On the Origins of Hardness of Cu-TiN Nanolayered Composites

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Abstract. We investigated the mechanical response of physical vapor deposited Cu-TiN nanolayered composites of varying layer thicknesses from 5 nm to 200 nm. Both the Cu and TiN layers were found to consist of single phase nanometer sized grains. The grain sizes in the Cu and TiN layers, measured using transmission electron microscopy and X-ray diffraction, were found to be comparable to or smaller than their respective layer thicknesses. Indentation hardness testing revealed that the hardness of such nanolayered composites exhibits a weak dependence on the layer thickness but is more correlated to their grain size.

Keywords: multilayers; hardness; grain size; layer thickness.

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Metal/ceramic multilayers have come into greater focus due to their promising mechanical, physical and chemical properties, making them practically useful in a wide range of temperatures, mechanical loadings, and environmental conditions [1-5]. One primary scientific interest stems from the large difference in strength and ductility between their constituent phases. In general, the mechanical properties of such composites have lower strengths than the ceramic constituent and a lower ductility than the metal component. However for layered composites comprised of individual layers of less than a few nanometers, both strength and ductility could be improved relative to their non-layered counterparts. For example, metal-metal nanolayered composites show higher strengths than either constituent and display appreciable ductility [6, 7]. Experimental [8-10], theoretical, and modeling [11] studies of these metal-metal multilayers have indicated that the enhancement of both strength and ductility is related both to the structure and properties of the interfaces between the layers, as well as the thicknesses and properties of the individual layers [6].

For metal-ceramic multilayers, the ceramic component has poor plasticity at room temperature and low fracture toughness, because of a high lattice friction stress on most slip systems at low homologous temperatures. Most studies from both experiment and modeling aspects have indicated that such metal-ceramic composites show no appreciable ductility [1, 3-5]. However, compressive stress-strain curves obtained from micro-pillar compression of Al-TiN multilayers have shown that plastic co-deformation may occur as the bilayer thicknesses are reduced to a few nanometers [12]. Similarly *in situ* indentation in a high-resolution transmission electron microscope has also indicated dislocation activity in both metal and ceramic layers in Al-TiN multilayers [13]. The improvement of the ductility in nanolayered metal/ceramics composites has been ascribed to plastic co-deformation mechanisms [14]. Atomic-scale

modeling has revealed unit processes (involving single or a few dislocations) occurring at the metal-ceramic interfaces during deformation [15, 16].

It is worth pointing out that such mechanisms are related to interfaces and layered structures where the individual layers have high aspect-ratio grains, i.e., the grain size in the layers is over 30 times the layer thickness in the accumulative roll bonded (ARB) Cu-Nb nanolaminates [17] and 2~10 times the layer thickness in the physical vapor deposited (PVD) Cu-Nb nanolaminates, [18, 19] and in Al-TiN metal/ceramics multilayers [12, 13, 20]. However, it has been noticed that ceramic layers produced by sputtering at room temperature often have a small grain size due to their low diffusivity and high melting temperatures. In particular, if the metal has a weak chemical affinity to the ceramic, then three-dimensional island growth is favored for the ceramic during sputtering, resulting in a nanometer-scale grain size, that may be even smaller than the layer thickness [21, 22]. Thus the scientific issue motivating this study is which factor(s) amongst grain size, layer thickness, and interfacial character determines the mechanical properties of such layered composites.

Our recent density functional theory (DFT) studies suggest that Cu has a weaker affinity to bond with TiN, as compared to Al [23]. Thus in the Cu-TiN system, both Cu and TiN are expected to exhibit a tendency towards three-dimensional island growth mechanism resulting in nanocrystalline grain sizes. In this work, we deposited Cu-TiN multilayers and achieved nano-grained Cu and TiN layers, where the grain size was smaller than (or comparable to) the respective layer thickness. In contrast, the smallest length scale of interest for the Al-TiN multilayer system studied in earlier reports [12, 20, 24, 25] is their layer thickness (the grain sizes of Al and TiN are 2-10 times their corresponding layer thickness). This study compares the hardness responses in these two metal-ceramic multilayer systems (Cu-TiN and Al-TiN) with the

aim of determining the correlation between the measured hardness values to the corresponding smallest length scale of interest (layer thicknesses and/or grain sizes) in the samples.

