AFRL-SR-BL-TR-99-
0074

REPORT DOCUMENTATION PAGE

ved *-0188*

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
February 1999

3. REPORT TYPE AND DATES COVERED
Final Technical Report 1 Aug 97 to 31 Jul 98

4. TITLE AND SUBTITLE
Preparation and Characterization of Superhard Materials of Crystalline Carbon Nitride

5. FUNDING NUMBERS
F49620-95-1-0384
61102F
2306/BS

6. AUTHOR(S)
Yip-Wah Chung

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Northwestern University
Materials and Life Science Bldg
2225 N. Campus Drive
Evanston, IL 60208-3108

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Office of Sponsored Research/NA
801 N. Randolph Street, Rm 732
Arlington, VA 22203-1977

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-95-1-0384

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited.

12b. DISTRIBUTION CODE
A

13. ABSTRACT *(Maximum 200 words)*
Prompted by the prediction of Cohen and coworkers that beta carbon nitride may have properties similar to diamond, there have been many attempts to synthesize this hypothetical metastable material. We successfully synthesized this material via epitaxial stabilization using TiN(111) and ZrN(111) as the growth template. The coatings were CN/TiN or CN/ZrN multilayers grown in a dual-magnetron system. The existence of beta carbon nitride in these multilayers has been confirmed with cross-section electron diffraction, Rutherford backscattering, Raman spectroscopy and near-edge x-ray diffraction. Most important, these multilayers exhibit hardness in the 50 GPa, in spite of the large volume fraction (60-70%) of the softer TiN or ZrN component. Attempts to improve the hardness by using TiB2 (which is harder than TiN and ZrN) as the growth template did not work as well because TiB2 was markedly softened by the presence of nitrogen. Nevertheless, carbon nitride/TiB2 multilayers achieved hardness in the 30-40 GPa range. Lubricated tribo-testing indicated that these very hard coatings exhibit wear coefficients ten times better than conventional TiN coatings. This work was extended to include BNxCy by magnetron sputtering of B4C in a mixed argon/nitrogen ambient. Depending on the process conditions, one can obtain a mixture of h-BN+amorphous carbon nitride to c-BN with excellent electrical and tribological properties.

14. SUBJECT TERMS

15. NUMBER OF PAGES
7

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

22 FEB 1999

F49620-95-1-0384

PREPARATION AND CHARACTERIZATION

OF

SUPERHARD MATERIALS OF CRYSTALLINE CARBON NITRIDE

Final Technical Report

May 15, 1995 - November 14, 1998

by

Yip-Wah Chung

Northwestern University

February 1999

Prepared for

AFOSR/NA

Grant F49620-95-1-0384

Dr. Alexander Pechenik

110 Duncan Avenue

Bolling AFB, DC 20332-0001

1. Background

This research is prompted by the prediction that a hypothetical material β-C_3N_4, which has the same structure as β-Si_3N_4, has mechanical properties similar to those of diamond. As research groups around explored different ways of synthesizing this material, there was speculation that β-C_3N_4 is metastable. While variable non-equilibrium synthesis techniques were used, it was our belief that we must provide some sort of structural template to facilitate its nucleation and subsequent growth.

It turns out that several transition metals (Ti, Zr, Nb and Hf) and their nitrides (TiN, ZrN etc) may be used for this purpose. For example, TiN(111) is hexagonal and is lattice-matched to β-C_3N_4(0001) within a few percent. Other nitrides such as ZrN are even closer. Even if this method of epitaxial stabilization works, there will be a buildup of elastic strain because of the finite mismatch, increasing with the film thickness. Beyond a critical thickness, the system will be unstable. This problem can be solved by depositing alternating layers of these two materials. That is, before the critical thickness is reached, the template layer (e.g., TiN) will be deposited. The whole process can then be repeated until a sufficiently thick film can be synthesized for various applications.

In the course of these investigations, we noted that TiB_2(0001) is also lattice-matched to β-C_3N_4(0001) within a few percent. Bulk TiB_2 is hard (hardness = 35 GPa) and wear-resistant. In fact, TiB_2 is used as a strengthening precipitate for various high performance aluminum alloys. Therefore, we extend our research to include TiB_2 and an important boron-related system, viz. boron nitride. Time limitation precluded us from exploring in detail the boron nitride system. However, some exciting results were obtained that prompted continuing support from industry, as detailed below. In addition, as we continued to expand our research in nanolayered materials, we had a need to extend the capabilities of our existing deposition systems. We were fortunate to be able to acquire a new dual-cathode magnetron sputter-deposition system, funded through the DURIP/AFOSR program. Some of our films were made in this system.

In the following sections, rather than presenting the detailed technical results (which were described in detail in previous reports), we will simply highlight the key conclusion for each material system mentioned above (β-C_3N_4 /TiN, β-C_3N_4 /ZrN, β-C_3N_4 /TiB_2 , TiB_2, TiB_xN_y , and hexagonal BN). A summary of personnel information and publications will be included at the end of this report.

2. Experimental Techniques

All coating systems described in this report were synthesized by a dual-cathode magnetron sputter-deposition system. The system operated at a base pressure of mid-10^{-7} Torr. To avoid target poisoning, we controlled the flow rate by monitoring the partial pressure of the active gas (nitrogen in this case). Coating properties were optimized by adjusting the substrate bias. We did not deliberately heat the substrate, so the substrate temperature varied according to the process conditions (400-500K typical).

