Shallow and Deep Nanoindentation on W/NbN Nanolayers

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Abstract. Superlatice W(100)/NbN(100) with bilayer periods (Λ = 5.6 and 10.4 nm) was non-isostructural superlattice material and fabricated by depositing alternating layers of single crystal tungsten (W), a body-centered cubic metal, and niobium nitride (NbN), a face-centered cubic ceramic, on a MgO single crystal substrate. The lattice constants of the ceramic and metal layers are 0.439 nm and 0.315 nm respectively. The superlattice are nanocomposites that exhibit a hardness at small bilayer repeat periods which exceeds the hardness predicted by the rule of mixtures for normal composites by deep nanoindentation, while shallow nanoindentations does not demonstrate the superhardening. The results indicate that the elastic modulus does not influence the hardness of the superlattice materials. The superhardening results at deeper indentation depths is related to the nature of the interface between the layers in the superlattice materials. Normally, superlattice gains hardness by losing deformability, however, the superlattice demonstrated excellent deformability when reaching the superhardening.

Key words: nanolayers, nanoindentation, superhardening.

1 Introduction

Multilayered materials have been the focus of a significant amount of research. Madan and Barnett [1, 2] have explored several different types of nitride based superlattice thin films and have described the fabrication, the structure and the hardness behavior of various thin films. Chu et al. [3] examined polycrystalline transition metal nitride superlattice films and demonstrated that the hardness for several materials is inversely proportional to the bilayer repeat period and showed that there is an optimum bilayer repeat period that maximizes the hardness for some materials. They also discussed several possible explanations for the hardness behavior such as the supermodulus effect, coherency strains, grain size reduction and Koehler's model. Clemens et al. [4] reviewed the hardness of several metallic and superlattice materials and discussed the strain relaxation, interface morphology and Koehler's model. Anderson et al. [5] examined 50 vol% Cu-50 vol% Ni multilayered samples and discussed the propagation of dislocation loops confined between the layers and

the nucleation of dislocations at the interface. Thus, different classes of multilayered materials have been examined, and several theories have been proposed to explain the mechanisms that may operate to produce this increase in hardness in these materials: the supermodulus effect, coherency strains, the effect of interfacial misfit dislocations on dislocation guide, the reduction of grain sizes as a result of thickness of the alternating layers, and image forces (Koehler's model) at the interface which resist dislocation glide [3, 4]. However, while these articles describe the hardness increases as layer thickness goes down and when layer thickness in the range of a few nanometers, the hardness of the superlattice will research maximum. In this paper, we present the superharening only occurs when indenter penetrates more interfaces. Also we found the superlattice of NbN/W is much hard and deformable than NbN ceramics.

2 Experimental Procedure

The nanocomposite chosen for this investigation was W/NbN which is classified as an immiscible, non-isostructural superlattice material. To evaluate the influence of the layer thickness on the results, two samples of this nanocomposite with different bilayer repeat periods (Λ = 5.6 nm and Λ = 10.4 nm) were prepared for experiments. The structure of this superlattice material has been well documented in the literature [1, 2]. The samples were fabricated by depositing alternating layers of single crystal tungsten (W), a body-centered cubic metal, and niobium nitride (NbN), a face-centered cubic ceramic, on a substrate. The lattice constants of the ceramic and metal layers are 0.439 nm and 0.315 nm respectively. A pictorial representation detailing the composition of each sample is shown in Figure 1. Note that the ceramic, NbN, is the surface layer for both nanocomposite samples. Two additional samples were prepared for each individual material comprising the nanocomposites for comparison. All four samples were epitaxially grown as a thin film approximately 1 μm thick on an MgO (001) substrate using reactive DC magnetron sputtering.

The experiments were conducted using Hysitron's Triboscope® Nanoindenter in conjunction with Digital Instruments' Nanoscope IIIa AFM imaging system. Each sample was ultrasonically cleaned with acetone to remove any surface debris. Prior to indentation, each sample was scanned to find suitable areas for indentation. After indentation, the sample surface was scanned *in situ* to record the image of the surface topography. Diamond cubic pyramidal indenter tips with an included angle of 90° were selected for the experiments since a sharp tip radius was necessary to achieve sufficient penetration into the hard samples.

