

[Home](#) [Search](#) [Collections](#) [Journals](#) [About](#) [Contact us](#) [My IOPscience](#)

Field-emission properties of sulphur doped nanocrystalline diamonds

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2007 J. Phys.: Conf. Ser. 61 66

(<http://iopscience.iop.org/1742-6596/61/1/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 143.106.108.182

This content was downloaded on 22/06/2015 at 19:26

Please note that [terms and conditions apply](#).

Field-emission properties of sulphur doped nanocrystalline diamonds

V Baranauskas¹, MA Sampaio, AC Peterlevitz, HJ Ceragioli and JCR Quispe

Faculdade de Engenharia Elétrica e Computação, Departamento de Semicondutores, Instrumentos e Fotônica, Universidade Estadual de Campinas, UNICAMP, Av. Albert Einstein N.400, 13 083-852 Campinas – SP - Brasil

E-mail: vitor.baranauskas@gmail.com

Abstract. Nanostructured diamond doped with sulphur has been prepared using a hot-filament assisted chemical vapour deposition system fed with an ethyl alcohol, carbon disulfide, hydrogen, and argon mixture. The reduction of diamond grains to the nanoscale is relevant to create a network of defective grain boundaries which may be n-type doped to facilitate the transport and injection of electrons to the diamond grains located at the vacuum interface, enhancing the electron field-emission properties of the samples. The downsizing was produced by secondary nucleation and defects induced by sulphur and argon atoms in the chemical vapour deposition surface reactions. Sulphur also acts as an n-type dopant of diamond. Raman measurements show that the samples are nanodiamonds embedded in a matrix of graphite and disordered carbon grains and the morphology, revealed by field electron scanning microscopy, shows that the grains are in the range of 10 to 30 nm. The lowest threshold achieved for field emission was 13.20 V/ μm .

1. Introduction

Research on preparing nanostructured materials has been of high scientific and technological interest because they may have new or improved properties compared to those of the bulk. Nano-sized diamond structures may have interesting properties such as better optical transmission, higher density of defect cores, enhanced quantum electronic conduction, and better field electron emission (FEE), compared to micron-sized diamond [1-5].

Diamond attracts a great deal of interest 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 [6]. 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 this favorable electron affinity, crystalline diamonds are poor field emitters because the transport of electrons through the bulk for emission at the diamond-vacuum interface is difficult [7-8].

Possible solutions to improve diamond field emission are either (i) to downsize the diamond grains to nano-scale to maximize the network of defective grain boundaries of non-diamond carbon or (ii) to find an atomic element to n-dope diamond. Both solutions may facilitate the transport and injection of electrons to the diamond grains located at the vacuum interface.

Nanocrystalline diamond can be grown by a variety of methods based on processes with high rates of secondary nucleation, such as microwave plasma or hot-filament CVD [2-3, 9-10]. Fullerenes [11], or methane [9-10], or ethyl alcohol [2-3], have been used as carbon sources, diluted in hydrogen, nitrogen, argon or helium. Methane and H₂S diluted in hydrogen (50 – 500 ppm) have also been used to achieve the downsizing of the diamond grains and possible n-doping of the nanocrystallites with sulphur atoms [12-15]

In this work, we report the use of high purity carbon disulfide (CS₂) diluted in ethyl alcohol, hydrogen and argon to synthesize nanostructured diamond samples, using the hot-filament technique. 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

The nano-sized structures were synthesized by hot-filament chemical vapor deposition (HFCVD) using ethyl alcohol (C₂H₅OH) vapor as the carbon source, diluted in a mixture of hydrogen (29.5 % vol.) and argon (70 % vol.). High purity carbon disulfide (CS₂) was also diluted in ethyl alcohol and used as the source of sulphur atoms. An S/C concentration ratio of 1600 ppm in the doping feed-stock was used. A total flow rate of around 93 sccm, regulated by precision mass flow controllers, and a total pressure of about 20 Torr were maintained throughout. Polished silicon wafers (10 mm x 10 mm square) of 0.8 mm thickness, were used as substrates, placed below the hot-filament coil. The deposition temperature was measured by a thermocouple beneath the Si substrates and corrected to express the temperature at the deposition surface. The ideal temperature for the growth of diamond samples with ~1 μm crystallites without argon or CS₂ in the gas feed was experimentally determined by trial and error as T = 1300 K. Argon (70 % vol.) and CS₂ were then incorporated into the feed to shift the equilibrium towards the formation of diamond nanocrystallites or other carbon structures and the deposition temperature decreased to T = 1143 K. Deposition times of 6 h were used in all experiments.

