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Properties of electron field emitters prepared by selected area deposition of CVD diamond carbon films

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Abstract

Selected area depositions (SAD) of diamond films were successfully achieved on silicon by two different approaches. In the first case, a standard lift-off technique employing a patterned SiO_2 layer was used as a mask, and in the second case commercial ink-jet printer technology was adapted to be used to seed diamond nano-grit onto silicon. Patterned, boron-doped diamond pads roughly 5.6 μm in diameter were formed by CVD growth on patterned SiO_2/Si substrates and found to be composed of closely packed carbon clusters approximately 250–800 nm in size each containing 50-nm particles embedded in them. The patterned diamond film seeded by ink-jet printing formed after CVD growth with in situ boron-doping, dots (85 μm in diameter) containing poly-crystals in the nanometre range. The resulting patterned diamond films were characterised by Raman and scanning electron microscope (SEM) analysis and then configured as cold cathode field emitters to determine their electron emission performance. The results suggest that patterned diamond films produced by ink-jet printing offer a simpler method for fabricating planar diamond emitter arrays with field emission and conduction properties which could be tailored to improve the performance and fabrication cost of cold field emitters in state-of-the-art field emission displays.

Keywords: Selective area deposition; Diamond seeding; Electron emitters; Boron-doped; CVD diamond

1. Introduction

The patterning of the diamond will be a key process for applying diamond film technology to microelectronic devices such as planar electron field emitter arrays and photo-detector arrays. Area selective diamond growth has been reported in the literature [1–9] as the practical alternative to removing undesired parts of a CVD diamond film by mechanical cutting or chemical means. The methods for patterning diamond films onto non-diamond substrates that have been reported in the literature [1–9] generally require a series of surface pretreatment steps involving at some point the use of a photo-resist or a silk-screen mask to create the desired film pattern.

Selected area depositions (SAD) of diamond films is commonly achieved by either enhancing the nucleation rate on selected regions or by suppressing the formation rate of nucleating diamond particles on selected regions. Selective suppression of the formation of diamond nuclei has been obtained by pre-coating the selected regions with low nucleation rate materials such as amorphous silicon [10], silicon oxide [11] or silicon nitride [12]. Selective enhancement of the rate of diamond nucleation has been achieved by using ion beam milling to selectively roughen the substrate area [1].

In this work, we have developed a new seeding method for patterning synthetic diamond nano-grit onto polished substrates using a modified commercial ink-jet printer and ink. This patterning method has been found to be compatible with the most commonly used substrate materials for CVD growth and the processing of diamond thin films such as, single crystal silicon, fused quartz, AF45 borosilicate glass and metal foil [16]. We have performed CVD film growth experiments using

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this seeding method in a hot filament CVD (HFCVD) reactor and have found that the resulting patterned film accurately reproduces the underlying printed 'diamond seed image'. The electron field emission properties of the SAD of boron-doped diamond films produced on mirror p-silicon by HFCVD, were examined and compared with the emission characteristics of patterned, boron-doped diamond emitter cathodes, formed by microwave plasma-enhanced CVD (MPECVD) onto mirror p-silicon by the selective suppression method using a SiO_2 mask.

2. Experimental details

Demonstration of the ink-jet seeding technique for generating patterned CVD diamond film structures, was undertaken using a custom-built HFCVD reactor. The experimental CVD growth conditions that were used are detailed in Table 1. No voltage bias pre-treatment or bias growth was involved in achieving the patterned films on p-silicon. In addition a mirror-polished, silicon substrate was patterned using only the ink-jet ink and included in the CVD experiments. This control experiment was performed to establish whether the pigment particles present in the ink could contribute significantly to the seeding effect of the diamond nano-grit upon selective CVD growth. It was found that after a 22-h growth run the control sample had not nucleated a patterned film. Instead, the density of randomly nucleated particles was no greater than for a mirror silicon substrate subjected to CVD without any form of pre-treatment (i.e. $<1\times10^3$ cm^{-2}). Boron-doped films were produced using a temperature-controlled, heated crucible containing borax as the in-situ dopant source.

