Characterization of boron doped nanocrystalline diamonds

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Abstract. Nanostructured diamond doped with boron was prepared using a hot-filament assisted chemical vapour deposition system fed with an ethyl alcohol, hydrogen and argon mixture. The reduction of the diamond grains to the nanoscale was produced by secondary nucleation and defects induced by argon and boron atoms via surface reactions during chemical vapour deposition. Raman measurements show that the samples are nanodiamonds embedded in a matrix of graphite and disordered carbon grains, while morphological investigations using field electron scanning microscopy show that the size of the grains ranges from 20 to 100 nm. The lowest threshold fields achieved were in the 1.6 to 2.4 V/µm range.

1. Introduction
Diamond attracts a great deal of interest for field electron emission (FEE) since its surfaces possess low or even negative electron affinity (NEA), i.e. low energy or no energy at all is necessary to extract electrons from the diamond surface to a vacuum environment [1]. However the concentration of intrinsic electrons in the conduction band of diamond is very low and it is difficult to dope diamond crystals with electron-donor impurities to produce n-type diamonds. Therefore, even with favorable NEA, crystalline diamonds are poor field emitters as the transport of electrons through the bulk for emission to the diamond-vacuum interface is difficult [2]. A possible solution to improve diamond FEE is to downsize the diamond grains to nano-scale so as to maximize the network of defective grain boundaries of non-diamond carbon to facilitate the transport and injection of electrons to the diamond grains located at the vacuum interface. Nanocrystalline diamond can be grown in a variety of methods based on processes with high rates of secondary nucleation, using microwave plasma or hot-filament CVD [3-4].

In this work, we report the use of the hot-filament technique with feeds of mixtures of hydrogen, argon and ethyl alcohol heavily doped with boron for the synthesis of nanostructured diamond. Morphological data obtained by field emission scanning electron microscopy (FESEM), Raman spectroscopic analyses and field emission properties of the samples are given and discussed.

2. Experimental Section
Deposition of nanodiamond structures was carried out in a hot filament chemical vapor deposition (HFCVD) system, fed from mixtures of boron doped ethyl alcohol (C$_2$H$_5$OH) vapor (0.5 %vol.) diluted in hydrogen (29.5 %vol.) and argon (70 %vol.). The boron-doping source was made by
dissolving $\text{B}_2\text{O}_3$ in water/ethyl alcohol feed reservoir before the start-up of the reactor. The boron-carbon (B/C) concentration ratio in the feed was 5000 ppm. A total flow rate of around 100 sccm, and a total pressure of about 20 Torr were maintained throughout. Silicon wafers (10 mm x 10 mm square) of 0.8 mm thickness, previously etched in HF and dipped in a colloidal mixture of diamond dust (0.25 $\mu$m in diameter) dispersed by ultrasonic vibration in n-hexane, were used as substrates. The ideal temperature for the growth of diamond samples with ~1 $\mu$m crystallites without argon or B doping in the gas feed was experimentally determined by trial and error as 1300 K. Argon (70 % vol.) and $\text{B}_2\text{O}_3$ were then incorporated into the feed to change the equilibrium for the formation of diamond nanocrystallites or other carbon structures and the deposition temperature decreased to 1143 K. Deposition times of 7 h were used in all experiments.

Morphological analyses were made by FESEM using a JEOL JSM-6330F operated at 5 kV and 8 $\mu$A. Raman spectra were recorded at the ambient temperature using a Renishaw microprobe system, employing an argon laser for excitation ($\lambda = 514.5$ nm) at a laser power of about 6 mW. The characterization of field emission properties was performed in a specially designed vacuum system by the control of distance ($d$) and parallelism between anode-cathode (sample) surfaces using a precisely combined XYZ-angular micrometer stage. The measurement of the current density versus electric field ($J-E$) was done for $d = 980$ $\mu$m in a parallel plate configuration. A Cu rod of 3.3 mm diameter was used as the anode. The threshold field ($E_{th}$) was measured by the slope of linear fits of the bias (for a fixed electron current density) as a function of the anode-cathode distance.

3. Results and Discussion

Figure 1 (a)-(b) shows typical top-view FESEM images of as deposited boron-doped samples produced by the CVD process. The morphology observed in Figure 1 (a) is of aggregates of round-shaped features of less than 1 $\mu$m diameter, forming a continuous film but with some boundary ruptures. The magnified image of Figure 1 (b) shows that such aggregates are formed by an apparently random coalescence of nanocrystalline grains. Grains of 20 to 100 nm are identified.

