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THE NUCLEATION OF CRYSTALLINE FILMS FROM VAPOR PHASE REACTANTS

Final Technical Report

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I. INTRODUCTION

A variety of technologically important materials can be synthesized by chemical vapor deposition (CVD). Diamond has potential applications as hard coatings, as optically transparent coatings, in microelectronic devices, and for thermal management. CVD silicon nitride is potentially important for oxidation protection of carbon-carbon composites, as a composite matrix material that can be produced by chemical vapor infiltration, and for low-observable applications. We have also investigated the CVD of silicon oxynitride materials. Thin coatings of this SiO_XN_Y material has dramatically improved the oxidation resistance of silicon nitride.

Compared to many other materials, it is difficult to nucleate the desired phase during the CVD of both diamond and silicon nitride. In the case of diamond, one of the primary difficulties is that graphite is a thermodynamically more stable form of carbon. It is also difficult to form the desired phase during the CVD of crystalline Si_3N_4 ; in this case high deposition temperatures are necessary to avoid the formation of amorphous material. In addition to studying two different materials, we also studyied deposition in two different CVD systems. Diamond was synthesized by microwave-plasma enhanced CVD and Si_3N_4 and SiO_XN_Y were synthesized by conventional thermal CVD.

Understanding and controlling the nucleation of these materials was the primary objective of this research program. This work has made it possible form the desired phase under more favorable processing conditions, and has also lead to better control of the resultant film microstructures and properties. In this research we have focused on the use of thin interlayers to control and enhance nucleation. In the case of silicon oxynitride, we have also demonstrated the potential for using thin interlayers to enhance materials properties (i.e., oxidation resistance).

II. RESULTS

Diamond Nucleation

Most of our work in this area is described in attached papers. We have shown that biasenhanced deposition leads to nucleation on a thin amorphous carbon interlayer, and that this amorphous carbon layer forms by an ion-assisted deposition mechanism. We have also conducted detailed TEM with concurrent electron energy loss spectroscopy to characterize the structure of the interlayer. This work indicates that the thin amorphous layer consists of both sp² and sp³ carbon, and that the structure of the carbon layer changes as it grows. We have also constructed a mathematical model of the bias-enhanced deposition process that describes ion acceleration across the plasma sheath region, as well as reactions and atomic displacements that occur at the substrate surface. Detailed descriptions of this process are important for obtaining high nucleation rates during biasenhanced deposition, and for obtaining heteroepitaxial nucleation on certain substrates.

We also constructed an optical emission spectroscopy system to provide *in-situ* measurements of the plasma chemistry (primarily atomic hydrogen) during diamond CVD. Some of our results with this system are described in the attached paper, "Emission spectroscopy during direct-current-biased, microwave-plasma chemical vapor deposition of diamond" (Shigesato, et. al.) and in two different undergraduate theses (N. Sone in 1993 and E. Chen in 1994).

In general, nucleation and growth processes occur simultaneously during the initial stages of CVD. To deconvolute the nucleation and growth kinetics, it is useful to measure the growth kinetics independently. The negative-biasing described above leads to a complex multimodal distribution of diamond grain sizes. A relatively narrow size distribution occurs when conventional diamond scratching is used to enhance nucleation. It is much easier to interpret growth-rate measurements with this narrow size-distribution, thus diamond scratched samples were used to study the growth

kinetics. This work is presented in the attached paper entitled "Nucleation and Growth of Diamond on SiO_2 Substrates" (Rankin, et. al.). This work indicates that direct impingement of a gas-phase precursor is the rate-controlling growth mechanism, except at high nucleation densities where nonlinear growth rates occur because of limited mass-transport in the plasma. This work also demonstrates that SiO_2 substrates alter the local plasma chemistry, which subsequently affects the growth process.

We have also enhanced diamond nucleation on fused silica by using chemical surface pretreatments, instead of prescratching the surface with diamond or another abrasive. This is potentially important for the synthesis of optically tranparent, hard coatings. One approach that was explored is the use of a thin Mo film which makes it possible to apply a dc-bias and then enhance nucleation during microwave-assisted chemical vapor deposition. On uncoated silica substrates, we used a pretreatment step at a lower temperature and microwave power to enhance nucleation. The same pretreatment was applied to Si and Mo coated SiO₂ substrates without applying a bias-voltage, and significant diamond nucleation did not occur. This indicates that the oxide surface also alters the local plasma chemistry in a way that enhances diamond nucleation. Detailed TEM studies of the oxide substrates after the unbiased pretreatment step show 10-100 nm islands of amorphous carbon. Thus, the nucleation of diamond in this case is also preceeded by the formation of a solid, carbonaceous precursor.

