Patterned diamond particle films

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This article reports on a technique for patterning diamond nanogrit which utilizes commercial ink-jet printer technology. Diamond nanogrit as small as 50 nm has been successfully printed onto substrates of glass, silicon, copper, and fused quartz. The technique has been used to demonstrate a quick and simple means to seed patterned. nanocrystalline diamond films onto candidate substrates of potentially any conceivable size or shape. © *2000 American Institute of Physics.* [S0021-8979(00)09611-0]

I. INTRODUCTION

Diamond is considered to be an excellent candidate material for applications which might exploit its characteristic physical and chemical properties such as high atom density ($1.76\times10^{23}\,\mathrm{cm}^{-3}$), extreme hardness (100 GPa), high thermal conductivity (2100 W/m K), high dielectric strength (1×10^{6} V/cm), high resistivity ($10^{16}\,\Omega\,\mathrm{cm}$), wide band gap (5450 meV), high chemical resistance, etc. There are many potential applications especially in microelectronics, optoelectronics, and micromechanics for polycrystalline thin films that require minimum stress in thin films with good adhesion to the substrate and a high degree of smoothness.

Using chemical vapor deposition (CVD) and *in situ* doping methods, semiconducting diamond films have been synthesised using dopant impurities such as boron and phosphorus, to produce films containing small quantities of activated *p*-type[1] and *n*-type[2] charge carriers, respectively. As this capability to make semiconducting CVD diamond thin films becomes more refined, high performance electronic devices using this material will become more widespread.

The patterning of diamond will be a key process for applying diamond film technology to microelectronic devices such as planar electron field emitter arrays and photodetector arrays. Area selective diamond growth has been reported in the literature[3–11] 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 nondiamond substrates that have been reported in the literature[3–11] generally require a series of surface pretreatment steps involving, at some point, the use of a photoresist or a silk-screen mask.

In this article, we have developed a new seeding method for patterning synthetic diamond nanogrit 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, borosilicate glass, and metal foil. We have performed CVD film growth experiments using this seeding method in a hot filament CVD reactor and have found that the resulting patterned film accurately reproduces the underlying printed ''diamond seed image''. We have also employed this diamond seeding technique to print fine nanogrit onto glass substrates in order simplify the means to fabricate diamond cold cathode surface conduction emitter array structures.

Ink-jet printing has previously been used in the flat panel display industry to manufacture, among other things, color filters for liquid crystal displays[12] and to deposit luminescent doped polymer films for organic light emitting polymer displays.[13]

II. EXPERIMENT

In our experiment two grades of commercially available diamond nanogrit 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

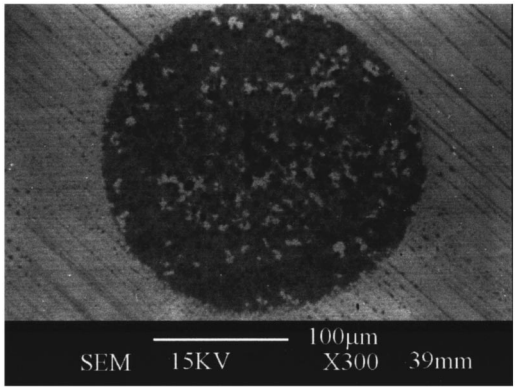

FIG. 1. SEM micrograph of an ink-jet-patterned dot composed of diamond nanoparticles and submicron ink pigment particles on *p*-silicon before CVD treatment.

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TABLE I. Growth conditions for boron-doped, patterned diamond deposition.

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

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 and quartz wafers 250 μm thick, were mounted on a high quality, 135 g A4 paper using adhesive tabs. The choice of substrate thickness and the use of a 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 cc of liquid soap dissolved in 100 cc of deionized 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.

Figure 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 nanoparticle distribution of diamond was consistently, and uniformly distributed as a monolayer with no particle clumping. This was also the case with the smaller grit size and it was found that within an ink-jet printed area, an average particle coverage of

