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PLASMA, PHOTON, AND BEAM SYNTHESIS OF DIAMOND FILMS AND MULTILAYERED STRUCTURES

Progress Report

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Abstract

Under the sponsorship of Department of Energy the diamond research program at Northwestern University has made major contributions to the field of diamond thin film science during the past three years. In the area of nucleation, it was discovered that C_{70} thin films are perfect substitutes for diamond seeds in the growth of diamond films. This research, along with a careful study of diamond growth on carbon ion implanted single crystal copper, have clearly demonstrated that structured carbon is the best precursor for nucleation and growth of diamond films on non-diamond surfaces. In addition, by using fluorine chemistry during diamond growth, it has been shown that diamond films can grow on carbide substrates without the pretreatment of diamond seeding. The growth rates are higher and the film adhesion is much improved. These discoveries have major impacts on the development of diamond films as an important energy material for the Department of Energy, the United States, and the rest of the world.

Introduction

During the past ten years, there has been a rapid increase in the research and development of chemical vapor deposition of diamond thin films. The prime driving force behind this push is the potential birth of a technology that will generate a multibillion-dollar market for many industries. Applications of the chemical vapor deposition technique include synthesis of diamond films, diamond fibers, and diamond composites. These new forms of diamond materials will be used in protective coatings, light-weight planes and vehicles, electronic and optical devices and systems, to mention just a few. Of special interest to the Department of Energy is the development of a new energy material for application in transportation systems, thermal management systems, corrosion-resistant coating, sensors, etc.

During the past three years, the DOE-sponsored diamond film research program at Northwestern University has made some major contributions to the understanding of diamond film growth on non-diamond substrates. In particular, it is discovered that structured pure carbon molecules such as C_{70} are excellent nucleation agents when placed on non diamond surfaces. This work has overcome a major barrier in hetero growth of diamond on non-diamond substrates. To date, diamond grit polish has been used as a pretreatment for the growth of diamond films on non-diamond substrates. Such a pretreatment is not desirable for coating large or nonplanar surface areas. In addition, it has been discovered that by using a fluorine bearing carbon precursor, such as CF_4, diamond films can be grown on carbide surfaces with improved adhesion and at a much increased rate. Significant accomplishments from the past 3 years are discussed below:

A. Properties of Boron Doped Diamond Films

The effects of the gas phase boron concentration and plasma deposition conditions on the morphological and electrical properties of polycrystalline diamond films have been investigated. The diamond films are prepared on both n and p type of Si substrates by microwave plasma assisted CVD using a tri-methylborate/methanol dopant source. DC conductivity vs. temperature measurements as well as secondary ion mass spectroscopy (SIMS), Raman spectroscopy, and SEM analysis are conducted on the films. Boron is found to have a significant effect on the morphology of the deposited films depending on the pressure at which the diamond is grown. At high deposition pressure (100 torr), the doping of the diamond film is varied to produce a highly doped p-type material with a minimum resistivity measured to be 0.05 ohm-cm and little change is observed in the morphology or Raman spectra among the films. At lower deposition pressures (50 torr), for the same gas composition and dopant level conditions, boron is found to affect both the conductivity and morphology of the deposited films. With increasing gas phase dopant concentration, both the resistivity and the grain size of the deposited diamond films decrease. Raman spectra of these highly doped films exhibit a 1130 cm^{-1} peak previously attributed to a microcrystalline form of diamond. The resistivity vs. temperature profile of these samples is distinctly different from that of semiconductor diamond. The above results have been discussed in terms of current models of electrical conduction in polycrystalline semiconductors, semiconductor diamond, and related doped carbon thin films.

B. Composite Diamond Films on Iron Surfaces

We reported for the first time that diamond composite films consisting of diamond particles, hydrogenated amorphous carbon, and/or fluorocarbon films could be successfully deposited on carbon steel and 304 stainless-steel substrates by plasma-assisted chemical vapor deposition. The use of thin (~200 Å) silicon buffer layer proved to be effective in inhibiting surface catalytic effect of iron and also prevented carbon species from diffusing into the bulk. The composite films adhered well to the substrates even upon imposing a scratch load of 68 newtons. They could also be bent up to 10° and still remain chemically inert and impermeable to salt solution. One of the potential applications of these films is for protective coating on sheet metal surfaces.