Thin multilayers composed of alternating Cu and TiN layers were deposited at room temperature using direct current (dc) magnetron sputtering on Si substrates (the Si substrates have a thin amorphous SiO₂ layer at the top) with the equal volume fraction of Cu:TiN = 1:1. The Cu layers were deposited at a base pressure of 2×10^{-8} Torr. The TiN layers were deposited using reactive sputtering of Ti in a gas mixture of Ar and N (Ar:N = 30:3 SCCM) with a bias of 20 watts RF on the substrate. The multilayers were deposited for six different individual (targeted) layer thicknesses: Cu (5 nm) – TiN (5 nm), Cu (10 nm) – TiN (10 nm), Cu (20 nm) – TiN (20 nm), Cu (50 nm) – TiN (50 nm), Cu (100 nm) – TiN (100 nm) and Cu (200 nm) – TiN (200 nm). The total film thicknesses for all samples were around 5 μ m. The actual layer thicknesses and grain sizes were characterized in a TEM for the as-deposited Cu (5 nm) – TiN (5 nm) and Cu (50 nm) – TiN (50 nm) samples. Cross sectional TEM samples of the as-deposited films were prepared by mechanical polishing to a final thickness of 20–30 μ m and a final finish of 1 μ m with diamond lapping film, followed by ion-milling using a Gatan™ PIPS® instrument operating at 3–5 kV. The samples were examined using a Tecnai TF 30TM 300 kV TEM. Grain size distributions were determined from the TEM micrographs by measuring grain diameters in one fixed direction parallel to the interface.

The grain sizes for the TiN layers in the other Cu-TiN samples were examined using X-ray diffraction (XRD). The grain size (D) of TiN grains in the Cu-TiN multilayers was determined from the Bragg-Brentano theta-2theta diffractogram, using the Sherrer method [26, 27]: $D = \frac{K\lambda}{\beta \cos\theta}$, where λ is wavelength of X-ray, β is the full width at half maximum (FWHM), θ is Bragg's angle and K the constant of proportionality. The (111) peak for TiN, and a K value of

0.9, which corresponds to spherical crystallites [26], was used for calculating D . This estimation is a lower bound since some parameters, such as the possible presence of twins, crystal defects and microstrains, can also contribute to the peak broadening [26, 28]. The measurements from XRD using the Scherrer method were therefore cross-checked with TEM analysis on select layer thicknesses. The same XRD and TEM acquisition parameters were used for all the samples for an accurate comparison.

Characterization of the Cu-TiN multilayers revealed two major microstructural features: (a) the Cu-TiN composites had a wavy layered structure and (b) the grain size in the layers was comparable to or even smaller than the respective layer thickness (Figs. 1 and 2). These small grain sizes are consistent with our expectation for this study.

Figure 1 shows an SEM (scanning electron microscope) image of the Cu (50 nm) – TiN (50 nm) multilayers, clearly showing the layered arrangement and wavy nature of the deposited layers of Cu and TiN. This waviness is almost absent for the first few layers seen at the bottom close to the substrate, but becomes more prominent with increasing thickness of the film. In contrast to the metallic multilayers and Al-TiN multilayers, there is no obvious columnar structure (where the column boundaries are represented by aligned homophase grain boundaries from layer to layer). This could be ascribed to the three dimensional island growth mechanism for TiN on Cu.