In our experiment two grades of commercially available diamond nano-grit in aqueous suspensions were selected for testing; a water-based polycrystalline diamond suspension containing 50-nm particles (Allied High Tech Products Inc., product code 90-31995-A) and another containing 250-nm particles (Struers, code SAPUQ). These suspensions were mixed in a 1:1 ratio with the water-based, ink-jet ink to formulate a printable diamond suspension. This solution was then subjected to 15-min sonification to ensure that the ink and diamond were thoroughly mixed. The reformulated ink solution was then transferred into an empty refill ink-jet cartridge and mounted in a Canon BJ10 printer. This printer was chosen for these tests because the orientation of the print head and media feed are able to accommodate inflexible, thin substrate materials such as glass and silicon without major modification. For these experiments silicon wafers, 310 μm in thickness, were mounted on a high quality, 135 g A4 paper using adhesive tabs. The choice of substrate thickness and the use of a supporting paper 'backing' allowed the substrates to be fed through the printer without image smearing, retaining the page-to-page positional accuracy and the reproduction quality of the printed image.

A surfactant formulated from 10 cm^3 of liquid soap dissolved in 100 cm^3 of de-ionised water was prepared and applied to the glass and silicon substrates in order to ensure that the reformulated printing ink 'wet' the substrate surface uniformly, during the printing operation. The surfactant was allowed to air dry before ink-jet printing commenced.

Fig. 1 shows a scanning electron microscope (SEM) image of a single printed dot containing diamond and ink particles using the 250-nm diamond seeds. The nano-particle distribution of diamond was consistently, and uniformly distributed as a monolayer with no particle clumping. This was also found to be the case with the smaller grit size and it was established that within an ink-jet printed area, an average particle coverage of 5×10^6 cm^{-2} on mirror silicon could be achieved using the 50-nm diamond seeds.

A variety of pattern designs were printed ranging from arrays of discrete dots, the smallest being 80 μm in diameter (Fig. 2), to patterned squares several centi-

Table 1
Experimental HFCVD growth conditions

	Typical CVD diamond deposition parameters
Source gas (CH_4 in H_2) (%)	1
Hydrogen gas flow (sccm)	250
Borax crucible temp. (°C)	400–900
Pressure (torr)	20
Filament-sample dist. (mm)	5
Deposition temperature (°C)	960
Filament temperature (°C)	1950

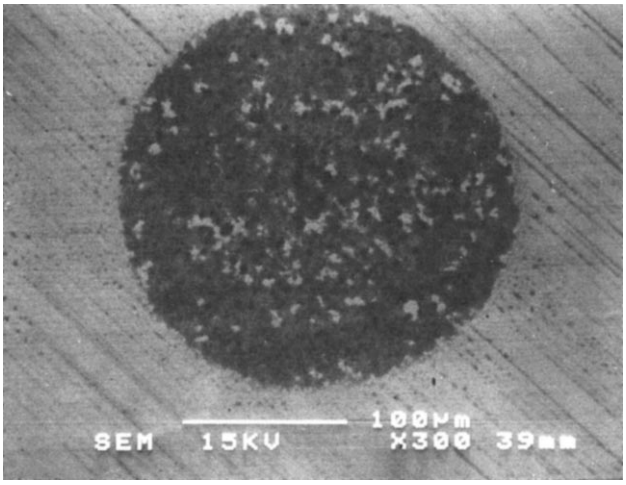

Fig. 1. SEM imaging of an ink-jet-patterned dot comprised of diamond nano-particles and sub-micron ink pigment particles on p-silicon before CVD treatment.

