PROPERTIES AND FRACTURE OF TUNGSTEN-ALUMINA ATOMIC LAYER DEPOSITED NANOLAMINATES

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ABSTRACT

Thin film coatings are often applied to microelectronic and MEMS devices to improve their tribological properties. However, as device complexity increases, it becomes necessary to deposit coatings over intricate structures. For these geometries, atomic layer deposition (ALD) represents an ideal method due to its inherent surface reaction growth mechanism. Interestingly, recent work has shown that nanolaminated film structures may display both increased hardness and fracture toughness as compared to single blanket films. Therefore, we have initiated a mechanical study of atomic layer deposited nanolaminate-based composites using alternating layers of nanocrystalline tungsten and amorphous aluminum oxide to take advantage of the high hardness and low frictional coefficients offered by the two-film systems. Using nanoindentation techniques, we have determined that the elastic modulus and hardness range from 183 to 284 GPa and 7.0 to 8.2 GPa respectively depending on laminate structure. Additionally, nanoscratch tests revealed a strong reverse length-scale effect in the fracture behavior of the laminated films. It was observed that as the layer period decreased, the apparent toughness of the film decreased. The results will be used to show how structure controls properties and fracture of ALD nanolaminates. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

1 INTRODUCTION

In many current microelectromechanical systems (MEMS) and microelectronic devices, coatings are often applied to improve component lifetime and performance. Ideally, these coatings should have both low frictional coefficients in order to minimize lateral forces and a high hardness to decrease permanent damage and wear. Limited success has been achieved by combining individual coatings that exhibit either a desirable frictional coefficient or desirable wear resistance. Ideally, a single robust coating would both increase the wear resistance and decrease the friction coefficient. In addition to meeting these requirements, it is critically important that the coating have both high fracture toughness and substrate adhesion. Although deposition techniques currently exist which may be used to create candidate planar films, atomic layer deposition (ALD) represents an ideal technique for the deposition of wear resistant coatings in complex geometry devices such as MEMS.

ALD is a modified chemical vapor deposition process where the reaction pathways are split into chemical half-reactions. These half-reactions are self-limiting at the sample surface, where saturation of available surface sites limits the adsorption, and consequent growth, of the reactive species. Through sequential exposures of half-reactions, a film may be grown to any given thickness. As a direct result of the self-limiting surface reactions, ALD is both a highly controllable and conformal film deposition technique with documented depositions occurring with submonolayer growth control and uniform film deposition over features with aspect ratios in excess of 100:1 (Mayer et al. [1]). ALD nanolaminates are of particular interest as they offer the unique ability to engineer both the laminate chemistry (with respect to the individual laminate layers) and sample structure (with respect to the individual layer thickness).

As early as 1970, Koehler [2] had proposed that by modifying both layer thickness and the ratio of shear moduli, it would be possible to design strong microstructures. Indeed, multiple research groups have observed that nanolaminated microstructures do display a functional relationship showing increasing hardness with decreasing layer spacing (Xhang et al. [3]; Chu and Barnett [4]; Misra et al. [5]). There have been several attempts to model this hardening response in laminated structures using both Hall-Petch scaling relations as well as independent energy-based designs; however, the models tend to diverge from experimental results at very small length scales (Freidman [6]; G-Berasategui et al. [7]). It has also been observed that increased wear resistance is directly related to the bilayer thickness with increasing resistance at smaller thickness (Ruff and Lashmore [8]). Additionally, *in-situ* TEM observations of crack bridging in nanolaminates imply that these structures could display increased fracture toughness compared to single component blanket films (Kramer and Foecke [9]). Interestingly, Koehler predicted that increasing the difference in the shear moduli of the layers would increase the hardness of the system, yet the majority of published literature deals with metal-metal or ceramic-ceramic laminate structures where the shear moduli are similar. In the current study, we have produced multilayers using nanocrystalline tungsten and amorphous aluminum oxide, where the difference in the shear moduli is approximately 77 GPa. Here we will look at the effect of nanolaminate structure on hardness, modulus and fracture toughness.

2 EXPERIMENTAL PROCEEDURES

The ALD nanolaminates used in this study were deposited in a flow reactor at a temperature of 130 ºC onto (0001) sapphire wafers. A 5 nm amorphous layer was present on the sapphire surface from mechanical polishing during processing. The ALD laminate samples were composed of alternating layers of amorphous aluminum oxide and nanocrystalline tungsten. For a more thorough description of this deposition process, refer to (Costescu et al. [10]). As a result of the low temperature growth, a density gradient develops during the first 4 nm of growth. As determined from x-ray reflectivity, in the alumina films this gradient ranges from 40 percent of fully dense alumina at 2 nm and plateaus at 80 percent density after 4 nm have been deposited. Similarly, the tungsten shows a gradient in density that ranges from 40-50 percent at 2 nm with a plateau between 80-90 percent of bulk density for thicknesses greater than 4 nm. The sample set was composed of 100-nm-thick 4, 8 and 16 bilayer alumina/tungsten samples. In all the samples, the alumina layer was held constant at 4 nm and the metal layer was adjusted to fill the remaining volume as shown in Table 1.