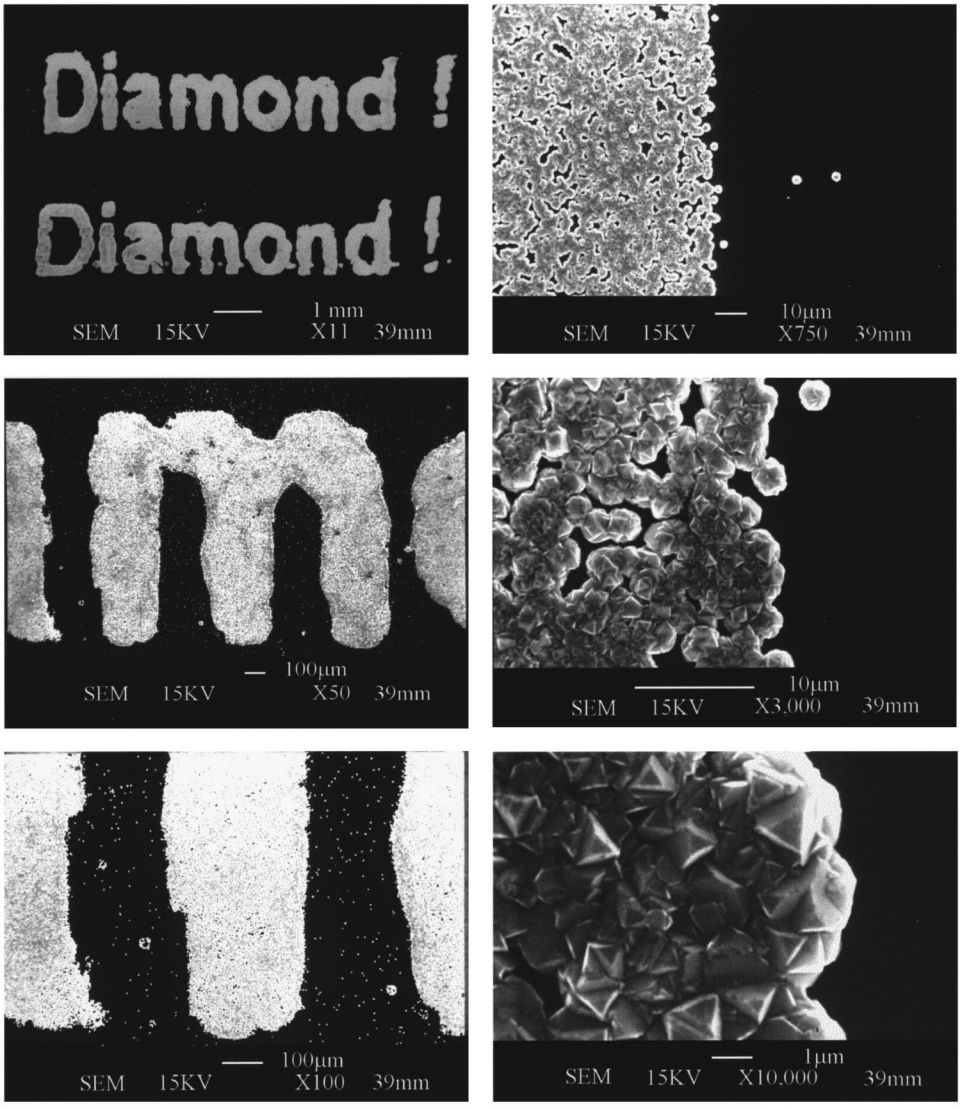


FIG. 2. SEM micrographs of ink-jet-seeded, CVD growth to form the word ''diamond'' on mirror *p*-silicon detailing with increasing magnification, (top left to bottom right) a region of selective growth.

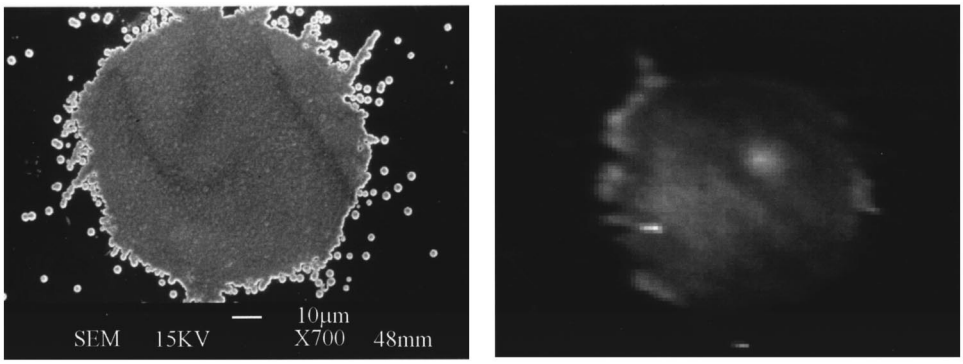


FIG. 3. (a) SEM micrograph and (b) Raman image of the patterning of diamond seeds by ink jet onto copper followed by CVD growth for 22 h.

$5\times10^{6}\,\mathrm{cm}^{-2}$ on silicon and polished, fused quartz 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 microns in diameter, to patterned squares several centimeters along a side. In comparison with electrophoretically deposited nanogrit patterning, using similar process conditions to Panitz *et al.*,[14] it was noted that the drying time for an equivalent substrate size and pattern was many times faster and did not give rise to localized densification of the particle distribution due to nonuniform evaporation of the solvent and/or high field areas generated when a mask-patterned substrate surface was employed.