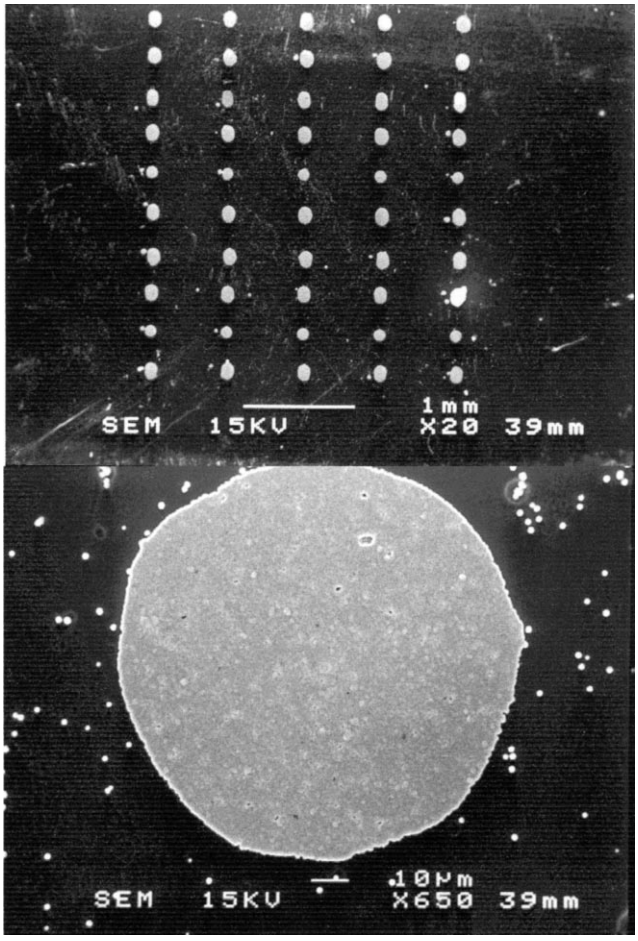

Fig. 2. SEM imaging of ink-jet-seeded diamond dots, 85 μm in diameter on mirror p-silicon after HFCVD growth for 4.5 h.

metres along a side. As a further example, Fig. 3 shows some printed text as a patterned nano-crystalline film after HFCVD growth for 22 h, using the conditions given in Table 1. SIMMS analysis indicated that the boron content in the patterned film was evenly distributed at a concentration of 1.4×10^{19} boron atoms cm^{-3}.

The MPECVD system used for depositing the patterned diamond films by the selective suppression method was an ASTeX model 5400. P-type Si mirror silicon substrate material was coated with 500 nm of thermal oxide. The substrate was next patterned using standard photolithography. The silicon oxide layer was then wet-etched using buffered, oxide etchant. Following the stripping away of the photo-resist, the patterned silicon substrate was next cleaned using acetone and then de-ionised water. Diamond films were deposited by a two-step process which involved using a negative bias during nucleation with the oxide mask present, and after the removal of the masking material, a zero voltage bias for the growth step. The process conditions are detailed in Table 2. The boron content of this patterned film