Morphological analyses were made by Field Emission Scanning Electron Microscope (FESEM) using a JEOL JSM-6330F operated at 5 kV, 8 μA. Raman spectra were recorded at the ambient temperature using a Renishaw microprobe system, employing an Argon laser for excitation (λ = 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 the distance (d) and parallelism between anode-cathode (samples) surfaces using a precisely combined XYZ-angular micrometer stage. Measurement of the current versus bias voltage (I-V) was undertaken for a fixed anode-cathode distance of d = 700 μm in the parallel plate configuration. A Cu rod of 3 mm diameter was used as anode. The threshold field (E_{th}) was measured by the slope of the bias (for a standard electron current density of 500 nAcm⁻²) versus anode-cathode distance curves, fitted by straight lines.

3. Results and Discussion

Figure 1 (a)-(d) shows typical top-view FESEM images of as-deposited samples produced by the CVD process with argon and CS₂, as described in Section 2. The morphologies observed in Figure 1 (a) are of aggregates of round-shaped features of ~ 1 μm diameter, forming a continuous film but with some boundary ruptures. The round-shaped features are formed by an apparently random coalescence of carbon nuclei. The magnified images of Figure 1 (b) and Figure 1 (c) show that such nuclei display grain dimensions of less than 100 nm, without any identifiable form. Magnification of the image shown in Figure 1 (c) (see Figure 1 (d)) shows that grains of 10 to 30 nm are identifiable. A typical growth rate of ~ 0.3 μm h⁻¹ was calculated by measuring the thickness of the deposited films after the cross-sectional fracture of the samples.

Figure 2 shows a typical Raman spectrum taken with a laser wavelength of 514.5 nm. The spectrum shows peaks at 1140 cm⁻¹, 1335 cm⁻¹, 1360 cm⁻¹, 1470 cm⁻¹ and 1550 cm⁻¹, which are