As noted in the literature, the surface roughness of the sample can significantly influence the experimental results when conducting nanoindentation experiments [6, 7]. This is particularly important for shallow nanoindentations where the penetration of the indenter into the material is less than 25 nm. To minimize this influence, the sample surface was scanned *prior to* nanoindentation, the image was recorded, and the actual surface roughness of the scanned area was determined to be less than
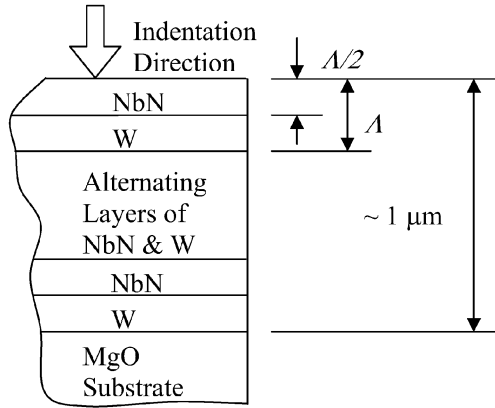
Fig. 1. Structure of the nanocomposite samples used for experimentation. Sample W/NbN (Λ = 5.6 and 10.4 nm).
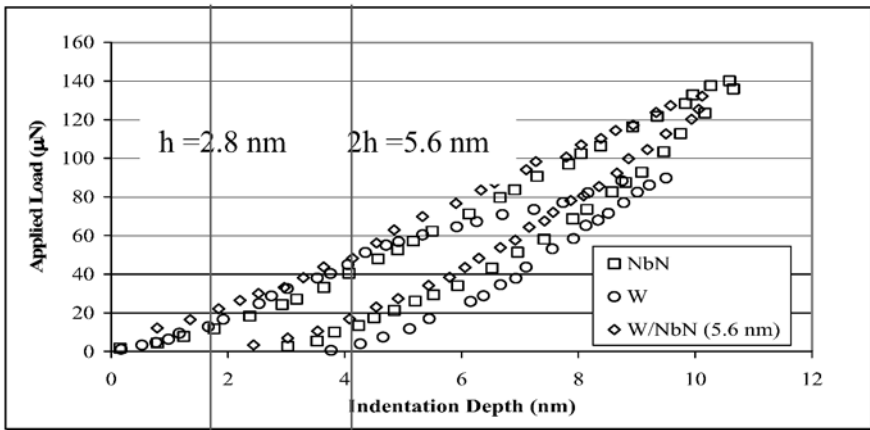
Fig. 2. Load vs. displacement curves during shallow nanoindentation when nanoindentor penetrates the 1st interface at $h = 2.8$ nm and the 2nd interface at $h = 5.6$ for sample W/NbN ($\Lambda = 5.6$ nm). The nanolayer shows very similar behavior to NbN single crystal.

0.5 nm from the recorded image utilizing the Roughness Analysis feature of the NanoScope IIIa software.

3 Experimental Results

A comparison of the load versus displacement curves for NbN and W at shallow indentation depths and the nanocomposites, W (100)/NbN (100) (bilayer thickness $\Lambda = 5.6$ nm), are shown in Figure 2. The comparison of the load versus displacement curves indicate that the superlattice materials, W/NbN ($\Lambda = 5.6$ and 10.4 nm),
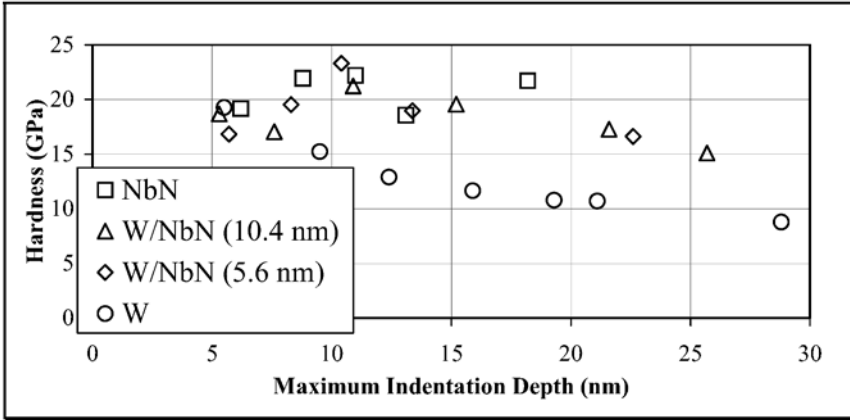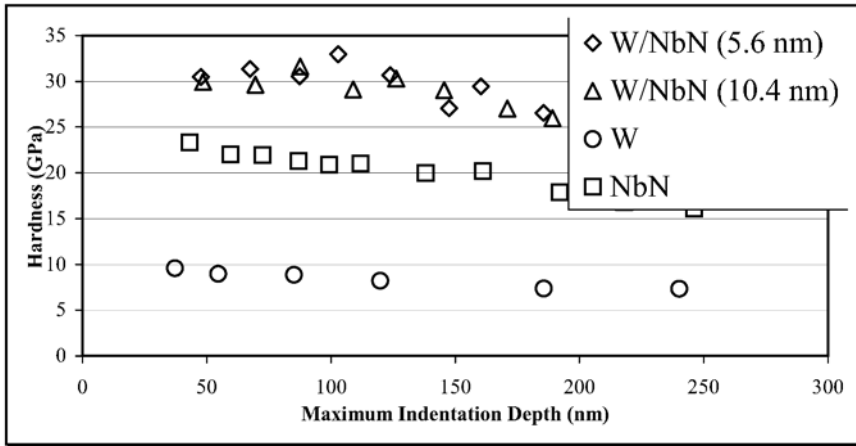
Fig. 3. Hardness as a function of maximum indentation depth (shallow indentations).