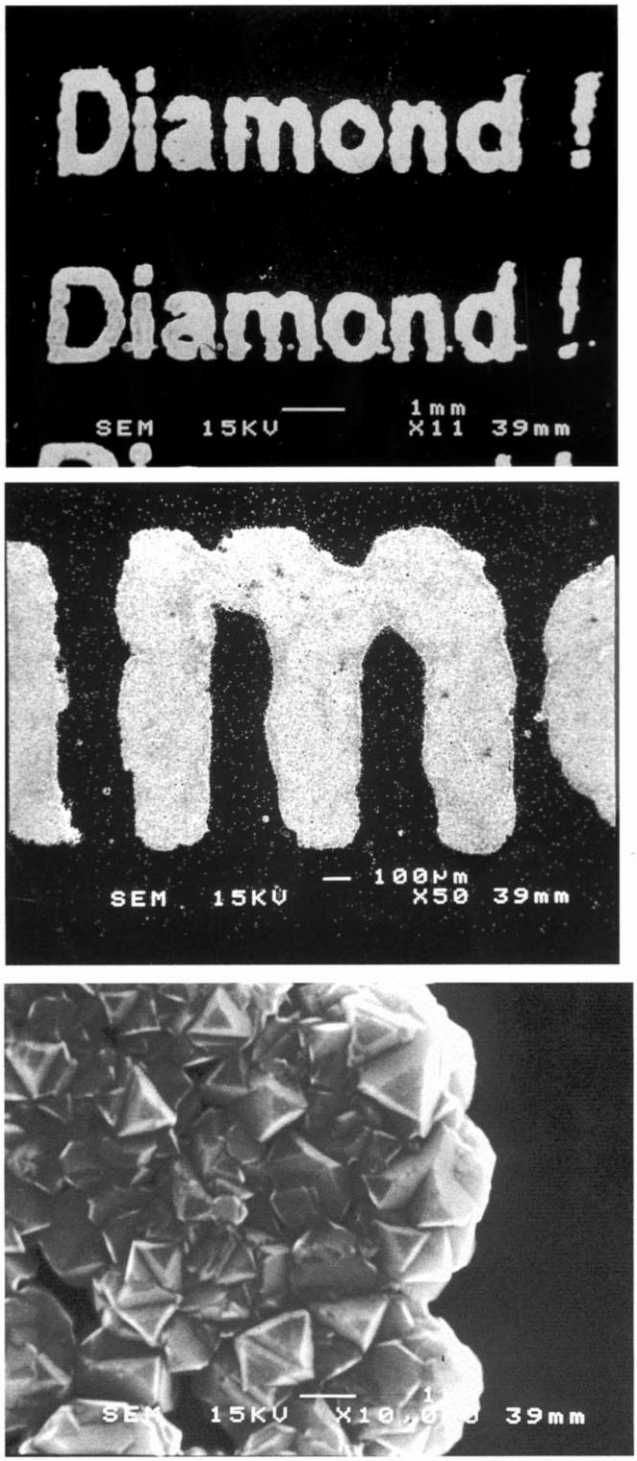

Fig. 3. SEM imaging of ink-jet-seeded CVD of the word 'diamond' on p-silicon detailing a region of selective growth at successively higher magnifications.

material was determined by SIMMs analysis to be of the same order as for the HFCVD material.

The patterned diamond films were characterised using a JEOL 6400 SEM and a Renishaw 2000 system. The latter system was used to examine the Raman spectral

Table 2
Experimental MPECVD growth conditions

	Nucleation step	Growth step
Source gas (CH_4 in H_2) (%)	3	6
Hydrogen gas flow (sccm)	300	300
Hydrogen gas flow through $B(OCH_3)_3$ liquid at 10°C (sccm)	0	9
Pressure (torr)	75	75
Microwave power (W)	2500	2500
Voltage bias to substrate (V)	−170 (d.c.)	0 V
Time (s)	5	30

profiles of the films, to establish the line intensity, peak width and peak position of the first order Raman mode of diamond. This information was then used to set up the Ramanscope for imaging, using the built-in filter system to perform the Raman imaging at a filter setting corresponding to the position of the diamond peak for a given patterned CVD film. For the two types of patterned film samples studied in this paper, the diamond Raman peak positions in Fig. 4 are: (a) 1332.8 cm^{-1}, and (b) 1333.2 cm^{-1}. Fig. 4 also shows that the MPECVD material appears to contain a significant proportion of non-diamond carbon. It is believed that the non-diamond signature can be attributed to the observation that during nucleation, the diamond nuclei formed on the patterned oxide mask are composed of loosely packed spherical carbon clusters approximately 250 nm in size, and that each cluster contains numerous diamond and non-diamond grains of the order of 50 nm in size [14]. This fact made it impossible to resolve a diamond Raman line image of this patterned sample. The ink-jet seeded HFCVD film shown in Fig. 4, exhibits a Fano-type interference [15] of the diamond Raman peak indicative of the boron incorporation, and a lower non-diamond content due to the use of diamond nano-grit to nucleate a continuous film.