To demonstrate the usefulness of this seeding technique for generating patterned CVD diamond film structures, hot filament CVD was conducted using a custom-made CVD reactor system from Applied Vacuum Engineering Ltd. CVD growth was performed on patterned silicon and quartz substrates employing the conditions detailed in Table I. 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 nanogrit 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 pretreatment (i.e., $<1\times10^{3}\,\mathrm{cm}^{-2}$). Boron-doped films were produced using a temperature-controlled heated borax crucible as the *in situ* source.

III. RESULTS AND DISCUSSION

Figure 2 illustrates examples of the SEM images of the diamond films obtained using this seeding method after 22 h of CVD growth for similarly printed features to those shown in Fig. 1 (see Fig. 3). The x-ray diffraction (XRD) analysis of boron-doped CVD films seeded using 250 nm nanogrit by the ink-jet method and by electrophoresis, are shown for comparison in Fig. 4. This figure illustrates that a preferred (111) polycrystal orientation can be achieved on an ink-jet seeded, patterned film area. This is primarily attributed to the hot filament CVD growth conditions. In Fig. 5 a typical Raman spectrum is presented to show how the presence of nanocrystalline diamond seeds can influence the diamond film quality obtained following CVD growth. The ink-jet seeded hot filament (HF) CVD film shown in Fig. 5, exhibits a Fano-type interference[15] of the diamond Raman peak indicative of the boron incorporation, and a lower nondiamond content due to the use of diamond nanogrit to nucleate a continuous film. The corresponding SEM images are illustrated in Fig. 6. It is noted that, the diamond-seeded regions are composed of submicron polycrystals and that nonseeded diamond particles nucleating adjacent to them are in the micron range.

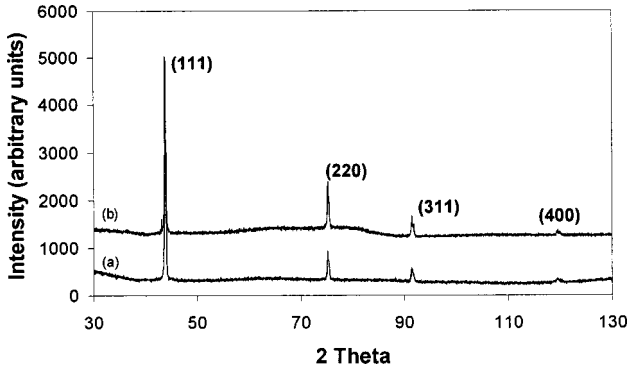


FIG. 4. XRD plot of boron-doped patterned CVD diamond films seeded using: (a) Electrophoresis, (b) ink-jet printer.

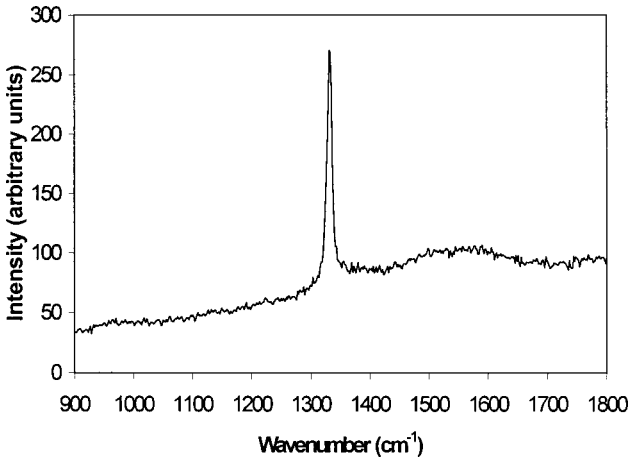
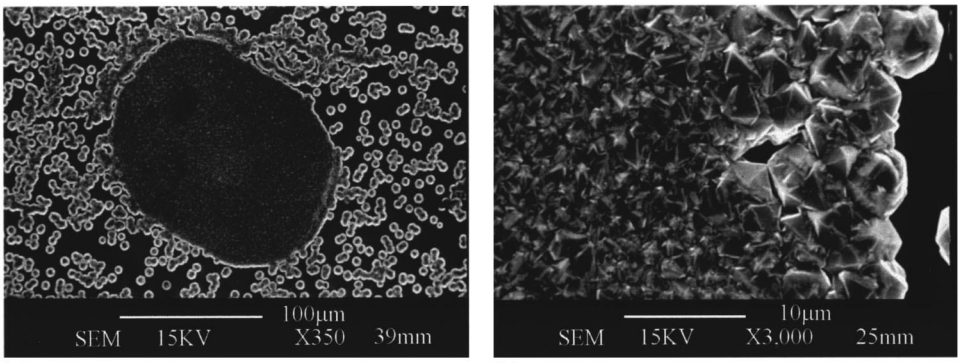


FIG. 5. Raman spectra taken using a laser wavelength of 488 nm for the patterned, boron-doped CVD film on mirror *p*-silicon.