C. Diamond Nucleation and Growth on Copper Surfaces

The nucleation and growth of diamond crystals on single crystal copper surfaces has been studied. Microwave plasma enhanced CVD was used for diamond deposition. The single crystal Cu substrate was implanted at elevated temperature (~820 °C) with carbon ions prior to diamond growth. This procedure leads to the formation of a graphitic film on the Cu surface which greatly enhances the diamond crystallite nucleation. From our study we construct a simple lattice model for diamond growth on graphite as <111> diamond parallel to $\langle 0001 \rangle_{graphite}$ and $\langle 110 \rangle_{diamond}$ parallel to $\langle 1120 \rangle_{graphite}$

D. Nucleation of Diamond on Surfaces Using Fullerenes

A unique method for nucleating diamond films on surfaces using fullerenes has been invented. The process substitutes the need for diamond polish pretreatment of substrates prior to diamond film growth, as currently practiced in low-pressure (<1 atm) chemical vapor deposition methods. We have used C_{70} films as diamond nucleating layers on single-crystal Si, SiO_2 and Mo surfaces. It is shown that a thin layer (approximately 1000 Å) of pure carbon C_{70} is sufficient for the nucleation and growth of fine grain polycrystalline diamond films. The enhancement of nucleation by the C_{70} layer is nearly ten orders of magnitude over untreated surfaces. It also follows that fullerenes can be used as a one-step lithographic template for growing diamond on selected regions of the substrate. In addition, insight into the mechanism for diamond nucleation from fullerenes has been obtained.

E. A New Plasma Enhanced Laser Ablation System

Funding support received from the State of Illinois allowed us to design and construct a new microwave plasma enhanced laser ablation system for the purpose of studying the growth of diamond-like thin films and multilayers. Our UHV compatible system is one of a kind in the world. This system is currently in operation and diamond-like films have been deposited on an array of substrates, including plastic, stainless steel, silicon, etc.

F. Properties of Amorphous Diamond Films

We have deposited hydrogen-free diamond-like amorphous carbon (amorphous diamond) films by ArF (193nm) pulsed laser ablation of a graphite target. The deposition process is performed with the laser power density of only 5×10^8 w/cm^2 at room temperature without any auxiliary energy source. The resulting films possess remarkable physical, optical and mechanical properties which are close to diamond and distinctly different from the graphite target used. The films have a mechanical hardness up to 38 GPa, an optical energy band gap of 2.4 eV with excellent thermal stability. Analysis of electron energy loss spectroscopy reveals the domination of diamond-type tetrahedral bonding structure in the films with the SP^3 bond fraction over 95%. The experimental results show that the laser wavelength or photon energy plays a crucial role in controlling the properties of the pulsed laser deposited diamond-like carbon films.

G. Diamond Growth on Carbide Surfaces Using Fluorine Chemistry

We have made preliminary studies on how diamond films can be grown on carbide surfaces without using the standard diamond grit abrasion pretreatment on carbide substrate surfaces. Our approach is to first use fluorine as a selective etchant to preferentially remove the metal of the carbide surface layer. This treatment leaves a carbon rich surface on the substrate for nucleation and growth of diamond thin film. In practice, we have used CF_4 as a source of fluorine for etching and carbon for growing diamond. Thus in place of the usual CH_4, we substitute a few percent of CF_4 in our experiments. Using this procedure we are able to grow diamond on tungsten carbide and silicon carbide. We have successfully grown diamond films on tungsten carbide tool inserts with much improved performance. A patent based on this process has already been filed.

Other Federal Funding

Agency: Dept. of the Navy, Office of Naval Research (ONR)
Current funding: $110,000
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Status of students

Andrew Yee, Ph.D. Candidate
Expected graduation date: Sept. 1994

Fulin Xiong, Postdoctoral Associate
About 50% on this project

Publications/presentations supported by this Grant:

A. Talks

1. "Plasma Enhanced Chemical Vapor Deposition of Thin Diamond Films", R.P.H. Chang, TMS Annual Meeting, Anaheim, CA, Feb. 1990

2. "Plasma Enhanced Chemical Vapor Deposition of Diamond Films", R.P.H. Chang, University of Minnesota, MN, Jan. 1990

3. "Diamond Film Science and Technology", R.P.H. Chang, Midwest Chinese Society, Evanston, IL, April 1990

4. "Plasma Processing for Advanced Thin Film Technology in the 21st Century", R.P.H. Chang, Chinese Materials Research Society (CMRS) Meeting, Beijing, June 1990