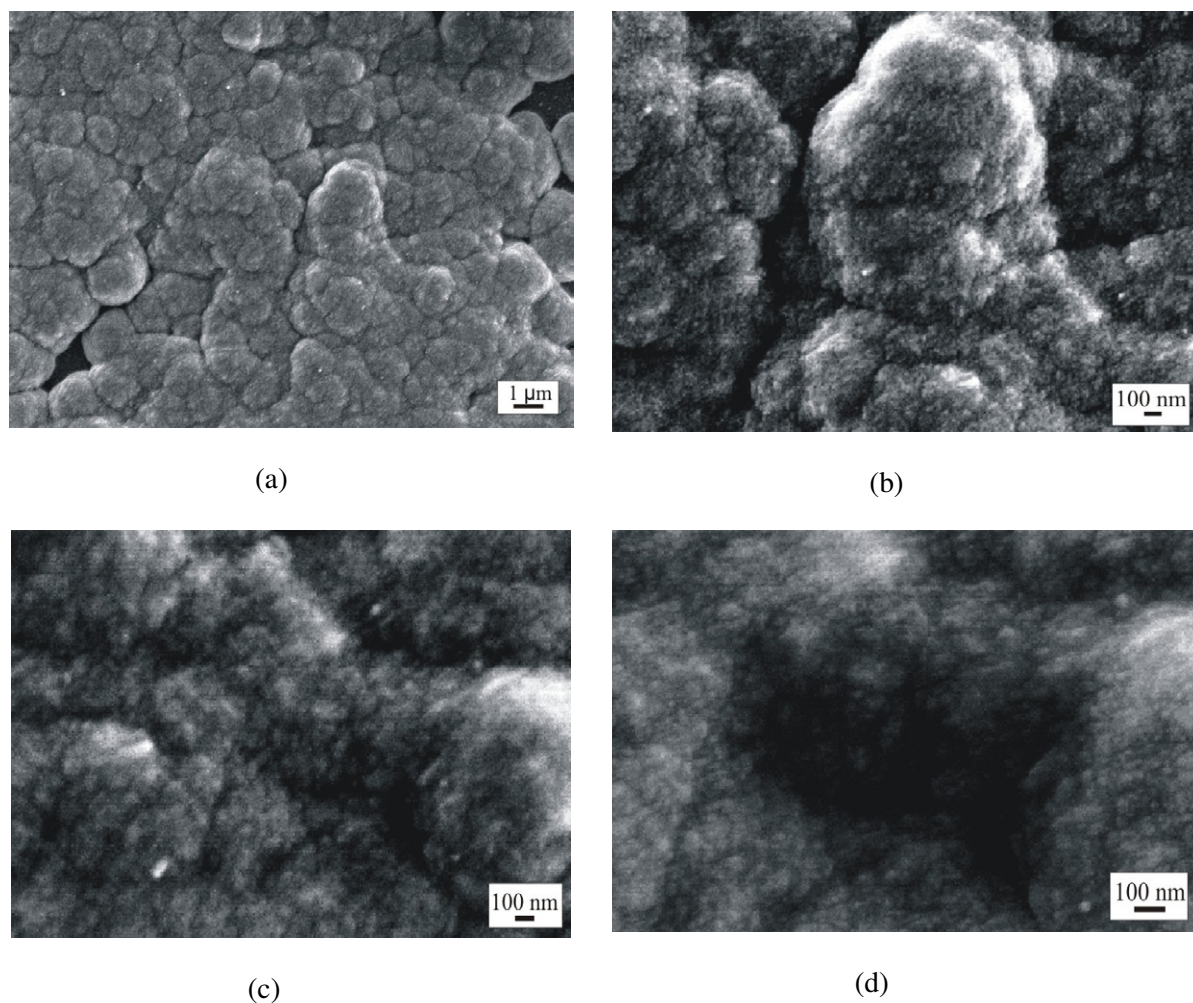


Figure 1. Typical FESEM images of the as-deposited samples at different magnifications

expected features for nanocrystalline diamond. The peak that appears at 1337 cm^{-1} is characteristic of diamond C-C sp^3 bonds, and is close to the accepted value (1332 cm^{-1}) for natural diamond. The peaks at 1350 cm^{-1} and 1550 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 [16-18] since some authors believe that it originates from confined phonon modes in nanocrystalline diamond and others claim that it is associated with C-C sp^2 vibrations at hydrogenated grain boundaries, where polyacetylene may be present [17-18]. The peak at 1470 cm^{-1} may also be assigned to polyacetylene [18] or nanocrystalline diamond [17].

Typical electron emission results are shown in Figure 3 (a)-(b) by plotting the current versus bias voltage (I-V) data for a fixed cathode-anode distance of $700\text{ }\mu\text{m}$ (Figure 3 (a)) and plotting the typical threshold voltage (V_{th}) versus the distance necessary to produce a standard threshold current density of about 500 nAcm^{-2} (Figure 3 (b)). A linear fit to this data provides the typical threshold field (E_{th}) for each sample. The lowest threshold field achieved was $13.20\text{ V}/\mu\text{m}$. This value is close to those achieved for S-doped microcrystalline diamond films ($12.0\text{ V}/\mu\text{m}$) prepared with H_2S doping [12]. However, most of the samples (77 % of $n = 9$) presented threshold fields above $20\text{ V}/\mu\text{m}$. The best threshold fields for electron emission of nanotubes, graphenes and nanostructured diamond are in the range of 1 to $10\text{ V}/\mu\text{m}$ [2-3, 9, 12, 19-20].

