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13. ABSTRACT (Maximum 200 words)

Significant progress has been made in producing large area, heteroepitaxial diamond films. Work has been directed at heteroepitaxial nucleation of diamond on nickel in a hot-filament chemical vapor deposition (CVD) reactor; and high rate, textured growth in a flat flame acetylene combustion reactor. In addition, a detailed kinetic model of the combustion reactor has been developed and validated by gas microprobe sampling. Comparisons of model predictions and experimental observations of growth rate and morphology have been used to develop a full understanding of the deposition process. Future studies will begin examining dopant effects on the diamond nucleation and growth process.

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CHARACTERIZATION OF DIAMOND FILM GROWTH IN A COMBUSTION FLAME

FINAL REPORT

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May 22, 1998

Summary: This research has investigated the growth of diamond films in the combustion flame of an oxyacetylene torch. As a result of this research we now have a good understanding of the parameters that affect the growth of high quality diamond films and a better understanding of the nucleation process. Research resulting in the growth of highly textured, high quality diamond films on Si (100) substrates is reported.

This final report presents progress made during ARO contract #31720-MS, covering the period from 1 April 1993 - 31 March 1998.

(1) LIST OF MANUSCRIPTS:

Book Chapters:

1. "Combustion Synthesis of Diamond", C.A. Wolden and J.T. Prater, Chapter 8 in Diamond Thin Films Handbook (Eds. J Asmussen and D. Reinhard) Marcel Dekker Inc, NY (1997)

2. "Combustion Flame Deposition of Diamond", C.A. Wolden, Z. Sitar and R.F. Davis, Chapter 3 in Low Pressure Synthetic Diamond: Manufacturing and Applications (Eds. B. Dischler and C. Wild) Springer-Vertag, Heidelberg, in press (1997).

Journal and Proceedings Publications:

1. "The Influence of Nitrogen on the Morphology, Growth Rate and Raman Spectra of Combustion Grown Diamond", C.A. Wolden, C.E. Draper, Z. Sitar and J.T. Prater, accepted for publication in Diamond and Related Materials (1998).

2. "Transmission Electron Microscopy Analysis of Oriented Diamond on Nickel Substrates", W. Liu, P. Yang, C.A. Wolden, R.F. Davis, J.T. Prater and Z. Sitar, J. of Applied Physics, Vol.83, No 12 (15 June 1998).

3. "Heteroepitaxial Nucleation of Diamond on Nickel", Z. Sitar, W. Liu, P.C. Yang C.A. Wolden, R. Schlesser and J.T. Prater, Diamond and Related Materials,7, (1998), p.276-82.

4. "Surface Melting in the Heteroepitaxial Nucleation of Diamond on Ni", P.C. Yang, W.Liu, R. Schlesser, C..A. Wolden, R.F. Davis, J.T. Prater and Z. Sitar, Journal of Crystal Growth, 187 (1998) p.81-88.

5. " Flat Flame Diamond CVD: The Effect of Pressure and Operating Conditions for Specific Applications", C.A. Wolden, R.F. Davis, Z. Sitar and J.T. Prater, Diamond and Related Materials, 7 (1998), 133-38.

6. "The Influence of Reactant Composition and Substrate Material on the Combustion Sythesis of Diamond", C.A. Wolden, C.E. Draper, Z. Sitar and J.T. Prater, accepted for publication in Journal of Materials Science, (1998).

7. "Highly Oriented Diamond Deposited with a Low Pressure Flat Flame", C.A. Wolden, S.K. Han, M.T. McClure, Z. Sitar and John Prater, Vol 32, No 1, Materials Letters, 9-12 (1997).

8. "In-situ Mass Spectrometry During Diamond Chemical Vapor Deposition Using a Low Pressure Flat Flame", C.A. Wolden, R.F. Davis, Z. Sitar and J.T. Prater, Journal of Materials Research, Vol.12, No. 10, 2733-42 (Oct. 1997).

9. "Control of Diamond Heteroepitaxy on Nickel by Optical Reflectance", P. Yang, R.

Schlesser, C.A. Wolden, W. Liu, R.F. Davis, J.T. Prater and Z. Sitar, Applied Physics Letters, 70 (22), 2960-62 (1997).