The TEM micrographs of the Cu (50 nm) – TiN (50 nm) and Cu (5 nm) – TiN (5 nm), along with their corresponding diffraction patterns, are shown in Figs. 1 and 2, respectively. For the Cu (50 nm) – TiN (50 nm) sample as shown in Fig. 1, the individual layer thicknesses of the Cu and TiN layers are measured to be ~ 64 nm and ~ 38 nm, respectively. The grain size is plotted in Fig. 1b, showing that the average grain size in the TiN layers is about 4 nm and in the

Cu layer is about 25 nm. The diffraction pattern in Fig. 1 indicates that there is no strong orientation relation between Cu and TiN layers. For the Cu (5 nm) – TiN (5 nm) sample as shown in Fig. 2, the individual layer thicknesses of the Cu and TiN layers are measured to be ~ 7.3 nm and ~ 5.2 nm, respectively. The grain size is plotted in Fig. 2b, showing that the average grain size in the TiN layers is about 3.6 nm and in the Cu layer is about 5 nm. The diffraction pattern in Fig. 2 is more diffuse than that for the thicker Cu (50 nm) – TiN (50 nm) multilayers, again indicating a lack of texture in the Cu and TiN layers. The TiN grain sizes were also estimated using XRD, and are summarized in Table 1. The XRD measurements indicate that the TiN grain size is more or less independent of layer thickness. Thus, we can conclude that the TiN grain sizes are around 4 nm or smaller (range 1.5-4.5 nm) for all multilayer samples, and the Cu grain size is comparable to or smaller than the layer thickness.

These observations are in sharp contrast to those reported for Al-TiN [12, 20, 24, 29], where the multilayers showed large sized in-plane through-thickness grains and a columnar structure. For example, the column size and the grain sizes in the Al-TiN sample have been reported to be 75-120 nm for a 9 nm thick Al layer [20], which increases to ~ 300 nm or higher as the Al layer thickness increases to 250 nm [24]. Thus the layer thicknesses for the Al-TiN multilayers are the smallest length scale of interest in these samples (i.e. they are smaller than the Al and TiN grain sizes), and the mechanical properties of Al-TiN multilayers are expected to show a strong correlation to changes in their layer thicknesses.

The hardness measurements were conducted using a diamond Berkovich tip. 50 tests per sample were made in each nanoindenter machine using a 10 sec (loading) – 10 sec (hold) – 10 sec (unloading) cycle. Tests were done to a maximum displacement of 200 nm for the Hysitron Triboindenter™ (instrument limit) and up to a maximum displacement of 200 and 400 nm for the

Agilent XP™. These choices of indentation depth ensured that in each case the indenter was sampling regions within and beyond at least one bilayer thickness (2λ).

Figure 3 shows the plotted hardness values of Cu-TiN and Al-TiN as a function of the inverse square root of their bilayer thickness (2λ). It is clearly revealed that the Al-TiN samples show a Hall-Petch-type dependence of hardness on the bilayer thickness for $2\lambda \geq 50$ nm. The best fit line to the Hall-Petch equation ($H = H_0 + k(2\lambda)^{-0.5}$) for Al-TiN multilayers of $2\lambda \geq 50$ nm is given by $H = 1.05 + 29.9 * (2\lambda)^{-0.5}$ GPa. According to this fit, as λ approached infinity, hardness $\sim$ 1 GPa, which is similar to hardness reported for Al thin films of average grain sizes in the range of 50- 80 nm [30, 31]. For $\lambda < 50$ nm the hardness becomes constant at around 6.3 GPa. However, compared to Al-TiN, the Hall-Petch behavior is relatively weaker in the Cu-TiN multilayers. The Cu-TiN films with the bilayer thicknesses of $2\lambda < 200$ nm show a narrow range of hardness values (from 4.9 to 5.7 GPa). Only the largest Cu-TiN bilayer thickness of $2\lambda = 400$ nm shows a slight decrease in hardness (4.3 GPa) as compared to the saturated hardness values. Additional samples with $2\lambda > 400$ nm are needed to demonstrate the Hall-Petch strengthening in Cu-TiN multilayers. With the exception of one ($2\lambda = 400$ nm), the other six samples had $2\lambda < 200$ nm with nearly constant grain size less than the respective layer thickness.