As part of this program, we also worked with Dr. Michael Capano at the Air Force Wright Research Lab. Dr. Capano is an expert in x-ray diffraction and synchrotron-based methods of analyzing the atomic structure of materials, and we supported his researh by providing him with several relatively thick diamond coatings on specific substrates.

Low Temperature CVD of Crystalline Silicon Nitride

The CVD of crystalline Si_3N_4 is typically conducted at temperatures exceeding 1300°C. In general, CVD at lower temperatures is less expensive. Also, the ceramic fibers that are used in ceramic matrix composites typically degrade at temperatures above 1200°C (e.g., Nicalon). Therefore, chemical vapor infiltration of a crystalline Si_3N_4 matrix is only viable if the deposition temperature is below 1200°C. In previous research, temperatures this low have usually produced amorphous material, which has poor mechanical properties and poor oxidation resistance compared with crystalline material. In a few instances crystalline Si_3N_4 has been observed at temperatures below 1200°C, but this was formed at very slow growth rates (< 1 µm/hr) and continuous crystalline coatings were not obtained.

We have synthesized continuous, crystalline Si_3N_4 coatings at relatively low temperatures and at relatively high growth rates (e.g., > 50 µm/hr. at 1150°C). Our initial results were reported in the attached paper entitled "Nucleation and Growth of CVD Polycrystalline Si_3N_4 Films at Low Temperatures" (Lauten, et. al.). More detailed results will be reported in Mr. Lauten's thesis, and in several other papers that that will be submitted for publication in the next year.

The CVD methodology that we have developed consists of two stages. Initially, an amorphous/nanocrystalline interlayer is deposited (as determined by TEM, electron diffraction, and FTIR spectroscopy). Large crystalline grains nucleate on top of this interlayer during the second stage of the process. During the first step, the N_2/SiH_4 ratio in the feed gas was relatively low. X-ray photoelectron spectroscopy (XPS) shows that the interlayer that forms during this initial step is silicon rich. If this Si rich layer is not formed first, then the subsequent nucleation of crystalline material does not occur (unless higher deposition temperatures are used). Interestingly, crystalline Si₃N₄ does not form on top of a pure Si interlayer. Thus, the pretreatment step must produce an interlayer that is Si rich, but that also contains some nitrogen. TEM shows that the interlayer has a granular

structure, and that this structure becomes coarser as the layer grows. Based on these experimental observations, it is clear that the evolution of the interlayer creates a surface where crystalline nucleation becomes favorable. We believe that a Si rich interlayer has higher atomic mobilities (compared to material with a higher nitrogen content), and is thus able to undergo the necessary structural evolution during deposition. Clearly this is a complex process that requires further investigation.

The general phenomena observed during the low-temperature CVD of Si_3N_4 that was investigated is similar to the processes observed during the early stages of diamond formation. Specifically, the nucleation of both materials proceeds after the formation of a disordered layer, and the structure of this layer evolves as it is deposited. The nature of the interlayers that form are considerably different. With diamond the interlayer is relatively thin (~10 nm), and the sp²/sp³ content apparently varies as the layer is deposited. With Si₃N₄ the interlayer is much thicker (~1 µm), contains evidence of crystallinity, and shows changes in both the Si/N ratio (by XPS) and the morphology (by TEM).

Surface Treatments to Enhance Silicon Nitride Oxidation Resistance

We have applied silicon oxynitride coatings to Si_3N_4 by using a range of gas compositions. This includes reacting an $N_2O/NH_3/H_2$ mixture directly with the Si_3N_4 substrate, and also depositing SiO_XN_Y from a mixture of $SiH_4/N_2O/NH_3/Ar$. Oxidation results at 1370°C in air show that the silicon oxynitride surface layer improves the oxidation resistance by almost an order of magnitude in some cases. This improvement depends on the composition and the thickness of the SiO_XN_Y material. Both XPS and FTIR were used to establish the relationship between the oxynitride composition and the processing conditions. Oxidation experiments show that improved oxidation resistance is only obtained when the predeposited films have a relatively large nitrogen content. Relatively thick

oxynitride layers behave like a bulk phase, and do not lead to improved oxidation resistance. The theoretical analysis described below indicates that most of these materials should exhibit improved oxidation resistance at longer times (after the oxynitride layer becomes thinner). In general, the oxynitride layers slow the oxidation process when they act as a moving intermediate layer between the Si_3N_4 substrate and the outer SiO_2 scale (i.e., not when they act as a conventional coating on top of the Si_3N_4). This occurs during conventional Si_3N_4 oxidation and when a thin oxynitride layer is predeposited. When a thick layer is predeposited, it initially acts like a distinct phase that oxidizes as though it were silicon oxynitride (i.e., there is little or no oxidation of the underlying Si_3N_4). Only after significant oxidation of the oxynitride, does the underlying Si_3N_4 begin to oxidize at an appreciable rate, such that the remaining oxynitride acts a diffusion barrier that moves into the solid as oxidation proceeds. Only at this stage does the behavior of the material resembles conventional oxidation or oxidation with a thin predeposited layer.