After deposition, coatings were characterized by a wide range of techniques as indicated below:

composition - Auger electron spectroscopy, Rutherford backscattering spectroscopy
bonding - FTIR, Raman, near-edge x-ray absorption, electron energy loss spectroscopy
hardness/modulus - nanoindentation
wear - pin-on-disk testing
structure - x-ray diffraction, high-resolution transmission electron microscopy
surface roughness/morphology - atomic force microscopy

The optimum properties (high hardness, smooth morphology and low wear) were obtained through statistical design of experiments. Results described below represent these optimum materials.

3. β-C_3N_4 - related systems

(a) β-C_3N_4 / TiN

When the carbon nitride thickness is more than 1-2 nm, the hardness of the coating is low (20 GPa or less). Electron microscopy shows that the coating is amorphous. When the carbon nitride thickness is 1 nm or less, the coating is fully crystalline, with hardness in the 50 GPa regime. Electron diffraction reveals extra diffraction peaks matching those from β-C_3N_4. In addition, there is a strong correlation between the occurrence of this high hardness and the predominantly (111) texture of TiN. This observation is consistent with our hypothesis that TiN(111) facilitates the nucleation and subsequent growth of β-C_3N_4.

(b) β-C_3N_4 / ZrN

The results from β-C_3N_4 / ZrN superlattice coatings are essentially similar to those of β-C_3N_4 / TiN. In this case, we made major efforts to determine the structure and local bonding characteristics of the β-C_3N_4 layers via several techniques. Transmission electron diffraction clearly reveals extra diffraction peaks which can be indexed to β-C_3N_4. Raman spectroscopy shows the absence of amorphous features in the 1400-1600 cm^{-1} range. Instead, it shows evidence of a C-N stretch around 1100 cm^{-1}. Near-edge x-ray absorption shows that the carbon atoms are in the sp^3 state. The latter two observations are consistent with carbon atoms in β-C_3N_4. Finally, Rutherford backscattering concludes that the carbon nitride layers have a N/C atomic ratio of 1.3 ± 0.1, consistent with the composition of β-C_3N_4. Taken together, these results provide the strongest evidence to date that we have successfully synthesized β-C_3N_4.

(c) β-C_3N_4 / TiB_2

With the above two systems, the transition metal nitride component is relatively soft (hardness $\approx$ 20-25 GPa), thereby lowering the hardness of the overall coating. By switching to TiB_2, we were hoping to increase the hardness further. Unfortunately, the two components are not compatible using the dual-cathode magnetron system. To produce carbon nitride, we sputtered a graphite target in an argon/nitrogen ambient. To produce

TiB_2, we sputtered TiB_2 in an argon ambient. Therefore, in order to deposit β-C_3N_4 / TiB_2 superlattice coatings, we should have a way to switch the two gases. Such a capability did not exist with our system. Instead, we kept a fixed argon/nitrogen ambient. As discussed in the next section, while oriented, crystalline and hard TiB_2 films can be made by sputtering TiB_2 in argon, presence of nitrogen tends to amorphize and soften TiB_2. In spite of the various tricks we used to reduce the nitrogen partial pressure in front of the TiB_2 target, we were unable to produce a fully crystalline TiB_2 component in the β-C_3N_4 /TiB_2 superlattice coatings. The hardness of these coatings is $\approx$ 30-40 GPa.

(d) TiB_2 and TiB_xN_y

DC magnetron sputtering of TiB_2 by argon can produce crystalline, smooth and highly (0001) textured TiB_2 films, provided that an optimum combination of pressure and substrate bias was employed. Under these conditions, we were able to synthesize TiB_2 films with hardness $\approx$ 45 GPa and r.m.s. surface roughness < 3Å. These films were shown to have wear performance significantly better than TiN. Addition of the smallest amounts of nitrogen to the sputter gas resulted in the reduction of hardness and crystallinity.

(e) Hexagonal BN_xC_y

By performing magnetron sputtering of boron carbide ($B_{13}C_3$) in an argon/nitrogen ambient, it is possible to produce BN_xC_y thin films. These films have a bluish color, with typical hardness $\approx$ 20-30 GPa. Transmission electron microscopy studies showed that the films have a turbostratic structure, i.e., hexagonal BN planes lining up perpendicular to the substrate surface. Even without further optimization, these films are extremely useful for dielectric and wear-protection applications. They have electrical resistivity $> 5 \times 10^{10}$ ohm-cm and dielectric strength $> 5 \times 10^6$ V/cm. Further optimization with proper choice of x, y and deposition conditions may yield BN-based coatings with much enhanced properties. The result of this initial work has attracted the interest of IBM, which is interested in developing new materials not only as protective overcoats for hard disk drives, but also for read-write heads. A research contract was awarded by IBM to explore the use of turbostratic boron nitride and aluminum oxide for specific magnetic recording applications.

4. Personnel Information

Principal investigators:

Yip-Wah Chung, professor of materials science and engineering; Fellow, ASM International; Fellow, Japan Society for Promotion of Science; Board of Directors, American Vacuum Society.

William Sproul, currently with Sputtered Films, Inc, California

Ming-Show Wong, currently chair of materials science and engineering at Hau Tung University, Taiwan.

Students:

Dong Li, graduated in 1995, PhD (MS&E), currently with Motorola

Mei-Ling Wu, expected to graduate in 1999, PhD (MS&E)

Elizabeth Cheang, undergraduate, expected to graduate in 1999, BS (MS&E)

Visiting scholar:

Tong-Jun Zhang, 7/95-5/96, currently at Hauzhong University, China

Postdoctoral fellow:

Ray Chia, 1/96 - 4/96, currently with Western Digital Corporation

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