To allow large areas of the patterned films to be imaged, the Renishaw microscope was set to use a 5× objective instead of the more usual 50× objective. Consequently, a longer exposure time was required to obtain a clear image of the patterned nano-crystalline diamond films. Typically, exposure times of 500–900 s were needed. The resulting images could then be compared with the SEM pictures to assess the intensity and distribution of the diamond signal across the patterned nano-crystalline film (Fig. 5).

Electron field emission measurements were undertaken using demountable vacuum glassware linked to a Leybold TMP50D turbo-molecular pump. Patterned diamond films were mounted within the glassware on a micrometer stage, which acted as the cathode of a vacuum diode test cell. A screen coated electrophoretically with a low voltage phosphor (mean particle size 2 μm), was electrically connected as the anode screen.

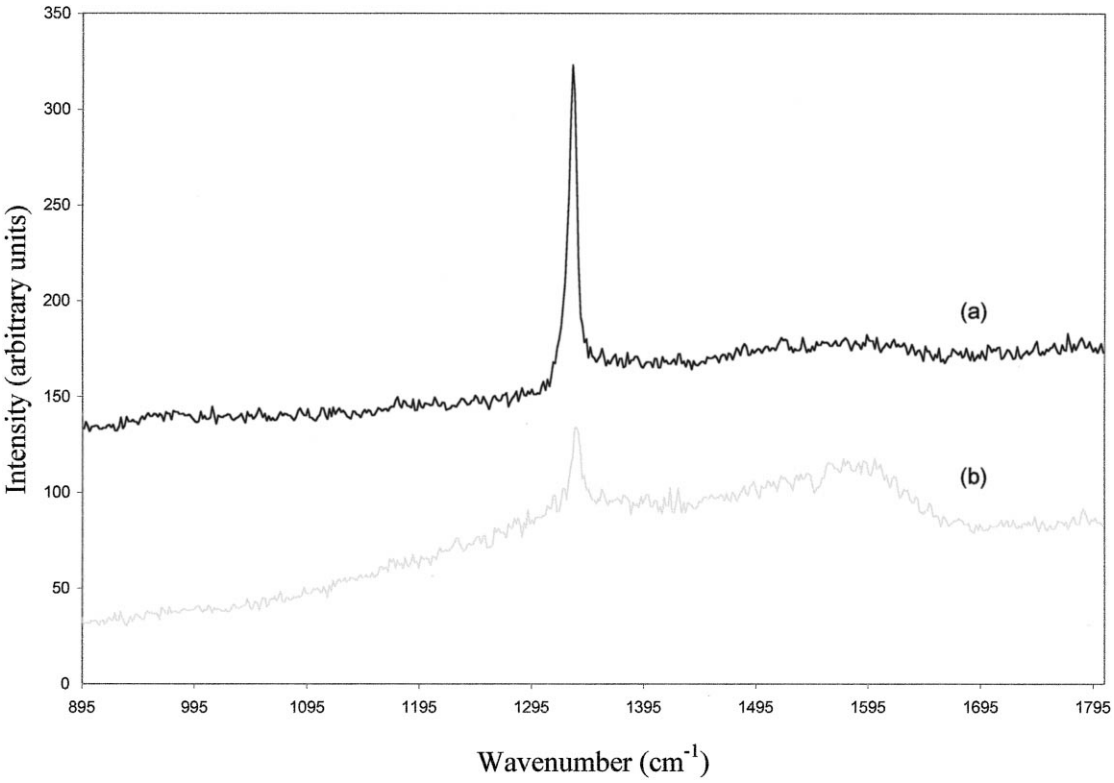

Fig. 4. Raman spectra recorded from patterned films on p-silicon produced by: (a) ink-jet seeded, HFCVD; and (b) biased nucleation, MPECVD with a SiO_2 mask.

