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DEPOSITION AND PROPERTIES OF
NOVEL NITRIDE SUPERLATTICE COATINGS

Progress Report

for Period September 27, 1990 - May 27, 1992

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Deposition and Properties of Novel
Nitride Superlattice Coatings

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Proposal Continuation Request

Progress Report

We have demonstrated that polycrystalline TiN/NbN superlattice thin films on tool steel substrates can have hardnesses H as high as $5200 \text{ kg mm}^{-2} \text{ HV}_{0.05}$ (52 GPa). This is more than twice the hardness of polycrystalline sputtered TiN ($H \approx 2200 \text{ kg mm}^{-2}$) and NbN ($H \approx 1400 \text{ kg mm}^{-2}$) deposited using the same conditions, and matches the highest H observed for single-crystal TiN/NbN superlattices. Initial parametric studies showed that H increased with decreasing superlattice period down to 4 nm, similar to the dependence for single-crystal TiN/NbN. These results are the first indication that polycrystalline superlattices with high hardness can be deposited on practical substrates.

The initial results have resolved the question of whether ion irradiation of the depositing film, normally needed to obtain dense nitrides, could be employed without ion-induced intermixing of the superlattice layers. Our XTEM and XRD results show that ion irradiation with appropriate energy ($\approx 150 \text{ eV}$) and flux ($\approx 4.2 \text{ mA cm}^{-2}$) produced dense nitride superlattices with well-defined layers even for periods down to 4 nm; these conditions yielded the highest H values. Decreasing the ion energy and/or flux decreased both the density and H . The initial results thus show that both high density and well-defined superlattice

layers are required to achieve high H.

Unique process control capabilities were also crucial for achieving high hardnesses. It was necessary to separately control the reactive gas partial pressure at each of the sputtering targets in order to prepare stoichiometric layers of both the TiN and NbN. Splitting of the partial pressure resulted in a 50% increase of the film hardness compared to a uniform partial pressure throughout the deposition chamber. Cross contamination of the targets and the alternating superlattice layers during deposition was minimized using a baffle or an extra-large cylindrical substrate holder; within the limits of detection of energy-dispersive spectroscopy, there was no cross-contamination of the layers. The superlattice period was determined by the substrate holder rotation speed and the power to the sputtering targets and checked by x-ray diffraction (XRD) and cross-sectional TEM (XTEM). The XRD peaks for the TiN/NbN films also showed that they were polycrystalline. XTEM showed a strong composition modulation with the layer morphology varying from undulating to planar depending on deposition conditions.

Papers Submitted

During the first year of this program, one paper entitled, "Deposition and Properties of Polycrystalline TiN/NbN Superlattice Coatings," has been submitted to the Journal of Vacuum Science and Technology A for publication. An oral version of this paper was presented at the Annual Symposium of the American Vacuum Society, which was held in Seattle from November 11-15, 1991.

In addition to the above listed paper, a patent application is being prepared titled "Nitride Superlattice Thin Films Exhibiting Ultra-High Hardnesses: A New Protective Coating."

Proposed Research

In the next year, we will further investigate effects of processing and superlattice parameters on properties, carry out more complete characterization, and investigate new superlattice materials. Superlattice parameters to be varied will include the superlattice period and relative TiN and NbN layer thicknesses, while deposition parameters including deposition rate and ion flux will be varied. Additional characterization to be conducted will include scratch adhesion testing and nano-indentor elastic modulus and hardness measurement. In addition to continuing the study of TiN/NbN films, we will explore the additional superlattice systems of TiN/VN, TiN/Ni, and TiN/NiCr. We expect that these systems will require the same care in preparation that was necessary with the TiN/NbN films in order to achieve the very high hardnesses. Split partial pressure control will be used during the preparation of these films, and the flux and energy of the bombarding substrate ions be controlled.

One of the unresolved questions from our initial work on polycrystalline films is the possibility of intermixing at the interfaces between the individual layers. While our XTEM results show distinct layers, we expect that energetic ion bombardment during film growth must cause some intermixing. During the next year of this program, we will use high resolution analytical XTEM to study the interfaces between the individual layers to determine the degree of intermixing. Effects of process parameters on layer morphology will also be studied by XTEM.

Graduate Students

This program is supporting the efforts of one graduate student, Mr. Xi Chu. He has a bachelor of science degree from Carnegie Mellon University, and he is currently in his second year of graduate studies at Northwestern University. It is expected that he will complete his doctoral studies by June, 1994.

Budget

The budget for the second funding period for this program is enclosed. The amount is \$80,080, and the time period covers ten months from May 28, 1992 through March 27, 1993.

Other Federal Funding

Funding for Scott A. Barnett

National Science Foundation, \$240,000, "Mechanical Properties of Single Crystal Transition-Metal Nitride Strained-Layer Superlattices Exhibiting Extremely High Hardnesses," February 1989 to January 1992.

Electric Power Research Institute, \$326,406, "Novel Solid Oxide Fuel Cells Based on Thin-Film Electrolytes," October 1989 to September 1992.

National Science Foundation, \$43,800, "Ion-Assisted Molecular Beam Epitaxy," March 1991 to February 1992.

Funding for William D. Sproul

NASA Marshall Space Flight Center, \$284,625, "Application of Hard Coatings to Substrates At Low Temperatures." The period of funding is from April 24, 1989 to April 23, 1992.

Department of Energy, Office of Transportation Materials Tribology Program, \$354,390, "Tribological Properties of Reactively Sputtered Nitrides and Carbides of Titanium, Zirconium, and Hafnium." The period of funding is from April 16, 1990 to April 15, 1994.

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