Table 1. Set of nanolaminates used during testing.

# bilayers	Alumina Thickness (nm)	Tungsten Thickness (nm)	Volume Fraction - Alumina	Volume Fraction - Tungsten
4	4	21.1	15.9	84.1
8	4	8.4	32.3	67.7
16	4	2.1	65.6	34.4

Nanoindentation tests were used to determine the elastic modulus and indentation hardness of the nanolaminate films. All the indentation tests were performed using a MTS Nano Indenter® DCM operated using the continuous stiffness method (CSM) with a Berkovich diamond indenter tip. The CSM was operated at 70 Hz with a displacement amplitude of 2 nm. Ten separate indents were performed on each sample to ensure a representative behavior was obtained. To determine

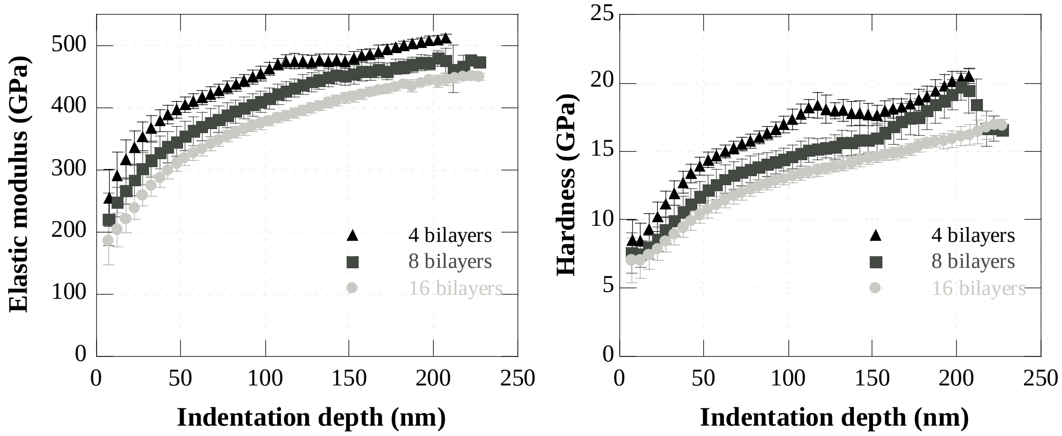

Figure 1. (a) Elastic modulus and (b) indentation hardness of the nanolaminate systems. The properties of bulk tungsten, alumina and sapphire are shown for comparison.

the scratch resistance of the laminate films, nanoscratch tests were performed using a MTS Nano Indenter® XP with both a Berkovich and 1 μm radius conical tip. These tests were performed by simultaneously driving the tips into the films at a rate of 250 μN/sec and across the films at a lateral rate of 0.5 μm/sec to a maximum normal load of 100 mN. The normal and tangential loads and displacements were continuously recorded during the entirety of the test. The resulting scratch tracks and film delaminations were examined using scanning electron microscopy.

3 RESULTS AND DISCUSSION

3.1 Elastic Modulus and Hardness

The nanoindentation results show that the elastic modulus increased with a decreasing number of bilayers. Previous experiments on blanket films of ALD tungsten and ALD alumina determined elastic modulus values of 280 and 145 GPa and hardnesses of 18 and 8 GPa, respectively (Moody et al. [11]). These values allow for a baseline approximation of laminate properties based on a simple rule-of-mixtures. As seen in Figure 1, the modulus for the laminates ranges from 183 GPa for the 16-bilayer sample to 248 GPa for the 4-bilayer composite at shallow displacements. These results compare well with what would be expected from a simple rule-of-mixtures approach. Since the total composite thickness is only 100 nm, a strong sapphire substrate effect quickly dominates properties; however by interpolating toward a zero penetration depth, approximations of the properties can be made. Similarly, the hardness response of the samples increased for a decreasing numbers of bilayers, however values of 7.0 to 8.2 GPa are below what would be expected based on the simple rule of mixtures approach, possibly due to effects from the density gradient. Discontinuities were observed in all three samples on both the elastic modulus and hardness curves at large indentation depth. These events were seen as indentation displacement discontinuities during loading and most likely correspond to either fracture or delamination within the nanolaminate stack; however, scanning probe microscopy did not reveal any features other than plastic pileup around the indents.