We have also conducted mathematical modeling of the multicomponent mass-transport and chemical reactions that occur during the oxidation of these materials. The conventional description of Si_3N_4 oxidation is based on diffusion of O_2 (or a nitrogen containing species) through two sequential stoichiometric oxides (Si_2N_2O and SiO_2), along with appropriate interface reactions. A thermodynamic analysis of this description, demonstrates that the oxynitride interlayer should be vanishingly small (< 1 Å thick). However, experimental measurements with TEM and XPS have shown that the conventional oxidation of Si_3N_4 is slowed by the presence of an oxynitride layer that is significantly thicker than this. Our analysis shows that this can be explained by an oxynitride layer that is kinetically stabilized. Specifically, the oxynitride is described as a solid solution with variable oxygen and nitrogen contents. The primary oxidation reaction occurs inside of this layer (rather than at an interface), such that interstitial oxygen reacts to replace network nitrogen. Thus, the oxidation rate depends on the kinetics of this reaction process, along with the diffusion rates through the

oxynitride. In addition to explaining the oxidation of conventional Si_3N_4 , this model also explains the effect that we have observed with predeposited oxynitride interlayers. These relatively thick interlayers create a thicker diffusion barrier for oxygen and nitrogen transport, and thus reduce the oxidation rate. As long as these thicker layers remain kinetically stable, these surface pretreatments can be used to obtain improved oxidation resistance.

III. PUBLICATIONS

- J. Rankin, Y. Shigesato, R.E. Boekenhauer, R. Csencsits, D.C. Paine, and B.W. Sheldon, "Early Stages in the Microwave-assisted Chemical Vapor Deposition of Diamond Films on Glass Substrates", <u>Novel Forms of Carbon - MRS Symposium Proceedings</u>, Vol. 270, edited by C.L. Renschler, J. Pouch, and D. Cox (Materials Research Society, Pittsburgh, PA., 1992), pp. 317-322.
- F.S. Lauten, J. Rankin, and B.W. Sheldon, "Nucleation and Growth of Polycrystalline Si₃N₄ During Chemical Vapor Deposition", to appear in <u>Silicon Nitride Ceramics - MRS Symposium</u> <u>Proceedings, Vol. 287</u>, ed. by I.-W. Chen et. al., (Materials Research Society, Pittsburgh, PA., 1993), pp. 315-320.
- B.W. Sheldon, T.M. Besmann, K.L. More, and T.S. Moss, "Epitaxical Nucleation of Polycrystalline Silicon Carbide During Chemical Vapor Deposition", J. Mater. Res. 8, 1086-92 (1993).
- 4. Y. Shigesato, R.E. Boekenhauer, and B.W. Sheldon, "Emission spectroscopy during directcurrent-biased, microwave-plasma chemical vapor deposition of diamond", *Appl. Phys. Lett.* 63, 314-16 (1993).
- 5. B.W. Sheldon, Y. Shigesato, R.E. Boekenhauer, and J. Rankin, "Diamond Nucleation during Bias-enhanced Chemical Vapor Deposition", in *Proceedings of the Third International Symposium on Diamond Materials*, edited by J.P. Dismukes and K.V. Ravi (Electrochemical Society, Pennington, N.J., 1993), pp. 229-235.
- R. Csencsits, J. Rankin, R.E. Boekenhauer, M.K. Kundmann, and B.W. Sheldon, "Early Stage Microstructure Evolution during the Chemical Vapor Deposition of Diamond Films", to appear in <u>Evolution of Surface and Thin Film Microstructure - MRS Symposium Proceedings, Vol</u> <u>280</u>, edited by H.A. Atwater, E. Chason, M. Grabow, and M. Lagally, (Materials Research Society, Pittsburgh, PA., 1993), pp. 695-700.
- B.W. Sheldon, R. Csencsits, J. Rankin, R.E. Boekenhauer, and Y. Shigesato, "Bias-enhanced nucleation of diamond during microwave-assisted chemical vapor deposition", *J. Appl. Phys.*, 75, 5001-8 (1994).
- 8. F.S. Lauten, Y. Shigesato, and B.W. Sheldon, "Diamond nucleation on unscratched substrates", *Appl. Phys. Lett.*, **65**, 210-2 (1994).
- J. Rankin, R.E. Boekenhauer, R. Csencsits, Y. Shigesato, M.W. Jacobson, and B.W. Sheldon, "Nucleation and growth during the chemical vapor deposition of diamond on SiO₂ substrates", J. Mater. Res., 9, 2164-2173 (1994).
- 10. F.S. Lauten, Ph.D. thesis, Brown University (expected completion in 1995).
- 11. R.E. Boekenhauer, Ph.D. thesis, Brown University (expected completion in 1995).
- 12. N. Sone, undergraduate honors thesis, Brown University, 1993.

