DOE/ER/45434--4

048849

DOE/ER/45434-4

DEPOSITION AND PROPERTIES OF NOVEL NITRIDE SUPERLATTICE COATINGS

Progress Report

for September 28, 1990 - October 1994

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October 1994

Prepared for

The U. S. Department of Energy
Agreement No. DE-FG02-90ER45434

The major effort during this report period was to elucidate the hardening mechanisms in polycrystalline superlattices. Since the last progress report, we have been working on theoretical modeling of hardening mechanisms in superlattices and have carried out detailed studies of two new polycrystalline superlattice coatings, NbN/VN and CrN/TiN, which were produced using an opposed, dual-cathode, high-rate, reactive, unbalanced-magnetron sputtering system. Significant hardness enhancement the above rule-of-mixture hardness value was found for the CrN/TiN, but not for the NbN/VN. Correlating these results with prior results for TiN/NbN and TiN/VN shows that the major hardening mechanism in polycrystalline superlattices is the difference in layer elastic moduli, which is minimal in the NbN/VN case. The modulus difference provides a barrier to dislocation flow across the layers. In the absence of modulus-difference hardening in NbN/VN, it was found that other hardening mechanisms such as coherency strains and the small grain sizes observed in the superlattices play a minor role. The results achieved in this report period are described below along with publications and presentations.

A model was developed that explains the yield stress and hardness enhancements that have been observed in superlattice thin films. The stress required for dislocations to glide across layers with different shear moduli was calculated using an expression that accounts for core effects and all interfaces in trapezoidal or sawtooth composition modulations. The predicted strength/hardness enhancement increased with increasing superlattice period Λ, before reaching a saturation value that depended on interface widths. A second mechanism, where dislocations glide within individual layers, was important at large Λ and gave a decrease in strength/hardness with increasing Λ. The combination of these two mechanisms gives a strength/hardness maximum versus Λ in good quantitative agreement with experimental results for nitride and metal superlattices. The results indicate that superlattice strength/hardness depends strongly on interface widths and the difference in shear moduli of the two components for Λ values below the maximum, and on the average shear modulus for larger Λ.

A new transition metal nitride superlattice VN/NbN with little difference in shear modulus was investigated in order to test theories that relate the strength/hardness enhancements to the modulus difference. The NbN/VN superlattices were deposited on steel substrates in an opposed dual-cathode unbalanced magnetron sputtering system. Despite a large lattice mismatch of 5.7% between NbN and VN, XRD results show that the superlattice structure exists in all the films studied, where the superlattice period ranged from 2.4 nm to 60 nm. The structures and properties of the superlattices were investigated under different deposition and superlattice modulation parameters including nitrogen partial pressure, superlattice period, and relative layer ratio. Microhardnesses measured by both a Vickers microhardness and a nanoindentation tester showed no appreciable hardness enhancement as a function of superlattice period or relative layer ratio. The results were compared with TiN/NbN and TiN/VN superlattices, in which hardness enhancements of over 2 times either nitride layer was shown. This study supports the theory that the difference in layer shear modulus is a major factor affecting the superlattice hardness. Furthermore, they show that any other hardening mechanisms related, e.g. to coherency strains or grain sizes, were minimal.

The CrN/TiN superlattice system, with a larger modulus difference than that for previously reported nitride superlattice systems, is being investigated as another verification that the modulus difference is the main factor determining the hardness enhancement. A simulation program was developed in order to extract structure information from the X-ray diffraction patterns, which showed a significant fluctuation in d-spacing which can be related to ion bombardment effects. For 2 μm CrN/TiN coated samples, preliminary nanoindentation hardness results showed an increase in hardness of > 10 GPa over the rule of mixtures value for CrN and TiN, and scratch tests (on high-speed steel substrates) showed critical loads that exceeded 6 kgf.

