$ curve of W-1-NP with a turn-on field as low as 5 V/μm. These results suggested that activated dopants other than defects might be responsible for the reduction of turn-on field in high quality implanted diamond films followed by annealing. No significant damage was observed in *N* and *P* implanted W-1 dia-

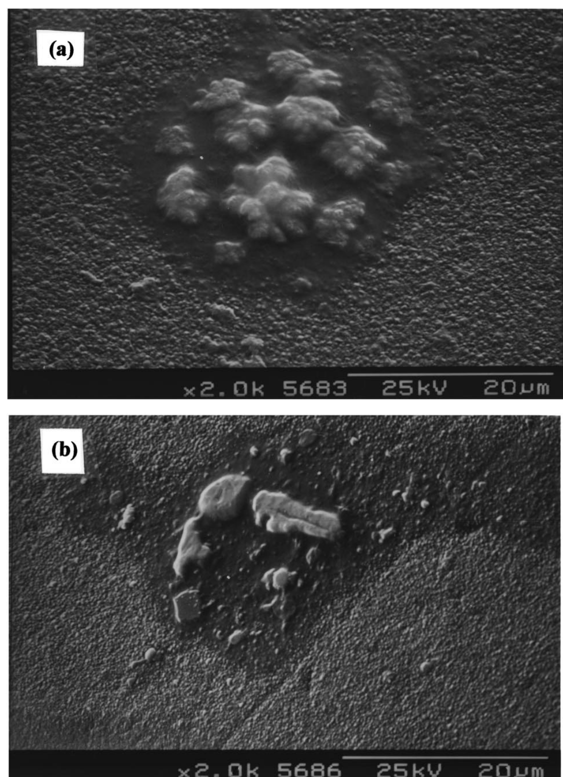


FIG. 2. SEM images of the surface morphology of a diamond film (a) deposited on $p$- and (b) on $n$-type silicon substrates, respectively, after field emission tests by an applied field of 60 V/$\mu$m.

mond film after field emission tests with the applied electric field as high as 150 V/$\mu$m.

Undoped diamond films of higher graphite contents and defects gave lower turn-on field and higher emission currents. However, they are prone to serious breakdown by high electric field and emission current. In general, it was found that the RTA and laser annealing were both effective at reducing the defects present within a given CVD film. However, this improvement in diamond quality was gained at the expense of an increase in the applied electric field required to initiate electron emission. RTA or laser annealing after multiple $N$ and $P$ implantation in high quality diamond films were found to be able to restore the quality of the diamond and to activate the dopants. These $n$-type diamond films provided the best field emission performance and were less susceptible to dielectric breakdown.

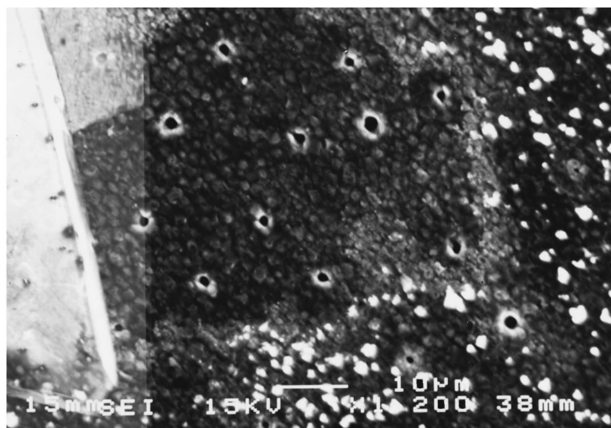


FIG. 3. The SEM image of a diamond surface created by the vacuum arc discharges.

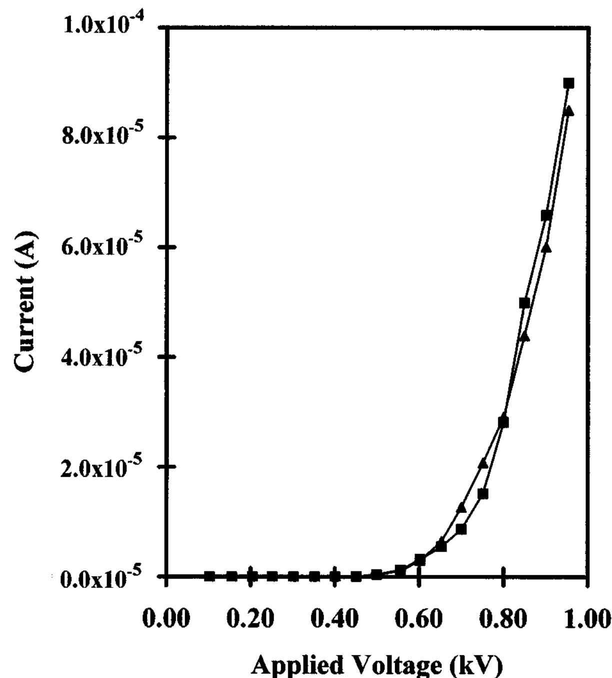


FIG. 4. The $I-V$ curve of W-1-NP with 50 $\mu$m anode-cathode gap.

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