NANOSCALE STRENGTHENING MECHANISMS
IN METALLIC THIN FILM SYSTEMS

By

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Nano-scale strengthening mechanisms for thin films were investigated for systems governed by two different strengthening techniques: nano-laminate strengthening and oxide dispersion strengthening. Films were tested under elevated temperature conditions to investigate changes in deformation mechanisms at different operating temperatures, and the structural stability. Both systems exhibit remarkable stability after annealing and thus long-term reliability.

Nano-scale metallic multilayers with smaller layer thicknesses show a greater relative resistance to decreasing strength at higher temperature testing conditions than those with larger layer thicknesses. This is seen in both Cu/Ni/Nb multilayers as well as a similar tri-component bi-layer system (Cu-Ni/Nb), which removed the coherent interface from the film. Both nanoindentation and micro-pillar compression tests investigated the strain-hardening ability of these two systems to determine what role the coherent interface plays in this mechanism. Tri-layer films showed a higher strain-hardening ability as the layer thickness decreased and a higher strain-
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Oxide dispersion strengthened Au films showed a marked increase in hardness and wear resistance with the addition of ZnO particles. The threshold for stress-induced grain-refinement as opposed to grain growth is seen at concentrations of at least 0.5 vol%. These systems exhibited stable microstructures during thermal cycling in films containing at least 1.0% ZnO. Nanoindentation experiments show the drop in hardness following annealing is almost completely attributed to the resulting grain growth. Four-point probe resistivity measurements on annealed films showed a significant drop in resistivity for the higher concentration ZnO films, which is proposed to be the result of a change in the particle-matrix interface structure. A model connecting the hardness and resistivity as a function of ZnO concentration has been developed based on the assumption that the impact of nm-scale ZnO precipitates on the mechanical and electrical behavior of Au films is likely dominated by a transition from semi-coherent to incoherent interfaces.
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CHAPTER 1: Introduction

1.1. Motivation

Increasing the useful lifespan of technical components is a recurrent objective and technical challenge for any engineering application. Many components fail as a result of mechanical degradation over time; this is often directly linked to operating conditions, whether that is through fatigue, wear, thermal cycling, high impact bombardment, radiation, or a gamut of other possibilities. In order to increase the lifetime of some components hard coatings can be applied as a mechanical barrier, which protects the main component underneath. These hard coatings are utilized in countless applications ranging from tribological to electrical, optical, or even radiological barriers.

Two of the most common sources of failure, and the particular focus of this thesis, are operational degradation from thermal annealing and wear. In either case the microstructure of the material is compromised and leads to softening, which in turn leads to macroscopic failure. In order to combat this type of degradation, hard coatings can be tailored to resist such microstructural changes. Nanocomposite materials have been known to show remarkable strength due to the small intrinsic length scales. The intrinsic size relationship for nanocomposites has been under investigation for decades, attempting to understand the underlying mechanisms responsible for deformation. These mechanisms continuously change as the length scale decreases from microscale to the nano-scale and are dependent on dislocation interactions with the increasing number of interfaces, whether they be grain-boundaries or interfaces. At extremely small length scales, the strength once again begins to decrease as dislocations overcome boundary barrier strengths.
One such system that has been studied extensively over the past few decades are nano-scale metallic multilayers (NMM) due to their atypically high strength and surprising durability in harsh environments. The strength and deformation response of these materials are directly related to the nature of their interfaces. Coherent interfaces, generally weaker, often exhibit greater ductility than incoherent systems. A mixed interface system has shown superior properties of both interface types leading to higher strength, greater ductility, and significant strain-hardening ability and is the focus of this investigation. Thus far, the reliability of these systems in conditions closer to actual operating environments has not yet been investigated and is a large focus of the current investigation. Since annealing inherently changes the interface of the multilayers, whether it is through triple point formation, alloying, or spheroidization, over time the yield behavior and deformation of the multilayers will be negatively affected. Annealing has the potential to negatively affect all forms of strengthening techniques, not just multilayers, especially when the number of interfaces increases.

1.2. Common Strengthening Mechanisms and Their Limitations

Many different techniques are typically used to increase the strength of a material, depending on the application and desired results. Some of these techniques include the control of grain size [1]–[4], deposition of nano-laminate structures [5]–[7], and the addition of solid solution impurities [3], [8]–[11], precipitates or oxide particles [9], [12], [13], all of which have the potential to degrade when used under elevated temperature service conditions. One of the most common techniques that has been studied for decades on a variety of different materials in both thin films as well as bulk materials is to decrease the grain size. The increased strength of the system with decreasing grain size was first observed and quantified by Hall [4] and Petch [2], who independently observed the strength of the materials increasing with the inverse square of the grain
size. While this relationship holds up across a wide range of materials and sample sizes, it begins
to break down for grain sizes or layer thicknesses on the order of tens of nanometers, leading to an
upper bound for this type of strengthening. However, additional energy introduced to the system
either through annealing or by plastic deformation can leading to grain growth and thus a decrease
in strength, making this a temporary strengthening mechanism if service conditions include
elevated temperatures or wearing bodies. Many studies suggest that grain growth is attributed to
grain-boundary sliding, diffusion, and grain rotation [14], [15]. Therefore, if the grain boundary
mobility is suppressed grain growth can be reduced, slowed or even stopped.