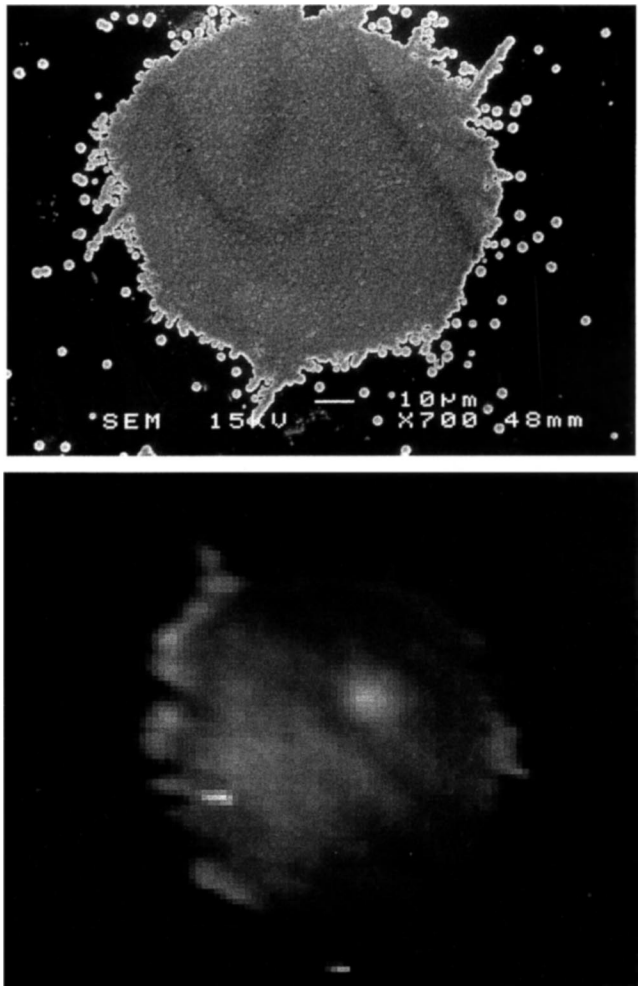

Fig. 5. Comparison of the SEM image and the corresponding Raman image at 1332.8 cm^{-1}, of an ink-jet-seeded diamond dot after HFCVD growth for 22 h.

The anode to cathode separation was controlled by the use of spherical glass spacers placed on each corner of the p-silicon substrates. For the ink-jet-seeded, patterned cathode a separation of 310 μm was employed for the current-voltage measurement. For the mask-patterned cathode, current-voltage measurements were carried out at a separation of 100 μm in order to use the same range for the voltage ramp.

A visual basic program was used to control a Brandenburg Alpha III high voltage d.c. supply and record the current-voltage outputs from the Keithley 2000 multimetre both suitably connected in circuit to the vacuum diode glassware [13].

3. Results and discussion

Examples of the arrays of patterned, boron-doped diamond features fabricated by the two SAD methods and employed for field emission measurement are shown