- 13. E.B. Chen, undergraduate honors thesis, Brown University, 1994.
- 14. J.A. Klahr, undergraduate honors thesis, Brown University, 1994.

IV. CONFERENCE PRESENTATIONS

- 1. R. Csencsits, J. Rankin, R.E. Boekenhauer, M.K. Kundmann, and B.W. Sheldon, "Early Stage Microstructure Evolution during the Chemical Vapor Deposition of Diamond Films", presented at the 1992 MRS Fall Meeting, Boston, MA, Nov. 30 Dec. 4, 1992.
- F.S. Lauten, J. Rankin, and B.W. Sheldon, "Nucleation and Growth of Polycrystalline Si₃N₄ During Chemical Vapor Deposition", presented at the 1992 MRS Fall Meeting, Boston, MA, Nov. 30 - Dec. 4, 1992.
- 3. B.W. Sheldon, "Early-Stage Microstructure Evolution During Vapor-Phase Synthesis of Diamond and Silicon Nitride", University of Connecticut, 31 March 1993 (invited).
- 4. B.W. Sheldon, Y. Shigesato, R.E. Boekenhauer, and J. Rankin, "Diamond Nucleation during Bias-enhanced Chemical Vapor Deposition", presented at the 3rd International Symposium on Diamond Materials, Honolulu, HI, May, 1993.
- 5. F.S. Lauten, J. Rankin, and B.W. Sheldon, "Nucleation and growth of CVD Silicon Nitride at Low Temperatures", F.S. Lauten, J. Rankin, and B.W. Sheldon, presented at the 1993 PACRIM Meeting of the American Ceramic Society, Honolulu, HI. Nov. 8-10, 1993.
- 6. B.W. Sheldon, Y. Shigesato, F.S. Lauten, R.E. Boekenhauer, and J. Rankin, "Diamond nucleation on fused silica substrates", presented at the 1993 PACRIM Meeting of the American Ceramic Society, Honolulu, HI. Nov. 8-10, 1993.
- R.E. Boekenhauer, J. Rankin, and B.W. Sheldon, "The Control of Diamond Nucleation during Bias-enhanced CVD", presented at the 1993 MRS Fall Meeting, Boston, MA., Nov. 29 -Dec. 3, 1993.
- 8. F.S. Lauten, J. Rankin, and B.W. Sheldon, "The Synthesis and Oxidation of Silicon Nitride Coatings", presented at the 1993 MRS Fall Meeting, Boston, MA., Nov. 29 Dec. 3, 1993.
- 9. F.S. Lauten, J. Rankin, and B.W. Sheldon, "The Synthesis and Oxidation Resistance of Silicon Nitride Coating", presented at the 18th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, FL., Jan 10 Jan 13, 1994.
- 10. F.S. Lauten, J. Rankin, and B.W. Sheldon, "Enhanced Oxidation Resistance of Silicon Nitride Coatings", presented at the 97th Annual Meeting of the American Ceramic Society, Indianapolis, IN., April, 1994.
- F.S. Lauten, R.E. Boekenhauer, and B.W. Sheldon, "Nucleation and Growth of Polycrystalline Si₃N₄ During Chemical Vapor Deposition", presented at the 1994 Fall MRS Meeting, Boston,

MA., Nov. 28 - Dec. 2, 1994.

- 12. R.E. Boekenhauer, F.S. Lauten, and B.W. Sheldon, "Diamond Nucleation on Unscratched Silica", presented at the 1994 Fall MRS Meeting, Boston, MA., Nov. 28 Dec. 2, 1994.
- 13. S. Nijhawan, F.S. Lauten, and B.W. Sheldon, "The Effect of Carbon Diffusion on the Nucleation of Diamond on Ni", presented at the 1994 Fall MRS Meeting, Boston, MA., Nov. 28 Dec. 2, 1994.
- 14. F.S. Lauten and B.W. Sheldon, "Enhanced Oxidation Resistance of Silicon Nitride", presented at the 1994 Fall MRS Meeting, Boston, MA., Nov. 28 Dec. 2, 1994.

V. PERSONNEL

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