One way in which grain-boundary mobility can be suppressed is by adding impurities into
the microstructure to act as stabilizers [11], [16], [17]. In one particular study, samples with lower
impurity concentrations exhibit significant grain growth in the deformed region of the sample
while the grain size in the un-deformed regions remains the same as the as deposited condition
[18], a classic example of stress-induced grain growth. In contrast, grain growth in the deformed
region of a high impurity concentration sample is suppressed, suggesting that impurities are
effective in decreasing grain growth by pinning grain boundaries, thus reducing grain boundary
sliding, rotation, and diffusion. This stabilization technique can be applied to both solid-solution
strengthened as well as oxide dispersion strengthened (ODS) materials. However, impurities in
solid-solution strengthened materials can segregate to the grain-boundaries over time or as a result
of annealing. While this doesn’t necessarily mean the material would no longer exhibit grain size
stabilization, it does reduce the solid-solution strengthening benefit.

Thin films can also be strengthened using oxide dispersion strengthening, where small
oxide particles are used to increase strength [30]. This technique increases the strength of the
material in a similar way as precipitation strengthening does, by creating barriers to dislocation
motion and additionally acting as Frank-Read dislocation sources. This type of mechanism is more stable than solid solution impurity strengthened materials because diffusion of the entire oxide particle is much less probable than the diffusion of individual impurity atoms, leading to less diffusion to the grain boundaries and therefore retains its strength. Additionally, ODS materials are less likely to undergo Oswald ripening: where atoms from smaller precipitates diffuse to larger precipitates causing them to grow at the expense of the smaller ones. This readily occurs in traditional precipitation strengthened materials, which in turn reduces the strength.

The ODS technique also shows great promise for increasing hardness without affecting conductivity as much as a solid-solution counterpart [12], which is particularly intriguing for hard Au films. When comparing the hardness and resistivity relationship of a Au-V alloy and Au-V_2O_5, the ODS Au showed both a larger increase in hardness as well as a smaller increase in resistivity as a function of V content in the film. This validates the hypothesis that ODS films are more effective in creating a hard Au film for electrical contacts, since high conductivity is still desired. If the oxide used in the ODS film is also conducting or semi-conducting, as is the case in the system used in this investigation, the increase in resistivity could be minimized while still gaining the benefits of particle strengthening.

Nano-scale metallic multilayers also have an intriguing ability to increase strength, similar to the way in which grain size reduction increases the strength of a material, with strengths far exceeding those of corresponding bulk metals [19]. The strength is highly dependent on the individual layer thickness, interface type, and material selection leading to a wide variety of properties, which could be tailored to suit specific applications. At larger layer thicknesses, down to a few hundred to several tens of nanometers, the strengthening relationship follows the Hall-Petch relationship ($\sigma \propto 1/d^2$) [4], which is also seen in non-layered microstructures. As the layer
thickness drops below a certain point, the strength increase more rapidly than the Hall-Petch model predicts, indicating a change in the deformation mechanism from traditional dislocation pile-up to a different mechanism depending on the interface structure.

The type of deformation mechanism occurring in the multilayers is highly dependent on the interface morphology and can be separated into two general categories: coherent and incoherent interfaces. Coherent interfaces occur in multilayer systems consisting of materials with similar crystallographic structures (i.e. Cu-Ni) but a lattice spacing mismatch. This mismatch causes a tensile strain in the layer with larger lattice spacing and a compressive strain in the other layer, which results in a coherency stress [20]. The stresses begin dropping off as the distance from the interface increases. Therefore, as the distance between two interfaces decreases, the less the stress is allowed to relax and the stronger the film becomes. Misfit dislocations are also likely to appear along the interface to relieve some of the stress which can act as barriers to other dislocations and further increase the strength. Additionally, since the crystallographic structures are the same in both layers, and many coherent systems grow epitaxially, slip systems are continuous. This leads to dislocation transmission across the interface and results in reasonable ductility as well as an increase in strength.