10. "Coalesced Oriented Diamond Films on Nickel", P. Yang, C.A. Wolden, W. Liu, R. Schlesser, R.F. Davis, J.T. Prater and Z. Sitar, Journal of Materials Research, **13** No. 5 (May 1998), p.1120.

11. "Low Temperature Deposition of Optically Transparent Diamond Using a Low Pressure Flat Flame", C.A. Wolden, R.F. Davis, Z. Sitar and J.T. Prater, submitted to Diamond and Related Materials (April 1997)

12. "Novel Approaches to Heteroepitaxial Nucleation of Diamond on Nickel", Z. Sitar, P. Yang, W. Liu, R. Schlesser, C.A. Wolden, and J.T. Prater, Advanced Materials '97, Proceedings of the 4th NIRIM International Symposium on Advanced Materials, Tsukuba, Japan, March 3-7, p.7-13 (1997).

13. "Growth of Highly Oriented Polycrystalline Daimond Films in an Enclosed Combustion Flame System", J.T. Prater, P.C. Yang, Shane Trent, Z. Sitar and R.F. Davis , Proceedings 20th Army Science Conference, p. 95 (1996).

14. "Experimental and Modeling Investigations of a Strained C2H2 O2-Ar Flame Used in Diamond Deposition", C.A. Wolden, Z. Sitar, R.F. Davis and J.T. Prater, submitted Combustion and Flame (November 1996)

15. "Nucleation and Growth of Oriented Diamond on Nickel Substrates", P. Yang, W. Liu, C.A. Wolden, Z. Sitar, R.F. Davis and J.T. Prater, Proceedings of Materials Research Society, Vol.423, 281-86 (1996).

16. "TEM Analysis of the Phases Observed During the Growth of Oriented Diamond on Nickel", W. Liu, P. Yang, C.A. Wolden, Z. Sitar, R.F. Davis and J.T. Prater, Proceedings of Materials Research Society, Vol.423, 457-62 (1996).

17. "Textured Diamond Growth by Low Pressure Flat Flame Chemical Vapor Deposition", C.A. Wolden, Z. Sitar, R.F. Davis and J.T. Prater, Applied Physics Letters, 69 (15), 2258-60 (1996).

18. "Growth of Diamond Films Using an Enclosed Combustion Flame", P.W. Morrison, Jr, A. Somashekhar, J.T. Glass and J.T. Prater, J. Appl. Phys., Vol. 78, No. 6 (1995), p. 4144.

19. "Nucleation and Growth of Oriented Diamond Films on Ni Substrates", P.C. Yang, T.J. Kistenmacher, D.A. Tucker, W. Liu, F.R. Sivazlian, S.P. Bozeman, B.P. Stoner, J.T. Prater, J.T. Glass, and R.F. Davis; Applications of Diamond Films: Third International Conference; edited by A. Feldman, Y. Tzeng, W.A. Yarbrough, M. Yoshikawa and M. Murakawa, (1995) p. 329.

20. "Effect of Native SiO2 Layer on the Nucleation of Diamond Using a Combustion Flame", M.T. McClure, J. A. von Windheim, J.T. Glass and J.T. Prater, Diamond and Related Materials, Vol. 3 (1994), p. 239-44.

21. "Nucleation Enhancement and Growth of Diamond Films Using an Enclosed Combustion Flame", P.W. Morrison, Jr, A. Somashekhar, J.T. Glass and J.T. Prater, Novel Forms of Carbon II, edited by C.L. Renschler, D.M. Cox, J.J. Pouch and Y. Achiba, MRS Symposium Proceedings Vol 349 (1994), p.403- 408.

(2) SCIENTIFIC PERSONNEL:

John T.Prater - P.I.
Robert F. Davis - co-P.I. (1996-98)
Zlatko Sitar - co-P.I. (1996-98)
Jeffrey Glass - co-P.I. (1992-95)
Shane Trent - Masters (1993-95)
Peichun Yang - Ph.D. (1995-97)
Wei Liu - (1997-present)
Colin Wolden - Postdoctoral Student

(3) INVENTIONS: None

(4) SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

Program Objective: The purpose of this research is to provide an improved understanding of the early nucleation and growth of high quality diamond films deposited by combustion flame synthesis. The immediate program objectives have been twofold: 1) to identify surface features and chemical effects that control the formation of epitaxially oriented diamond nuclei on Ni substrates, and 2) to determine processing methods that promote the continued growth of diamond films into uniform single-crystal films with a minimum of defects and entrapped impurities, and improved physical (optical, thermal and electrical) properties.