(a) (b)

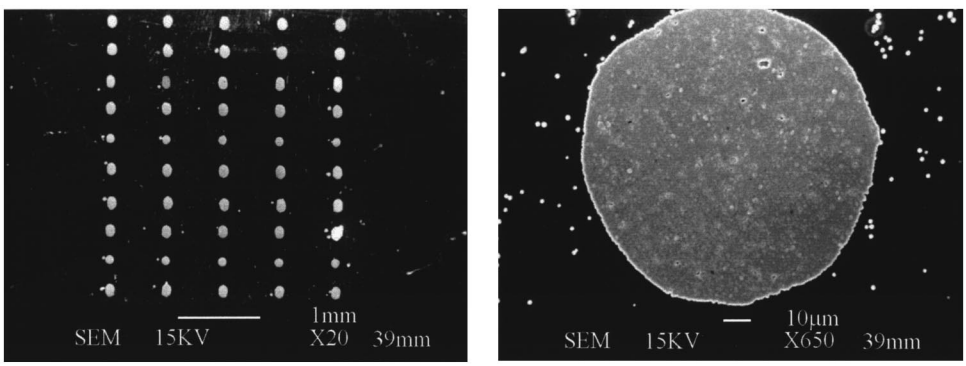
FIG. 6. SEM micrographs of diamond-seeded CVD after more than 24 h growth on *p*-silicon illustrating, (a) secondary nucleation around at patterned dot, (b) the relative size of these nucleated diamond particles compared to the adjacent printed area.

Figure 7 illustrates the application of this seeding method to fabricate a planar diamond nanoparticle electron field emitter structure. In this case the CVD growth was stopped after 4.5 h. It is seen that a near continuous film is produced in the selected areas and that the pattern definition is superior to the 22 h growth run due to the absence of diamond particle nucleation effects on the unpatterned areas of the mirror silicon. 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 conductive indium tin oxide glass screen coated electrophoretically with a low voltage phosphor (mean particle size 2 μm), was electrically connected as the anode. 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 microns was employed for the current–voltage measurement. A VISUAL BASIC program was used to control a Brandenburg Alpha III high voltage dc supply and to record the current–voltage outputs from the Keithley 2000 multimeter; both suitably connected in circuit to the vacuum diode glassware.[16]

Figure 8 shows a current–voltage plot taken from the results of electron field emission tests recorded from a forty-five element array of patterned diamond emitter pixels, each approximately 85 μm in diameter, produced by a 22 h HFCVD growth run. The doped patterned diamond array was configured as cathode and operated in a vacuum ambient of 7×10^{-8} Torr. Large integral emission currents were recorded from the pixel array at low applied fields. The peak integral current recorded from cycle to cycle varied by less than 6%. However, the emission voltage threshold was found to fluctuate during the 100 cycles between 552 and 691 V for the program controlled ramping up, and 548 and 665 V for the ramping down. 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 possible effect upon the conduction properties of this nanocrystalline material. The possible sources of this nitrogen are believed to be the synthetic, polycrystalline diamond nanogrit seed material, and the methane source gas.[17]

IV. CONCLUSIONS

In summary these results have 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 360 dpi, ~70 micron features can be seeded reproducibly. It



(a) (b)

FIG. 7. SEM micrographs of ink-jet-seeded hot filament CVD films obtained after 4.5 h of growth on mirror *p*-silicon substrates. (a) Patterned dot array, (b) magnified image of one dot.

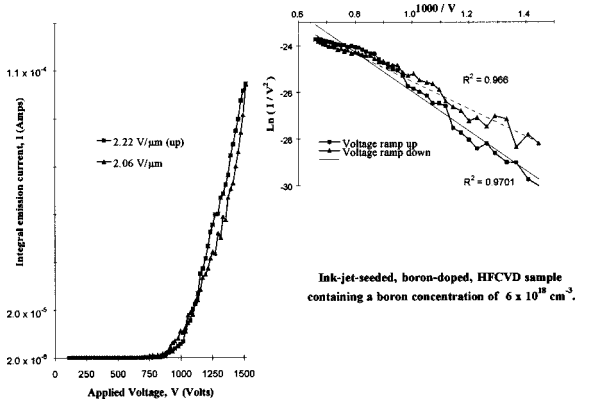


FIG. 8. Typical electron field emission result, cycle 56, extracted from a programmed sequence of 100 voltage ramp cycles.

is evident from this preliminary work that this printing technique could be coupled with suitable plasma CVD processing to fashion very high densities of pixellated diamond structures onto nondiamond substrates which may conceivably be any size.

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