On the other hand, incoherent interfaces are constructed of layers with different crystallographic structures (i.e. Cu-Nb), with no continuous slip plane and thus are much stronger barriers to slip transmission [21], much like grain boundaries with transmission only occurring when the strength overcomes the barrier strength. While this type of interface is often stronger than the coherent system, it is also more brittle due to shearing of the interface. The deformation mechanism for this type of interface at small layer thicknesses is the confined-layer-slip (CLS) mechanism, which has been observed in many different systems [21]–[23]. As there is no longer
sufficient room for dislocations to build up against the interfaces, dislocations instead glide through a single layer, bowing along the interface and leaving dislocation debris, in the form of misfit dislocations. This debris in turn interacts with passing dislocations leading to an increased flow stress and strain-hardening. Once the layer thickness decreases below a few nanometers, dislocations can no longer bow due the extremely small radius of curvature of the propagating dislocation. At this point, the strength in the film is high enough to overcome the interface strength and dislocations can cut straight through. In some cases, there is actually a softening in these extremely thin layers which has been shown to be a result of increased dislocation nucleation and propagation [24]. A summary of this strength to layer thickness trend is schematically shown in Figure 1-1.

![Figure 1-1. Schematic of controlling deformation mechanisms occurring in multilayers with incoherent or weak interfaces at different layer thicknesses.](image-url)
Tri-layer systems have a combination of both coherent and incoherent interfaces and have been suggested to possess properties of both types of interfaces through dislocation dynamic simulations [14, 21-23]. These films suggest that the strong incoherent interface in combination with the coherent interface can lead to additional strain-hardening [26]. The Cu-Ni-Nb tri-layer system has been investigated using two different nanoindentation techniques to investigate the extent of strain-hardening occurring in these layers. The first technique tests the hardness of the material using tips with two different included angles, which create different effective strains under the indenter tip [29]. Results from bulge testing (~0.2% strain) and nanoindentation with a Berkovich (~8% strain) and cube-corner (~22% strain) tip were used to approximate the stress-strain curve of Cu-Ni, Cu-Nb, and Cu-Ni-Nb multilayers, Figure 1-2. Tri-layer system started with the lowest strength at 0.2% effective strain, but managed to surpass both other bi-layer films, suggesting a higher strain-hardening behavior.

![Stress-strain curves approximated from nanoindentation and bulge testing techniques on Cu-Ni, Cu-Ni and Cu-Ni-Nb multilayers with individual layer thicknesses of 20 nm. Lines are curve fit approximations from the data points [24].](image)

Figure 1-2. Stress-strain curves approximated from nanoindentation and bulge testing techniques on Cu-Ni, Cu-Ni and Cu-Ni-Nb multilayers with individual layer thicknesses of 20 nm. Lines are curve fit approximations from the data points [24].
Additionally, scanning probe microscopy images of the indents show tri-layers having less pile up than both bi-layer systems, indicating increased strain-hardening ability. Both of these results substantiate each other, experimentally indicating that tri-layer films would show a higher strain-hardening exponent than bi-layer systems. However, molecular dynamic simulations indicate a different trend where the strength for the tri-layer system actually starts higher than both bi-layer systems at small strains and lies in between Cu-Ni and Cu-Nb at larger strains [27], suggesting a lower strain-hardening ability than the Cu-Nb system. Since these results are inconsistent with the experimental results discussed previously, more direct measurements of the strain-hardening ability of these films is required. The differences in these predictions of strain-hardening behavior could be a result of small variations in interface structure or loading conditions, which suggests a more robust understanding is needed.

Tri-layer films generally follow the same deformation mechanism as incoherent interfaces, where confined-layer-slip is dominated at small layer thickness. The dislocation is contained in the Cu/Ni bi-layer and bows along the Ni-Nb and Cu-Nb incoherent interface. The presence of the coherent interface in the center of this threading dislocation causes a “super threader” dislocation [30]. As these super threaders propagate, dislocation debris is deposited at the incoherent interface, causing this weak interface to shear. The sheared interface then produces internal shear stresses in the system and combined with elastic mismatch between the two materials, causes cross-slip to occur. This cross slip acts as an additional barrier to dislocations, making propagation increasingly difficult and adding to greater strain-hardening behavior over the bi-layer systems [30]. This ability to cross-slip is not seen in the bi-layer systems, since the effect only occurs at high stresses with a
continuous FCC-FCC system. Without the added strength from the Nb layer, Cu-Ni bi-layers cannot reach high enough stresses to cross-slip, and therefore is unique to the tri-layer system.