These distinctive differences in the hardness values suggest that mechanical properties of Cu-TiN multilayers have a weak dependence on layer thickness. Since the TiN grain sizes in these samples are the smallest length scale of interest (see Table 1), we surmise that the strength of these samples is instead determined by their grain sizes. Figure 4 shows some additional evidence; here the Cu-TiN hardness values are plotted against the inverse square root of their respective TiN grain sizes. The narrow range of hardnesses seen in the various Cu-TiN

multilayers appears to be dictated by the small nanocrystalline grain sizes (ranging from 1.5 to 4.5 nm) of the TiN layers in the multilayered composite.

Such differences in the hardness and strength determinants of the two multilayer systems – where the layer thickness and the interface character determines the hardness for Al-TiN, while the TiN nano-crystalline grain sizes control the same for Cu-TiN – are expected to have major consequences for deformation mechanisms in these two systems. For example, the Al-TiN multilayers have been found to exhibit plastic co-deformation (without cracking) at individual layer thickness below ~5 nm [12, 20, 24, 29]. This change in deformability from brittle to ductile, particularly for the ceramic layer, has been explained by a high density of interfaces in the thin layered (<5 nm individual layer thickness) Al-TiN system where interactions between dislocations in the two adjacent interfaces results in the locally high resolved shear stress in ceramic layers, facilitating dislocation transmission across the interface [14]. However the Cu-TiN multilayers, due to the small grain size of its components and a consequent lack of epitaxy, is not expected to have any strong orientation relation between adjacent layers. Thus the interfaces in multilayered Cu-TiN may not play a significant role in determining the metal-ceramic co-deformation response in this system.

In summary, we studied the hardness of nanocrystalline, nanolayered Cu-TiN composites. Although these composites consisted of continuous layered structures, the hardness of such nanolayered composites exhibited a very weak dependence on the layer thickness and is better correlated to the grain size. This is ascribed to the small (nanometer) grain sizes in both Cu and TiN layers that are comparable to or smaller than the layer thickness.

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Figure(s)

Figure 1. (a) Cross-sectional TEM of the Cu (50 nm) – TiN (50 nm) sample with corresponding diffraction pattern and (b) grain size distribution. (inset) BSEM micrograph showing layering of the Cu (50 nm) – TiN (50 nm) system.

Figure 2. (a) Cross-sectional TEM of the Cu (5 nm) – TiN (5 nm) sample with corresponding diffraction pattern and (b) grain size distribution .

Table 1. Grain size (D) measurements (from TEM and XRD) for the Cu-TiN multilayered films. TEM was used for the Cu (5 nm) – TiN (5 nm) and Cu (50 nm) – TiN (50 nm) samples; while XRD was used only for measuring the TiN grain sizes.

Cu-TiN nominal layer thickness	D in Cu (nm)	D in TiN (nm)
5 nm	5.3 (TEM)	3.6 (TEM)
10 nm		1.5 (XRD)
20 nm		2.8 (XRD)
50 nm	24.5 (TEM)	3.2 (XRD)/4.4 (TEM)
100 nm		3.4 (XRD)
200 nm		4.5 (XRD)

Figure 3. Hardness vs. (bilayer thickness, 2λ)^{-0.5} for Cu-TiN (orange circles) and Al-TiN (blue diamonds). The bilayer thickness values are marked for each data point. The blue dotted line shows the best fit of the Hall-Petch equation for the Al-TiN multilayers. The orange dotted line shows the saturation in hardness values for Cu-TiN multilayers of $2\lambda < 200$ nm. The error bars denote the standard deviation of the hardness measurements.

Figure 4.

Replotted values from Fig. 3 using the smallest length scale of interest for each system. Thus the hardness values for Al-TiN are plotted against $(\text{bilayer thickness, } 2\lambda)^{-0.5}$, while for Cu-TiN the plot is Hardness vs. $(\text{TiN grain size})^{-0.5}$.