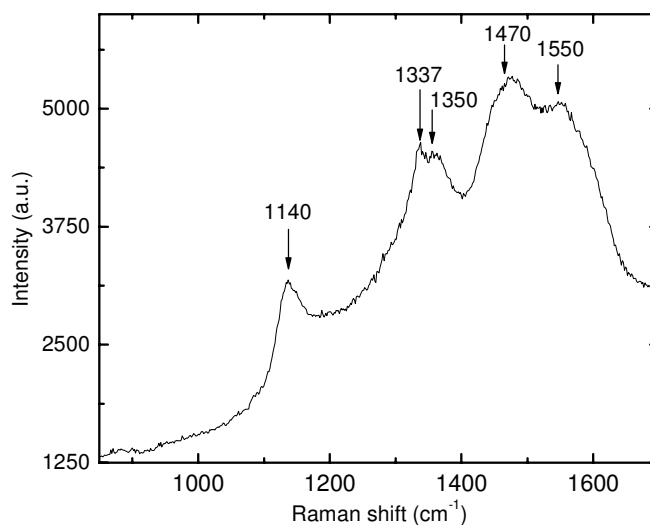


Figure 2. Typical Raman spectrum taken with a laser wavelength of 514.5 nm.

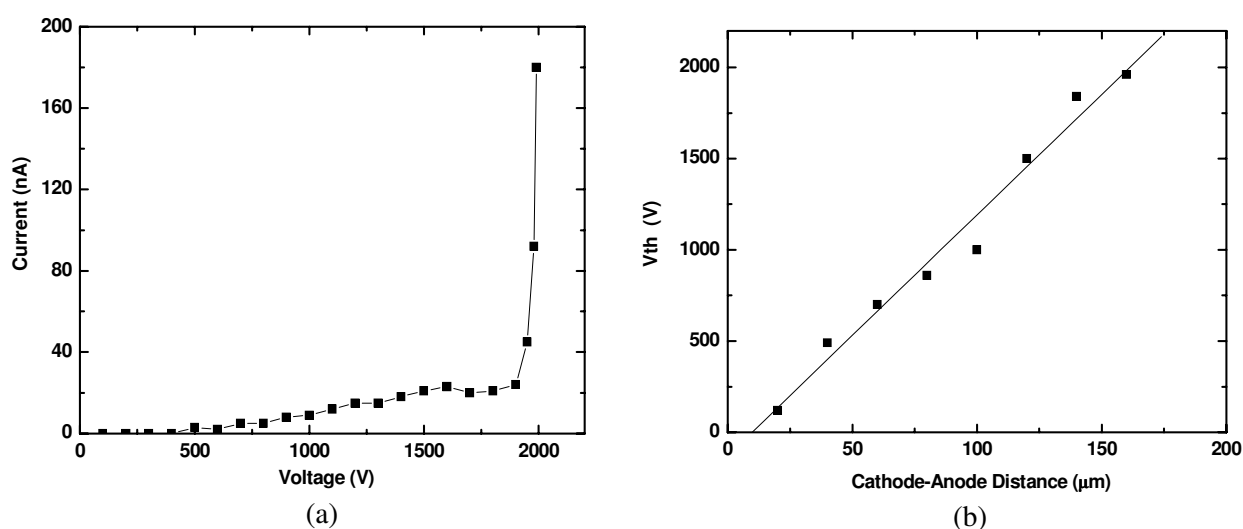


Figure 3. (a) Typical field emission current-voltage data, (b) Threshold voltage (V_{th}) versus distance necessary to produce a standard threshold current density of about 500 nAcm^{-2} .

Nanocrystalline CVD diamond is characterized by a small grain size, and described as sp^3 bonded grains (nanodiamond) embedded in a matrix of sp^2 bonded carbon (nanographite) [15]. 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. Grain size is also reduced due to the participation of sulphur-containing species in the deposition reactions, such as CS, and the incorporation of sulphur in the film structure and at grain boundaries [12-13]. Sulphur also enhances diamond secondary nucleation [14]. The Raman scattering and FESEM images (Figure 1 (a)-(d)) reveal very small crystallites, consistent with a highly sulphur-doped carbon deposition in an argon-rich feed gas mixture.

