FINAL REPORT

DOE GRANT No. DE-FG02-99ER45796

Proposal Title: Studies of the Growth and Doping of Diamond Thin Films

Principal Investigator: Dr. Gerardo Morell
UPR - Dept. of Physical Sciences
PO Box 23323, San Juan, PR 00931
Ph 787-645-0685, Fax 787-756-7717
Email gmorell@rrpac.upr.clu.edu

Co-Investigators: Dr. Brad R. Weiner, Dr. Antoni[o Mar][illegible]

Total DOE Funding: $234,999.00

Duration of Award: Oct 1999 - Sep 2002

Reporting period: Oct 1999 - Sep 2002

Abstract:
The objective of this research is to fabricate diamond thin films suitable for device fabrication, and to dope these films in order to obtain n-type semiconducting behavior. Chemical vapor deposition (CVD) is used to grow the films, and *in situ* ellipsometry is used to monitor the growing surface. Sulfur doping is accomplished by the addition of trace amounts of H_2S. Hall conductivity measurements show that the sulfur-incorporated films are n-type with conductivities around 100 S/cm. The surface roughness and growth rate were simultaneously improved by a factor of ten as a result of sulfur addition. The as-grown films look transparent and shiny. The surface roughness of these films is 20-50 nm, as measured by AFM, which is one order of magnitude lower than typical CVD microcrystalline diamond. Since the presence of sulfur changes the overall surface and gas reaction kinetics, systematic growth studies as a function of sulfur concentration, methane concentration, substrate temperature, and gas pressure are needed and underway. The results obtained enable the fabrication of small device structures (1 μm interdigit spacing) on diamond films and make diamond a more viable material for commercial applications. Moreover, the hot filament chemical vapor deposition system employed is much easier to upscale than other types of enhanced CVDs, and it has the additional advantage of being relatively insensitive to the presence of molecular nitrogen, which is the major source of unintentional doping in microwave CVDs. In the second phase of this research project, prototype electronic device structures will be fabricated on semiconducting diamond films in order to evaluate their UV sensing and electron field emitting characteristics.

Summary of Accomplishments:

- Sulfur-incorporated films are n-type with conductivities around 100 S/cm.
- Growth rates were increased by a factor of ten to around 15 μm/hr.
- Surface roughness was lowered in one order of magnitude to around 20-50 nm.
- The as-grown films are transparent and shiny, requiring no polishing.
- Smooth semiconducting diamond films enable the fabrication diamond electronic devices.

DISCLAIMER

Collaborations Developed:

Brookhaven National Laboratory
- Dr. Jack Miller, Brookhaven National Laboratory, P.O. Box 5000, Upton, NY 11973-5000, (631) 344-3830

National Institute of Standards and Technology
- Dr. George Lamaze, National Institutes of Standards & Technology, 100 Bureau Drive, Stop 8395, Gaithersburg, MD 20899-8395, Phone 301-975-6202

Pennsylvania State University
- Dr. Andrzej Badzian, Pennsylvania State University, 271 Materials Research Laboratory, University Park, PA 16801, Phone 814-865-1198, Email abadzian@psu.edu
- Dr. Larry Pilione, Pennsylvania State University, 262 Materials Research Laboratory, University Park, PA 16801, Phone 814-863-1967

Massachusetts Institute of Technology
- Dr. Ramachandra R. Dasari, Massachusetts Institute of Technology, George R Harrison Spectroscopy Laboratory, 6A-230 77 Mass. Ave., Cambridge, MA 02139, Phone 617-253-5377, Email rrdasari@mit.edu

University of Florida
- Dr. Rajiv K. Singh, University of Florida, Gainesville, FL, 32611, Phone 352-846-1194, Email: rsingh@mse.ufl.edu

Number of Postdocs: 1 (non DOE funded)

Number of Graduates: 5 (two DOE funded, one PhD and one MS theses produced)

Number of Undergraduates: 5 (one DOE funded)

Awards and Honors:
University of Puerto Rico Research Productivity Award
December 2000, Issued by UPR President's Office

Summary of Scientific Productivity:
- 25 Publications
  - 15 in refereed journals / 10 in conference proceedings
- 30 Presentations
  - 10 international / 12 national / 8 local
- 3 U.S. Patents (provisional patent already obtained, regular patent in process)
  - Sub 300^{o} C Diamond Growth (July 2001)
  - Nanocrystalline Carbon for Cold Cathode Applications (March 2002)
  - Nanocrystalline Carbon Microwave e- source (in conjunction with NCSU, April 2002)

Publications:

1. Ex Situ Spectroscopic Ellipsometry and Raman Spectroscopy Investigations on Chemical Vapor Deposited Sulfur Incorporated Nanocrystalline Carbon Thin Films, S. Gupta, B. R. Weiner, and G. Morell, Journal of Applied Physics, submitted March 2002.

2. Electron Field Emission Properties of Gamma Irradiated Microcrystalline Diamond and Nanocomposite Carbon Thin Films, S. Gupta, B. L. Weiss, B. R. Weiner, L. Pilione, A. Badzian, G. Morell, Journal of Applied Physics (2002) Accepted in June 2002.
3. Electrical conductivity studies of chemical vapor deposited sulfur incorporated nanocomposite carbon thin films, S. Gupta, A. Martínez, B. R. Weiner, and G. Morell, Applied Physics Letters 81, in press for July 2002.

4. Investigations of the Electron Field Emission Properties and Microstructure Correlation in Sulfur-Incorporated Nanocrystalline Carbon Thin Films, S. Gupta, B.R. Weiner, G. Morell, Journal of Applied Physics, 91, 10088 (2002).