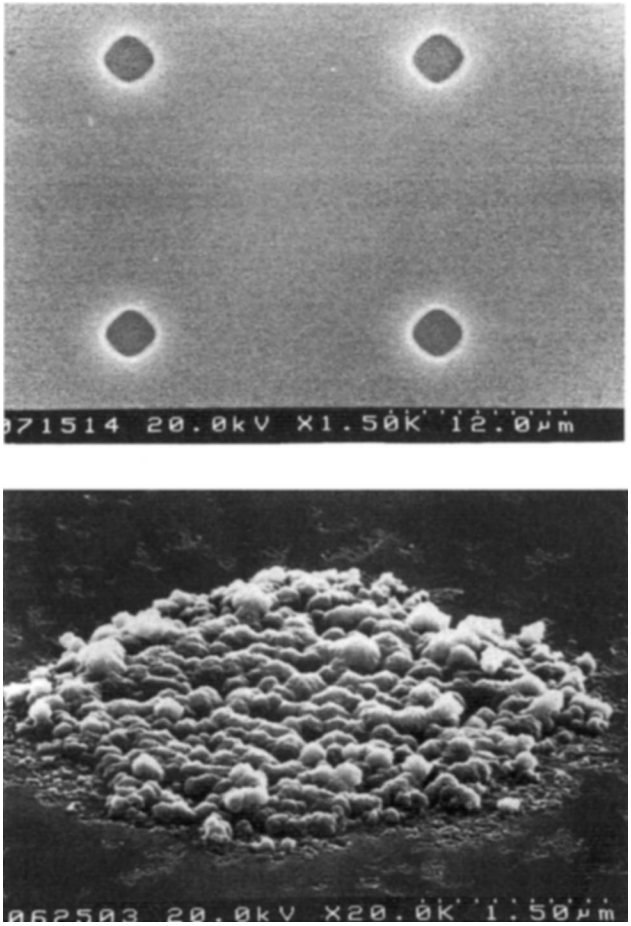

Fig. 6. SEM of the boron-doped, diamond pads formed by MPECVD for electron emission testing.

in Figs. 2 and 6. Comparison of the electron emission performance of these emitter array structures is summarised in Table 3. It may be noted that both emitter structures exhibit a low threshold field for field emission and are capable of generating high current densities at field strengths much lower than continuous CVD films. The ink-jet seeded diamond emitter structure demonstrated better emission performance. This may be attributed to the observation we have made from systematic seeded, patterned growth studies [16] that the diamond seeding facilitates the maintenance of the polycrystalline film quality at boron dopant levels above 200 ppm better than the bias-nucleated, MPECVD film. This may mean

Table 3
Comparison of electron field emission results

Sample	Threshold for field emission (V/μm)	Integral current density (μA/cm^2)
Ink-jet seeded B-doped diamond dots	2.2	5286 at 4.8 V/μm
SiO_2 mask B-doped diamond pads	7.8	1400 at 10.7 V/μm