5. "Flexible Diamond Composite Coatings for Steel", T.P. Ong, R.P.H. Chang, International Conference on the New Diamond Science and Technology (ICNDST), Washington, DC, Sept. 1990

6. "Plasma Enhanced CVD of Diamond Films", R.P.H. Chang, Joint Symp. of the American Vacuum Society/Electrochemical Society/North Texas Materials Characterization Society, Dallas, TX, June 1990

7. "Diamond Research at Northwestern University", R.P.H. Chang, Argonne National Laboratory, Argonne, IL, Feb. 1992

8. "Overview of Diamond Film Technology: Trends and Opportunities", R.P.H. Chang, Argonne National Laboratory, Argonne, IL, March 1992

9. "Overview of Diamond Film Technology: Trends and Opportunities", R.P.H. Chang, Annual Conference of the Chinese Society for Materials Science, Taiwan, April 1990

10. "Preparation of Nanocrystalline Diamond Films for Optical Coating Applications using a Pulsed Microwave Plasma CVD Method", T.P. Ong, W.A. Chiou, F.R. Chen, R.P.H. Chang, Workshop on the Science and Technology of Diamond Thin Films, Concord, OH, May 1990

11. "The Electrical Properties of B Doped Microwave Plasma CVD Diamond Films", R. Meilunas, R.P.H. Chang,

International Conference on Electronic Materials-90, Newark, NJ, Sept. 1990

12. "Overview of Diamond Film Technology: Trends and Opportunities", R.P.H. Chang, Illinois Chapter of the American Vacuum Society Fall Meeting, Naperville, IL, Sept. 1990

13. ibid, R.P.H. Chang, Northwestern University, Evanston, IL, Oct. 1990

14. "Recent Results of Plasma Enhanced Thin Diamond Film Studies at Northwestern University", R.P.H. Chang, Meeting of the Office of Naval Research Grantees, Penn State University, PA, Oct. 1990

15. "Overview of Diamond Film Technology: Trends and Opportunities", R.P.H. Chang, National Center for Manufacturing Science Day (Nov. 20), Northwestern University, Nov. 1990

16. ibid, R.P.H. Chang, Chicago-Milwaukee Section of American Ceramic Society, March 1991

17. "Preparation, Characterization and Application of Buckminsterfullerene", S. Liu, J. Hunter, V. Dravid, R. Meilunas, R.P.H. Chang, Manfred Kappes, Industrial Associates Meeting, Northwestern University, March 1991

18. "Recent Developments of Diamond Research at Northwestern University", R.P.H. Chang, Meeting of the Office of Naval Research Grantees, Arlington, VA, July 1991

19. "Diamond Nucleation Using Carbon Clusters", R.P.H. Chang, Japan Materials Research Society Meeting, Tokyo, Dec. 1991

20. "Nucleation of Diamond Films on Surfaces Using Carbon Clusters", R. Meilunas, R.P.H. Chang, S.Z. Liu, M. Kappes, Materials Research Society Fall Meeting, Boston, MA, Dec. 1991

21. "Structural Probes of C_{60} and C_{70}", S. Liu, R. Meilunas, Y.J. Lu, R.P.H. Chang, V.P. Dravid, J.A. Ibers, M.M. Kappes, Materials Research Society Fall Meeting, Boston, MA, Dec. 1991

22. "A Mechanism for Diamond Nucleation and Growth on Single Crystal Copper", T.P. Ong, R.P.H. Chang, C.W. White, The International Workshop on Science and Technology of Thin Diamond Films for the 21st Century, Northwestern University, Evanston, IL, July 1991

23. "Diamond Film: Science and Technology", R.P.H. Chang, Technology Reviews Seminar, Northwestern University, Evanston, IL, Nov. 1991

24. "Nucleation of Diamond Films Using Carbon Clusters", R.P.H. Chang, International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 1992

25. "Nucleation of Diamond Films on Surfaces Using Carbon Clusters", R.J. Meilunas, R.P.H. Chang, S. Liu, M.M. Kappes, Materials Research Society Spring Meeting, San Francisco, CA, April 1992

26. "A Mechanism for Diamond Nucleation and Growth on Single Crystal Copper Surfaces", T.P. Ong, F. Xiong, R.P.H. Chang, C.W. White, Materials Research Society Spring Meeting, San Francisco, CA, April 1992