5. Synthesizing Nanocrystalline Carbon Thin Films by Hot Filament CVD and Controlling Their Microstructure, S. Gupta, B.R. Weiner, G. Morell, Journal of Materials Research 17, (2002).

6. X-Ray Photoelectron and Raman Spectroscopy Studies of Sulfur Impurity Incorporated Nanocrystalline Carbon Thin Films Deposited By HFCVD for Electronic Displays, S. Gupta, B.R. Weiner, G. Morell, Materials Research Society Meeting Symposium Procedings F8.44 (2002).

7. Optical Characterization and Modeling of Sulfur Incorporated Nanocrystalline Carbon Thin Films Deposited By Hot Filament CVD, S. Gupta, B. R. Weiner and G. Morell, Mater. Res. Soc. Symp. Proc. 703, V11.9 (2002)

8. Role of sp^2 C Cluster Size on the Field Emission Properties of Sulfur-incorporated Nanocomposite Carbon Thin Films Grown by Chemical Vapor Deposition, S. Gupta, B. R. Weiner, and G. Morell, Applied Physics Letters 80, 1471 (2002).

9. Electron Field Emission from S-Incorporated Nanocrystalline Carbon Thin Films, S. Gupta, B. R. Weiner, B. L. Weiss, G. Morell, Applied Physics Letters 79, 3446 (2001).

10. Low-Field Electron Emission Properties from Intrinsic and S incorporated Nanocrystalline Carbon Thin Films Grown by Hot- Filament CVD, G. Morell, S. Gupta, B. R. Weiner, B. L. Weiss, K. Johnson O. Ortiz, Materials Research Society Symposium Proceedings Vol. 638, F16.2.1 (2001).

11. Effects of Sulfur Concentration on the Electron Field Emission Properties of Nanocrystalline Carbon Thin Films, S. Gupta, B. L. Weiss, B. R. Weiner, G. Morell, Materials Research Society Symposium Proceedings Vol. 675, W6.9.1 (2001).

12. Investigation of the Layered Structure of Polycrystalline Diamond Thin Films Grown by ECR-Assisted CVD by Spectroscopic Phase Modulated Ellipsometry, G. Morell, S. Gupta, B. R. Weiner, Materials Research Society Symposium Proceedings Vol. 648, P6.51.1 (2001).

13. Ex Situ Spectroscopic Ellipsometry Investigation of the Layered Structure of Polycrystalline Diamond Thin FilmsGrown by Electron Cyclotron Resonance-Assisted Chemical Vapor Deposition, S. Gupta, B. R. Weiner, G. Morell, Journal of Applied Physics, 90, 1280 (2001).

14. Spectroscopic ellipsometry studies of nanocrystalline carbon thin films deposited by HFCVD, S. Gupta, B.R. Weiner and G. Morell, Diamond & Related Materials 10, 1968 (2001).

15. Study of the Electron Field Emission and Microstructure Correlation in Nanocrystalline Carbon Thin Films, S. Gupta, B. L. Weiss, B.R. Weiner, G. Morell, Journal of Applied Physics, 89, 5671 (2001).

16. Study of the Effects of Low-Energy Electron Bombardment During the Chemical Vapor Deposition of Diamond, J. A. González, O. L. Figueroa, B.R. Weiner, and G. Morell, Journal of Materials Research 16, 293 (2001).

17. Structural Evolution During Chemical Vapor Deposition of Diamond Thin Films, G. Morell, L.M. Cancel, O.L. Figueroa, B.R. Weiner, Journal of Applied Physics 88, 5716 (2000).

18. Microstructural Studies of Diamond Thin Films Grown by Electron Cyclotron Resonance-assisted Chemical Vapor Deposition, S. Gupta, R. S. Katiyar, D. R. Gilbert, R. K. Singh, and G. Morell, Journal of Applied Physics 88, 5695 (2000).

19. In situ phase-modulated ellipsometry study of the surface damaging process of silicon under atomic hydrogen, G. Morell, I.M. Vargas, J.Y. Manso, J.R. Guzmán, and B.R. Weiner, Solid State Communications 116, 217 (2000).

20. Effects of low temperatures, low pressures and seeding over the crystalline quality, yield and stress of diamond films grown by ECR-assisted chemical vapor deposition, S. Gupta, G. Morell, R.S. Katiyar, D.R. Gilbert, R.K. Singh, Journal of Materials Science 35, 6245 (2000).

21. Electron Field Emission Characterization of Nanocrystalline Diamond Thin Film Cold Cathode Devices, B.L. Weiss, A. Badzian, L. Pilione, T. Badzian, W. Drawl, and G. Morell, Materials Research Society Symposium Proceedings Vol. 593, pp. 227-232 (2000).

22. Controlling the diamond film morphology by low-energy electron bombardment, J.A. González, O. L. Figueroa, B.R. Weiner, G. Morell, Materials Research Society Symposium Proceedings Vol. 585, pp. 283-288 (2000).

23. Effects of Seeding over the Microstructure and Stresses of Diamond Thin Films, S. Gupta, G. Morell, R.S. Katiyar, D.R. Gilbert, and R.K. Singh, Materials Research Society Symposium Proceedings Vol. 594, pp. 337-342 (2000).

24. In situ spectroscopic ellipsometry study of the oxide etching and surface damaging processes on silicon under hydrogen plasma, I.M. Vargas, J.Y. Manso, J.R. Guzmán, B.R. Weiner, G. Morell, Materials Research Society Symposium Proceedings Vol. 591, pp. 295-300 (2000).

25. In situ ellipsometry study of the diamond film evolution process, L.M. Cancel, O.L. Figueroa, B.R. Weiner, G. Morell, Materials Research Society Symposium Proceedings Vol. 580, pp. 351-356 (2000).