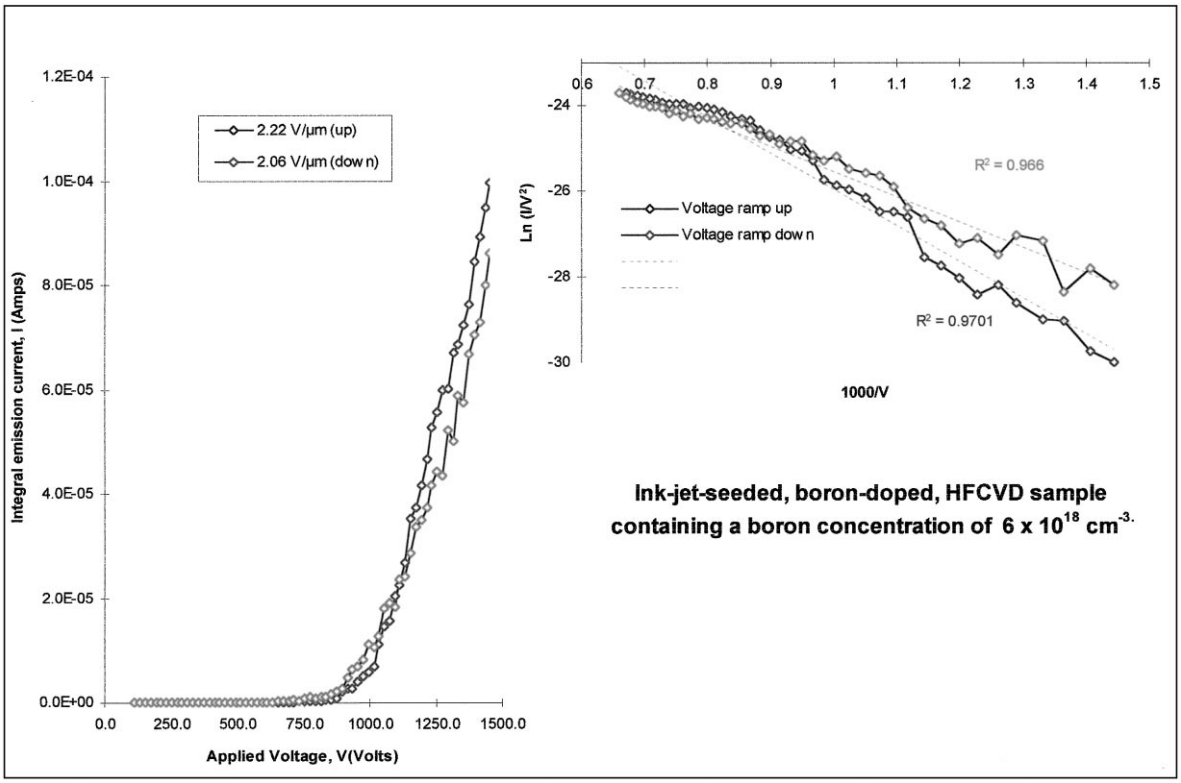

Fig. 7. Field-induced electron emission from a patterned, boron-doped, HFCVD film generated using the ink-jet (diamond) seeding method.

that boron is incorporated more efficiently into the diamond-seeded film improving the semiconductivity of the nano-crystals, which make up the diamond HFCVD thin film. An example current-voltage characteristic for the electron field emission from ink-jet-seeded, patterned HFCVD film is detailed in Fig. 7 for voltage ramp cycle 56, extracted from a programmed sequence of 100 cycles. This was recorded from an array containing 45 patterned dots, each approximately 85 μm in diameter. This test sample was one of a number of patterned arrays cleaved from the same processed SAD sample as the 100 element example array used for SEM analysis and detailed in Fig. 2. The emission voltage threshold was found to fluctuate during the 100 cycles between 552 V and 691 V for the program-controlled ramping-up, and 548 V and 665 V for the ramping-down. However, there was no pattern to this fluctuation and no evidence that it was linked to the creation or destruction of distinct emitter sites on given 'pixel' dots, as evidenced from observation of the phosphor dot pattern for successive cycles. SEM analysis of this sample after field emission testing identified that a small number of phosphor particles had been dislodged from the anode screen and come to rest within the area of the emitter dot array. This observation may be one of the explanatory factors for the fluctuation in threshold voltage. Another factor relates to the known presence of residual nitrogen impurity atoms in the patterned, boron-doped HFCVD film material and its effect upon the electron emitter properties of this nano-crystalline material. The possible sources of this nitrogen are believed to be the synthetic, polycrystalline diamond nano-grit seed material and the methane source gas [16,17].

4. Conclusions

In summary we have produced boron-doped, SAD diamond particle films on mirror p-silicon by two different methods and compared their field emission properties. Both methods nucleated SAD diamond films from nanometer-sized particles containing diamond.

The more stable and reproducible electron field emission performance was obtained from the patterned HFCVD film, selectively diamond seeded by ink-jet printer. When configured as a cold cathode emitter it exhibited an emission current density of 5280 μA/cm^2 at 4.8 V/μm. The low turn-on voltage of this material makes it a good candidate for planar diamond field emitter structures.

This result has demonstrated that large area patterning of synthetic diamond thin films is possible without the need for any form of mask design, and that with a bubble-jet printer, possessing a modest resolution of only 300 dpi, 80 μm features can be seeded reproducibly.

It is evident from this preliminary work that this seeding technique by ink-jet printer could be coupled with suitable large area plasma CVD processing to fashion very large areas and high densities of pixellated, diamond emitter array structures onto substrates which may conceivably be any size.

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