![Figure 1](attachment:image1.png)

**Figure 1.** Typical FESEM images of the as-deposited samples at different magnifications

Figure 2 shows a typical Raman spectrum taken with a laser wavelength of 514.5 nm. The spectrum show peaks at 1140 cm$^{-1}$, 1333 cm$^{-1}$, 1350 cm$^{-1}$, 1470 cm$^{-1}$ and 1570 cm$^{-1}$, which are expected features for nanocrystalline diamond. The peak that appears at 1333 cm$^{-1}$ is characteristic of diamond C-C sp$^3$ bonds, and is close to the standard value (1332 cm$^{-1}$) of natural diamond. The peaks at 1350 cm$^{-1}$ and 1570 cm$^{-1}$ correspond to the D and G modes of disordered carbon. The nature of the peak at 1140 cm$^{-1}$ has been of some controversy [5-6] since some authors believe that it originates from confined phonon modes in nanocrystalline diamond and others claim that it is associated with...
Figure 2. Typical Raman spectrum taken with a laser wavelength of 514.5 nm.

Figure 3. (a) Typical field emission current density \( J \) versus electric field \( E \), (b) Fowler-Nordheim plot from the emission current \( I \) versus voltage \( V \) data, (c) Threshold voltage \( V_{th} \) versus cathode-anode distance necessary to produce a threshold current density of about 120 nAcm\(^{-2}\).
C-C sp$^2$ vibrations at hydrogenated grain boundaries, where polyacetylene may be present [6]. The peak at 1470 cm$^{-1}$ may also be assigned to polyacetylene [6].

Typical electron emission results are shown in Figure 3 (a)-(c). Figure 3 (a) shows the emission current density versus electric field ($J$-$E$) for a fixed cathode-anode distance of 980 $\mu$m, and Figure 3 (b) shows the Fowler-Nordheim plot from the emission current ($I$) versus voltage ($V$) data. The Fowler-Nordheim plot is linear ($y = 14.229 - 60.422x$), indicating that there is no saturation of the emission current at higher applied fields. Figure 3 (c) shows the typical threshold voltage ($V_{th}$) versus distance necessary to produce a threshold current density of about 120 nAcm$^{-2}$. The typical threshold field ($E_{th}$) may be estimated from the $J$-$E$ plot (Figure 3 (a)) or from the slope of the threshold voltage ($V_{th}$) versus cathode-anode distance (Figure 3 (c)). Lowest threshold fields achieved were in the 1.6 to 2.4 V/$\mu$m range. Several samples (75% of $n = 12$), however, presented threshold fields > 20V/$\mu$m.

The Raman scattering and FESEM images are consistent with nanocrystalline diamond, characterized by small grain size, and described as sp$^3$ bonded grains (nanodiamond) embedded in a matrix of sp$^2$ bonded carbon (nanographite). The small grain size is attributed to a high renucleation rate due to the increase of C$_2$ formation in the argon rich feed gas mixture. The grain boundaries are altered by the heavy boron doping [7-8] and also a large concentration of boron is expected to be incorporated into the lattice of the nanocrystalline diamond grains, introducing lattice defects and electron acceptor sites. Thus boron doping may enhance the grain surface conductivity but also results in electron trapping in the nanocrystalline diamond acceptor sites. The electron transport through conductive paths at grain boundaries, and the increase in the density of emission sites due to the nanosizing of diamond crystallites, may be the dominant effects observed in low threshold field emission samples, and the electron trapping may be the dominant effect observed in high threshold field emission samples.

4. Conclusions

Heavily boron-doped nanocrystalline diamond films were synthesized by hot-filament chemical vapor deposition using B$_2$O$_3$ diluted in water/ethyl alcohol, hydrogen and argon. Argon and boron increased secondary nucleation and the local disorder of the diamond grain boundaries, which leads to grains in the 20 to 100 nm range. Raman measurements show that the nanodiamonds are embedded in a matrix of graphite and disordered carbon grains. The lowest threshold fields achieved were in the range of 1.6 to 2.4 V/$\mu$m. We suggest that the enhancement in field emission is due to the increase of electron transport through conductive paths at intergranular boundaries.

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