Progress: Significant progress was achieved under this 5 year program toward the goal of producing large area, hetero-epitaxial diamond films. Work has been directed in two areas: heteroepitxial nucleation of diamond on nickel in a hot-filament chemical vapor deposition (CVD) reactor; and high rate, textured growth in a combustion CVD reactor. The process we have developed to produce oriented diamond nuclei on Ni is very sensitive to the time-temperature history. To achieve better control, *in-situ* laser reflectometry was developed as a real time process monitor. It was found that the scattered light signal was sensitive to surface structures at the submicron level, and could be used as a process control parameter. A reproducible process for oriented diamond on nickel was developed in which experimental parameters were adjusted as a function of the scattered light signal. Subsequent optimization with this set up yielded an increase in nucleation density as shown in Figure 1, in which 90% of the nuclei demonstrate direct registry with the {100} Ni substrate. In addition, the mechanism underlying the process was extensively investigated using transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD). Cross section TEM and selected area XRD studies identified the presence of a Ni4C interfacial layer that is believed to play an important role during nucleation.

A limitation of the hot-filament CVD system is that growth rates are relatively slow (< 1 m/hr). One would like to rapidly grow the oriented nuclei shown in Figure 1 into a coalesced film with properties that approach that of single crystal diamond. For this purpose a flat flame acetylene burner was constructed that produces uniform deposition at rates > 5 m/hr. In addition, the apparatus was equipped with the capability to monitor the gas phase composition at the growth surface using microprobe sampling and detection by quadrupole mass spectroscopy. Quantitative mole fractions were measured as a function of reactor conditions (reactant composition, pressure, flow rate, burner-substrate distance). A detailed kinetic model of the reactor was developed and validated by the experimental measurements. Comparisons of model predictions and experimental observations of growth rate and morphology were used to develop an understanding of the deposition process. Based on these insights, experimental conditions were determined that yield {100} textured growth. Using substrates that were pretreated by bias-enhanced nucleation, highly oriented {100} films were deposited on silicon as shown in Figure 2. The high growth rate of the low-pressure combustion reactor produced continuous films with low angle grain boundaries after only 3 hours of growth.

(5) TECHNOLOGY TRANSFER:

A poster presentation was made at the 20TH ARMY SCIENCE CONFERENCE (25-27 June 1996) entitled "Growth of Highly Oriented Polycrystalline Diamond Films in an Enclosed Combustion Flame System . This proved to be an excellent forum for bringing the research to the attention of the entire Army research community.

AWARDS:

Best Student Poster Award, November 1996. Materials Research Society, North Carolina Section Fall Meeting.