Our prior studies have shown that the effect of deposition parameters on polycrystalline superlattice structure, hardness, and adhesion are analogous to the dependences observed for homogeneous nitrides such TiN, NbN, and VN. However, the hardness and adhesion values obtained under optimal conditions are much higher for the superlattices. Thus, in order to obtain polycrystalline superlattice coatings with the desired properties, the individual layer materials need to be optimized. Polycrystalline VN films were deposited onto M2 steel substrates in a high-rate reactive DC magnetron sputtering system. The crystal structure, surface morphology, and properties of the films were explored under several process parameters such as nitrogen partial pressure, target power, and negative substrate bias. Analytical techniques including X-ray diffraction and SEM were used to characterize the structure and morphology of the films, and the mechanical properties of the films were measured by a Vickers microhardness and a scratch adhesion testers. The nitrogen partial pressure was found to be the dominant deposition parameter for the formation of different crystalline phases. The film hardness was shown to depend on the crystalline phase, and maximum hardness of 30 GPa was found for the β-V_2N phase.

Publications and Presentations

1.X. Chu, M.S. Wong, W.D. Sproul and S.A. Barnett, "Deposition and Properties of Polycrystalline TiN/NbN Superlattices Coatings", J. Vac. Sci. Technol. A, 10(4) (1992) 1804-9.

2.X. Chu, M.S. Wong, W.D. Sproul and S.A. Barnett, "Superhard Nanocomposite of Nitride Superlattices Formed By Unbalanced Magnetron Sputtering", in Nanophase and Nanocomposite Materials, MRS Symposium proceedings V.286, (1993) 379-384.

3.X. Chu, M.S. Wong, W.D. Sproul and S.A. Barnett, "Reactive Unbalanced Magnetron Sputter Deposition of Polycrystalline TiN/NbN Superlattice Coatings", Surf. and Coatings Tech. 57 (1993) 13-18.

4.M.S. Wong, W.D. Sproul, X. Chu, and S.A. Barnett, "Reactive Magnetron Sputter Deposition of Niobium Nitride Films", J. Vac. Sci. Technol., A 11(4) (1993) 1528-1533.

5.X. Chu, M.S. Wong, W.D. Sproul and S.A. Barnett, "Mechanical Properties and Microstructures of Polycrystalline Metal/Ceramic Superlattices", Surface and Coatings Technology, 61 (1993) 251-256.

6.P. Yashar, X. Chu, M.S. Wong, W.D. Sproul, and S.A. Barnett, "Synthesis and Properties of Polycrysalline CrN/NbN Superlattices". to be presented at AVS 1994 (Oct.) Annual Meeting. (paper submitted).

7.X. Chu, M.S. Wong, W.D. Sproul, and S.A. Barnett, "Deposition and Properties of Polycrysalline VN/NbN Superlattices". to be presented at AVS 1994 (Oct.) Annual Meeting. (paper in preparation)

8.M.S. Wong, X. Chu, W.D. Sproul and S.A. Barnett, "Synthesis and Characterization of Superhard Polycrystalline Superlattice Coatings", presented at AVS 1993 Annual Meeting.

9.X. Chu, M.S. Wong, W.D. Sproul, and S.A. Barnett, "Reactive Magnetron Sputter Deposition of Vanadium Nitride Coatings", presented at AVS 1993 Annual Meeting. (paper submitted)

10.X. Chu and S.A. Barnett, "A Model of Superlattice Yield Stress and Hardness Enhancements" (Submitted to J. App. Phys. in Aug. 94)

11.X. Chu, S.A. Barnett, M.S. Wong, and W.D. Sproul, "Hardness Enhancement in Polycrystalline Transition-metal nitride superlattice films", presented at ICMCTF 1994, (paper in preparation)

Graduate Students

Xi Chu	(expected to complete his Ph.D in Dec. 1994)
Philip Yasher	(second year graduate student)

Research Direction for Next Reporting Period

Although we have been successful in elucidating the main mechanism of hardness enhancement in polycrystalline superlattices, we will carry further studies to refine the hardening theories and to understand in more detail the effects of other contributing hardening mechanisms such as coherency-strain and grain-size effects. Further studies in the CrN/TiN system are required to optimize deposition conditions and then determine if a larger hardness enhancement is obtained for a larger modulus difference. We will continue to study the fundamental factors affecting adhesion and attempts will be made to improve adhesion using metal/nitride superlattice interlayers. Also, materials factors affecting the layer structure and high-temperature thermal stability of superlattices will be investigated, and measurements of new property such as hot hardness, friction, wear and erosion resistance will be carried out.