exhibit loading and unloading patterns which are very similar to the behavior of NbN. Both comparisons also demonstrate that tungsten initially follows the same loading pattern but starts to deviate from the others at approximately 5 nm. Since the bilayer repeat periods for W/NbN ($\Lambda = 5.6$ nm) and for W/NbN ($\Lambda = 10.4$ nm) are so shallow, the indenter has penetrated only a couple of layers into the superlattice materials.

Hardness is a general measure of the resistance of a material to plastic deformation. As noted earlier, the hardness is normally defined as the ratio of the maximum applied load divided by the corresponding projected contact area. For nanoindentations, the hardness is normally defined as the maximum load divided by the projected area of the indenter in contact with the sample at the maximum load [8]. Thus, $H = P_{max}/A_C$, where, H, P_{max} and A_C are the hardness, the maximum applied load, and the projected contact area at the maximum applied load respectively. The experiment was divided into two sets of nanoindentations. The first set of nanoindentations, hereafter referred to as shallow nanoindentations, were conducted to evaluate the influence (if any) of the individual layers on the hardness of the nanocomposites. The second set of nanoindentations, hereafter referred to as deep indentations, was conducted to examine the behavior of the materials as a function of the indentation depth. For the shallow indentations, the applied loads were selected to achieve penetration of the indenter to a depth equal to the theoretical thickness of the individual layers of the nanocomposite materials. Since the focus was only on the first couple of nanolayers, the shallow nanoindentations were designed to achieve a penetration depth of less than 25 nm.

A comparison of the hardness as a function of the maximum indentation depth for all the material samples for the shallow nanoindentations is shown in Figure 3. A comparison of the results shows no significant difference in the hardness for the two superlattice samples (W/NbN, $\Lambda = 5.6$ nm and W/NbN, $\Lambda = 10.4$ nm) and the NbN sample for the shallow indentation depths (less than 25 nm). Also, the in-

Fig. 4. Hardness as a function of maximum indentation depth (deep indentations).

dentation size effect causes the hardness of W to increase until it is approximately the same as the hardness of NbN (at 5 nm). A comparison of the hardness as a function of the maximum indentation depth is shown in Figure 4 for the deep nanoindentations. An examination of this graph shows several trends. The results for the monolithic material samples, NbN and W, indicate the presence of the Indentation Size Effect (i.e. there is increase in hardness as the indentation depth decreases). The tungsten hardness ranges from approximately 7 GPa at an indentation depth of 240 nm and gradually increases to about 10 GPa at a depth of 40 nm. The niobium nitride hardness ranges from 17 GPa at a penetration depth of 250 nm to about 23 GPa at a depth of 40 nm. In contrast, the behavior of the nanocomposites differs from the behavior for the monolithic materials. The hardness for both nanocomposites is consistent over a range of indentation depths (50 nm to approximately 150 nm) before it begins to taper off slightly. The final observation is that the hardness for each sample at the deeper indentation depths approaches the microhardness reported [1]. An examination of the post-indentation surface topography shows significant pile-up of the material near the indentation site.

4 Discussion

Combining the results of the previous two graphs (Figures 3 and 4), some deductions can be made regarding the factors contributing to the observed hardness increase in the superlattice materials under deep indentation. Both W and NbN exhibit hardness around 20–23 GPa at an indentation depth of 5 nm. This is the approximate thickness of an individual layer in one of the superlattice materials and both superlattice materials exhibit similar hardness at the same indentation depths. The influence of the interfaces is minimal for the shallow indentations because only a few interfaces are