1997 Issai Lefkowitz Award (Army Research Office) to Dr. Prater

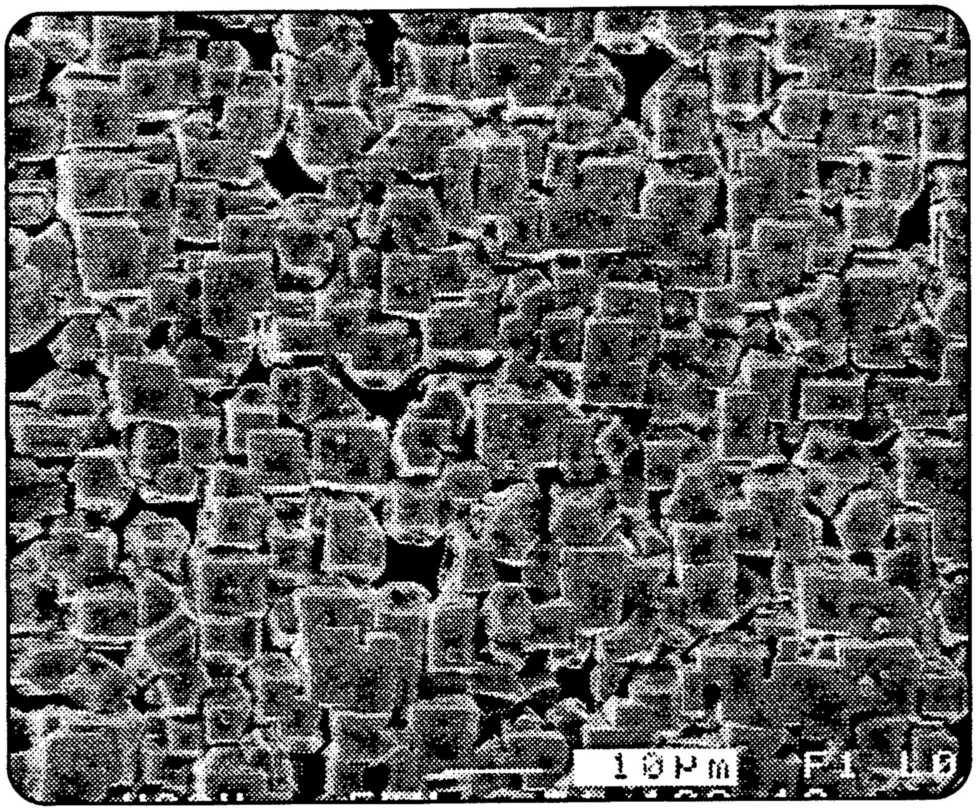

Figure 1: SEM micrograph of oriented diamond on {100} nickel produced after 6 hours of growth with the use of real time optical monitoring in a hot-filament CVD system .

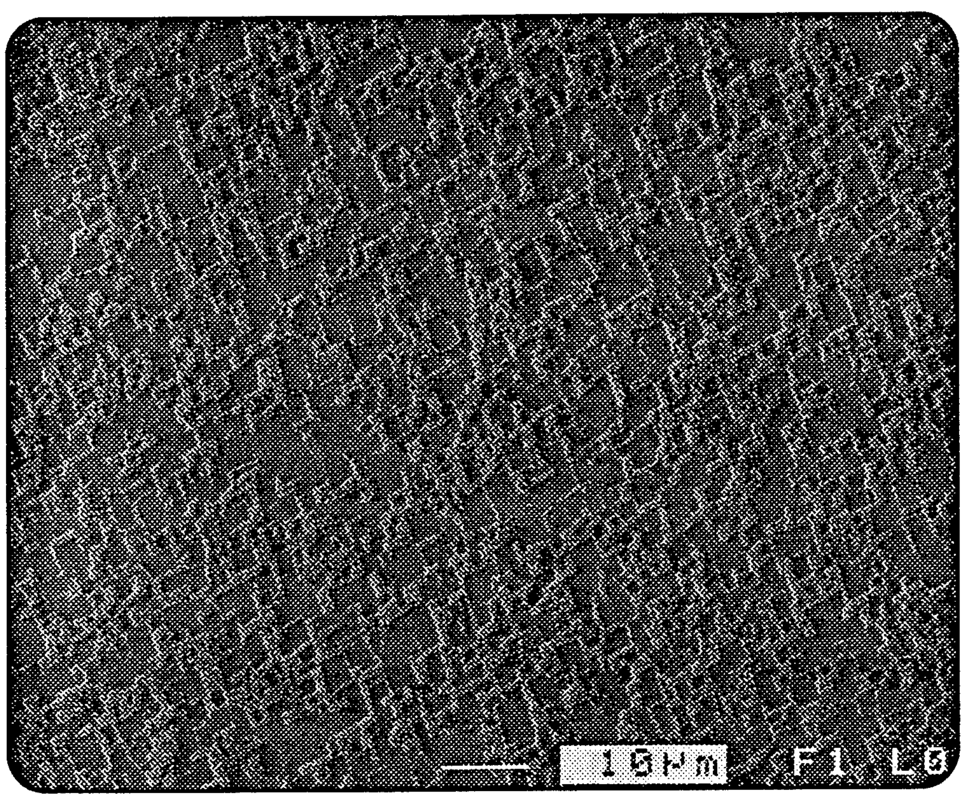

Figure 2: SEM micrograph of continuous, highly-oriented diamond on {100} silicon produced in a low pressure combustion system after 3 hours of growth.