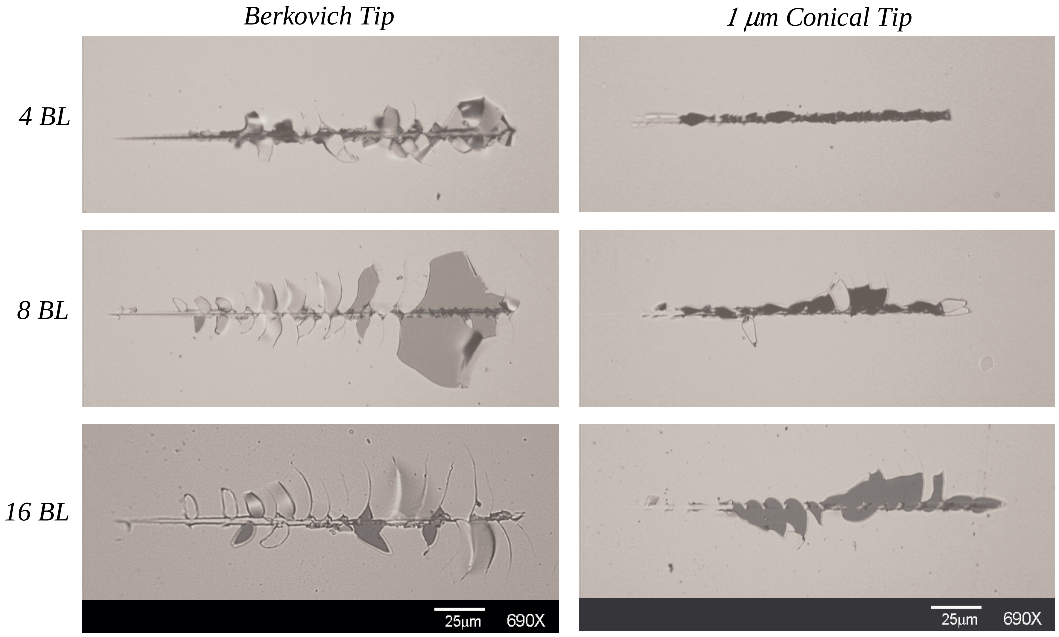

Figure 2. Scratch fracture and delaminations observed for both (a) Berkovich and (b) conical tips. The magnitude and extent of the fractures increases with decreasing layer period, and is noticeably larger for the Berkovich tip due to the increased lateral forces.

3.2 Scratch Testing and Film Fracture

In order to determine the fracture resistance of the laminate films, nanoscratch tests using both 50 nm radius Berkovich and 1 μm radius conical tips were performed. Representative images from these tests can be seen below in Figure 2, where it is immediately observed that for increasing number of bilayers the resistance to fracture and qualitatively the fracture toughness decreases. Additionally, the Berkovich tip generates increased channel crack formation compared to the spherical tip. It is hypothesized that this is due to the higher tangential stresses produced by the Berkovich tip. These higher tangential stresses result in a positive shift of the frictional coefficient, from 0.05 with a conical tip to slightly greater than 0.12 using the Berkovich, an increase of almost a factor of 3.

Unlike the results from single ALD tungsten films where scratch tests initiated extensive channel cracking and film debonding, there is no widespread delamination in the nanolaminate films. Rather, small channel cracks are localized near the scratch track and increase in magnitude as the normal and tangential loads increase. Interestingly, a strong reverse length scale is observed in the fracture behavior of the laminates. It can be seen that as the layer period decreases, the length of the channel cracks increase, contradicting the expected toughness results. One could argue that the toughness of the composite film is directly related to the total volume fraction of metal, where the metal acts to absorb energy plastically. Therefore, since the 16-bilayer system has a lower overall volume fraction of metal as compared to the 4- or 8-bilayer systems, the 16 bilayer system would have the lowest fracture toughness. Consequently, this argument would imply that a pure tungsten film would have the highest toughness when compared to the laminate films. However, this is in disagreement with previously observed results on ALD-W films

(Moody et al. [11]). Nevertheless, these results imply that a maximum in the fracture toughness exists between the single blanket film of ALD-tungsten and the 4-bilayer laminated structure of ALD-tungsten and ALD-alumina.

4 CONCLUSIONS

We have initiated a study of atomic layer deposited nanolaminate-based composites using alternating layers of nanocrystalline tungsten and amorphous aluminum oxide. Using nanoindentation techniques, we have determined that the elastic modulus and hardness range for 4- 8- and 16-bilayer systems from 284 to 183 GPa and 8.2 to 7.0 GPa respectively at shallow displacements. From nanoscratch tests, a strong reverse length-scale affect was observed in the fracture behavior of the laminated films. It was seen that as the layer period decreased, the apparent toughness of the film decreased. When these results are compared to similar tests on blanket films of ALD-tungsten, a maximum in the fracture toughness can be predicted with bilayer thicknesses somewhat larger than 21nm of ALD-tungsten and 4 nm of ALD-alumina.

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