in the load zone and the amount of deformation is small. However, at the deeper indentation depths, the superhardeing occurs for the superlattice. The hardness is much higher than the one predicted by the rule of mixtures for conventional composites concept [1, 2]. Since the number of interfaces in the load zone increases at deeper indentation depths, this indicates that the interface between layers is an important factor in the remaining increase in hardness observed in the superlattice materials. At shallow indentation depths, a few interfaces (about 1∼4) are penetrated and the dislocation movement required to accommodate the plastic deformation is minimal. However, as the penetration depth increases, the amount of dislocation activity increases. At some point, the behavior of the interface as a barrier to dislocation motion begins to affect the deformation characteristics of the nanocomposites leading to the observed increase in hardness. Also there are no common slip systems between NbN and W (bcc crystal). In B1 structure NbN, the primary slip system is $\{110\}\langle1\bar{1}0\rangle$, while the primary slip systems in W are $\{110\}\langle111\rangle$, with additional slip systems being $\{112\}\langle111\rangle$ and $\{123\}\langle111\rangle$. With the 45 degree rotation of the lattices, both the slip planes and slip directions are different. It is extremely difficult for dislocations propagate cross NbN/W interface. Moreover, since the lattice consts. Å for W/NbN are 3.1650/4.39, with 1.36% mismatch, interfacial dislocation or interfacial stress exist along the interface. All these above will make it harder for the indentor to penetrate through the interface. Consequently, hardness will increase with more interface participation.

In general, the elastic modulus should be constant regardless of the indentation depth, although some minor variation is to be expected due to material imperfections. The reduced elastic moduli for the deep and shallow indentations were calculated using the area functions calibrated on a standard quartz sample and compared for all the samples. The measured elastic modulus are between 270∼310 Gpa for both deep and shallow indentations. Since the moduli for all the samples are in the same approximate range, the influence of the elastic modulus on the hardness of the nanocomposites appears to be minimal. Consequently, it is not possible to attribute the increase in hardness observed in the superlattice materials to this particular material property.

Normally, nanolayers gains hardness by losing deformability [9], however, the superlatice demonstrated excellent deformability when reaching the superhardening. The NbN sample exhibits less material pile-up than the other materials. For a ceramic material, the energy of indentation is absorbed by local cracking in the deformation zone under the indenter tip. Hence, little material pile- up occurs during indentation. However, in the nanocomposites, the NbN layers surround the W layers. Due to the ductile properties of the W layers and the fact that the individual layers are only a few nanometers thick, the NbN layers are forced to bend with the W layers since the bending of the NbN layers is easier to achieve than fracture of the material. As a result, the presence of the W layers act to alter the deformation process of the NbN layers from fracture to bending.

5 Conclusions

The shallow indentations show little difference in hardness between the NbN sample and the two superlattice materials. However, an increase in hardness is observed at deeper indentation depths. This indicates that the interface has a strong influence on the increase in hardness.

Acknowledgements

References

1. A. Madan and S.A. Barnett, Fundamentals of nitride-based superlattice thin films, in *Materials Science of Carbides, Nitrides and Borides*, Y.G. Gogotsi and R.A. Andrievski (eds.), pp. 187–204.
2. A. Madan, Yun-yu Wang, S.A. Barnett, C. Engstrom, H. Ljungcrantz, L. Hultman and M. Grimsditch, Enhanced mechanical hardness in epitaxial non-isostructural Mo/NbN and W/NbN superlattices, *J. App. Phys.* **84**(2), 1998, 776–785.
3. X. Chu, M.S. Wong, W.D. Sproul, and S.A. Barnett, Deposition, structure and hardness of polycrystalline transition-metal nitride superlattice films, *J. Mater. Res.* **14**(6), 1999, 2500–2506.
4. B.M. Clemens, H. Kung and S.A. Barnett, Structure and strength of multilayers, *MRS Bulletin*, February 1999, 20–26.
5. P.M. Anserson, T. Foecke and P.M. Hazzledine, Dislocation-based deformation mechanisms in metallic nanolaminates, *MRS Bulletin*, February 1999, 27–33.
6. S.P. Baker, Between nanoindentation and scanning force microscopy: Measuring mechanical properties in the nanometer regime, *Thin Solid Films* **308–309**, 1997, 289–296.
7. W.W. Gerberich, W. Yu, D. Kramer, A, Strojny, D. Bahr, E. Lilleodeen and J. Nelson, Elastic loading and elastoplastic unloading from nanometer level indentations for modulus determinations, *J. Mater. Res.* **13**(2), 1998, 421–439.
8. W.C. Oliver and G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *J. Mater. Res.* **7**(6), 1992, 1564–1583.
9. M.Z. Li and S.X. Mao, Length scale (thickness) controlled ductile versus brittle transition in layered materials, *Material Science and Engineering* **A266**, 1999, 73–79.