27. "Generation, Separation and Spectroscopic Characterization of the Higher Fullerenes", S. Liu, A.L. Yee, R.P.H. Chang, R. Vu, M.M. Kappes, Materials Research Society Spring Meeting, San Francisco, CA, April 1992

28. "On the Use of C_{60} or C_{70} Clusters to Nucleate Diamond Crystals", R.P.H. Chang, 181st Electrochemical Society Meeting, St. Louis, MO, May 1992

29. "Physical Characterization of C_{76}, C_{78}, C_{84} and of Other Higher Fullerenes", S. Liu, A. Yee, V. Dravid, R. Michel, M. Kappes, R.P.H. Chang, Materials Research Society Fall Meeting, Boston, Dec. 1992

30. "Recent Advances in Diamond Research at Northwestern University", R.P.H. Chang, National Renewable Energy Laboratory Diamond Thin Film Symposium, Golden, CO, Sept. 1992

31. "Nucleation of Diamond Films on Surfaces Using Carbon Clusters", R.P.H. Chang, Illinois Institute of Technology, Sept. 1992

32. "Potential Technological Applications of Fullerenes", R.P.H. Chang, American Chemical Society Meeting, Niles, IL, Sept. 1992

33. "Applications of Fullerenes for Diamond Nucleation and Optical Second Harmonic Generation", R.P.H. Chang, Associated Colleges of the Chicago Area, Argonne Natl. Lab., Argonne, IL, Sept. 1992.

B. Publications

a. Proceedings

1. "Flexible Diamond Composite Films for Sheet Metal Coating Applications", T.P. Ong and R.P.H. Chang, NDST (New Diamond Science and Technology) Conference Proceedings, edited by R. Messier, J.T. Glass, J. Butler, R. Roy (Materials Research Society, Pittsburgh, PA, 1991) p. 797

2. "The Physical and Electrical Properties of Boron Doped Diamond Thin Films", R. Meilunas and R.P.H. Chang, Proceedings of the Second International Conference on Electronic Materials, edited by R.P.H. Chang, Michael Geis, Bernie Meyerson, David A.B. Miller, R. Ramesh (Materials Research Society, Pittsburgh, PA, 1990) p. 609

3. Proceedings of the Second International Conference on Electronic Materials, edited by R.P.H. Chang, Michael Geis, Bernie Meyerson, David A.B. Miller, R. Ramesh (Materials Research Society, Pittsburgh, PA, 1990)

b. Papers

1. "Properties of Diamond Composite Films grown on Iron Surfaces", T.P. Ong and R.P.H. Chang, Appl. Phys. Lett., **58**, 358 (1991)

2. "Oxidation Studies of Fluorine Containing Diamond Films", K.J. Grannen, D.V. Tsu, R.J. Meilunas, R.P.H. Chang, Appl. Phys. Lett., **59**, 745 (1991)

3. "Infrared and Raman Spectra of C_{60} and C_{70} Solid Films at Room Temperature", R. Meilunas, S. Liu, R.P.H. Chang, M. Kappes, J. Appl. Phys., **70**, 5128 (1991)

4. "Nucleation of Diamond Films on Surfaces Using Carbon Clusters", R. Meilunas, R.P.H. Chang, S.Z. Liu, M. Kappes, Appl. Phys. Lett., **59**, 3461 (1991)

5. "Activated C_{70} and Diamond", R. Meilunas, R.P.H. Chang, S.Z. Liu, M. Kappes, Nature, **354**, 271 (1991)

6. "Workshop Identifies Scientific, Commercial Opportunities for Future Thin Film Research and Technology", R.P.H. Chang, J.M. Poate, MRS Bulletin, **XVI**, 63 (1991)

7. "A Mechanism for Diamond Nucleation and Growth on Single Crystal Copper Surfaces", T.P. Ong, F.L. Xiong, R.P.H. Chang, Appl. Phys. Lett., **60**, 2083 (1992)

8. "Nucleation and Growth of Diamond on Carbon-Implanted Single Crystal Copper", T.P. Ong, F. Xiong, R.P.H. Chang, C.W. White, Journal of Materials Research , **7**, 2429 (1992)

9. "A Comparison Study of Diamond Films Grown on Tungsten Carbide Cobalt Tool Inserts with CH_4 and CF_4 Gas Sources", K.J. Grannen, F. Xiong, R.P.H. Chang, submitted to Surface and Coating Technology Journal (1992)

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