Since a high concentration of CS_2 was used in the CVD feed, a large concentration of sulphur is expected to be incorporated into the samples, but owing due to its large covalent radius sulphur may not easily substitute carbon in the diamond lattice to act as an ionized active electron-donor, but may

induce lattice and surface defects. 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.

4. Conclusions

Sulphur-doped nanocrystalline diamond films were synthesized by hot-filament chemical vapor deposition using carbon disulfide diluted in ethyl alcohol, hydrogen and argon. Sulphur and argon increased secondary nucleation and the local disorder of the diamond grain boundaries, which leads to grains in the range of 10 to 30 nm. Raman measurements show that the nanodiamonds are embedded in a matrix of graphite and disordered carbon grains. The lowest threshold achieved for electron field emission was 13.20 V/ μm . We suggest that the enhancement in field emission is due to the increase in electron transport through sulphur-doped grains and intergranular surface defects.

Acknowledgments

The electron microscopy work was performed with the JSM-5900 LV microscope of the LME/LNLS - Campinas. We wish to express sincere thanks to Prof. S. F. Durrant of UNESP in Sorocaba, SP - Brazil for his technical assistance. We also gratefully acknowledge the Brazilian agencies FAPESP, CAPES and CNPq for partial financial support.

References

- [1] Yang A T S, Lay J Y, Wong M S and Cheng CL 2002 *J. Appl. Phys.* **92** 2133.
- [2] Mammana VP, Santos TEA, Mammana A, Baranauskas V, Ceragioli HJ and Peterlevitz AC 2002 *Appl. Phys. Lett.* **81** 3470.
- [3] Baranauskas V, Fontana M, Ceragioli HJ and Peterlevitz AC 2004 *Nanotech.* **15(10)** S678.
- [4] Gruen DM 1998 *MRS Bull.* **9** 32.
- [5] Jin BM and Kim CC 1997 *Appl. Phys. A: Solid Surf.* **65** 53.
- [6] Himpsel FJ Knapp JA VanVechten JA and Eastman PE 1979 *Phys. Rev. B* **20** 624.
- [7] Bandis B and Pate BB 1996 *Appl. Phys. Lett.* **69** 366.
- [8] Okano K Yamada T Suave A Koizumi S and Pate BB 1999 *Appl. Surf. Sci.* **146** 274.
- [9] Kurt R Bonard JM and Karimi A 2001 *Diam. Rel. Mater.* **10** 1962.
- [10] Bonnot AM Deldem M Beaugnon M Fournier T Schouler MC and Mermoux M 1999 *Diam. Rel. Mater.* **8** 631.
- [11] Gruen DM Liu S Krauss AR Liuy A Luo J and Foster CM 1994 *J. Vac. Sci. Technol. A* **12** 1491.
- [12] Gupta S Weiner BR and Morell G 2002 *Diam. Rel. Mater.* **11** 799.
- [13] Gupta S Weiner BR and Morell G 2005 *J. Appl. Phys.* **97** 094307.
- [14] Morell G González-Berríos A Weiner BR and Gupta S 2006 *J. Mater. Sci: Mater. Electron* **17** 443.
- [15] Koeck FAM Zumer M Nemanic V and Nemanich RJ 2006 *Diam. Rel. Mater.* **15** 880.
- [16] Shroder RE Nemanich RJ and Glass JT 1990 *Phys. Rev. B* **41** 3738.
- [17] Birrell J Gerbi JE Auciello O Gibson JM Johnson J and Carlisle JA 2005 *Diam. Rel. Mater.* **14** 86.
- [18] Ferrari AC and Robertson J 2001 *Phys. Rev. B* **63** 121405(R).
- [19] Wu K Wang EG Cao ZX Wang ZL and Jiang X 2000 *J. Appl. Phys.* **88** 2967.
- [20] Proffitt SS Probert SJ Whitfield MD Foord JS and Jackman RB 1999 *Diam. Rel. Mater.* **8** 768.