1.3. Thermal Stability of Multilayer Systems

The thermal stability of these NMM systems is crucial if they are to be used as hard coatings in service conditions above room temperature. If the layered structure begins to degrade, the strengthening benefit would be seriously compromised. Many studies have been conducted on the annealing stability of NMMs, mostly focusing on incoherent interfaces [26-37]. An elevated temperature nanoindentation study on thin film Cu [43] showed a 60% reduction in hardness as the temperature increases by 100°C, coupled with a pronounced drop in modulus, whereas Cu-Nb multilayer studies conducted at elevated temperatures showed only a 40% drop in yield strength after a 200°C temperature increase [40]. This suggests the addition of a layered structure has the potential to decrease the temperature sensitivity, allowing the thin film to maintain a greater percentage of its strength at elevated temperatures. Since the thermal stability of thin films, especially multilayers, is controlled by the tendency to decrease the internal energy of the system, and multilayered structures have both high elastic strains and a high density of interfaces, it is more preferable to rearrange the interface structure to help reduce the total energy in the system. This can occur either through interfacial mixing, alloying, or layer breakdown due to triple joint formation from the reduction of interfacial energy [44]. The extent of which any of these mechanisms occur is dependent on the temperature, chemistry, and layer thickness.

Several detailed studies have been conducted on the thermal stability of Cu-Nb bi-layers [21], [36], [40], [42], examining both mechanical and structural changes in the layers using nanoindentation and micro-tensile testing. Due to their mutually low miscibility the Cu-Nb system shows remarkable resistance to thermal degradation, maintaining a layered structure to
temperatures over 600°C, but is dependent on layer thickness, with thinner layers breaking down at lower temperatures. Vacuum annealed freestanding Cu-Nb bi-layer films with individual layer thicknesses ranging from 15 to 75 nm [21] showed films with layer thicknesses larger than 35 nm maintained a layered structure up to 700°C for several hours, with the only deviation from the original structure being triple-joint formation, similar to that seen in Figure 1-3. Conversely, 15 nm layer thickness sample showed layer pinch-off and spheroidization after only half an hour at the same temperature. There was also a significant drop in hardness in the 15 nm films after annealing, whereas 75 nm layers showed a minimal drop in hardness, attributed directly to the change, or lack thereof, in the microstructure of the film.

![Diagram](image)

**Figure 1-3. Schematic showing how triple joints form in annealed bi-layer films with grain boundaries present in both layers.**

Similarly, Economy et. al. annealed Cu-Nb films with 20 nm and 100 nm layer thicknesses in a variety of atmospheres at 400°C for 30 minutes [36]. The 20 nm Cu-Nb samples showed a significant loss of hardness even though other studies have shown thermal resistance above 400°C, whereas the 100 nm sample maintained its structure and hardness. The different atmospheres had a negligible effect on the change in hardness, indicating oxidation is not a major contributing
factor. Since a breakdown of the layered structure generally isn’t seen until higher temperatures, the authors attribute the decrease in hardness to a change in the internal stress of the films, which is supported by x-ray diffraction (XRD) analysis, rather than a breakdown of the layers. Elevated temperature micro-tensile tests of freestanding Cu-Nb films in Ar showed a significant drop in tensile strength and elastic modulus as the testing temperature increased, with a corresponding increase in ductility [40]. The structure of the layers was examined post mortem in both the unstrained shoulder region and near the fracture surface. The unstrained, but annealed, shoulder showed the original layered structure with triple-joint formation (as was seen in previous studies), whereas the deformed region near the fracture surface showed grain elongation in Cu layers, suggesting power-law or diffusion-based creep, along with grain rotation of the Nb layers, suggesting grain boundary sliding. Strain rate tests were also conducted and suggest high temperature deformation occurs as a result of dislocation glide and climb, as was indicated by the calculated hardening exponent.

Elevated temperature testing on coherent interfaces is less common than for incoherent systems like Cu-Nb since they are generally more miscible, like the Cu-Ni system, and readily alloy at elevated temperatures [20], [45]. This completely eliminates the benefit of the layered structure, instead creating a solid solution Cu-Ni alloy. That being said, some elevated temperature studies have been conducted, both experimental and theoretical. Due to the diffusivity asymmetry between Cu and Ni, during the initial stages of annealing a transient interface sharpening along with a shift in position and increase of the composition gradient is likely [45]. Eventually the interfaces begin to broaden and there is complete mixing of the two regions, resulting in a loss of the layered structure and likely a drop in strength. Similarly, Bunshah et. al. conducted elevated temperature tensile testing of Cu-Ni multilayers, deposited at different temperatures and with layer
thicknesses over 100 nm [46]. Significant alloying was seen for samples that were deposited at a substrate temperature of 625°C and for samples annealed above 600°C, though no mechanical testing was conducted on these samples to determine the effect on hardness and yield strength to determine the relative strength drop as a result of alloying. This system also showed a greater retention of strength in the higher layer thickness samples, likely due to the smaller likelihood of complete alloying which would be seen in the thinnest layer samples.

1.4. Testing Techniques

1.4.1. Nanoindentation

Instrumented nanoindentation has become an increasingly popular way to test mechanical properties of thin films due to the ease and breadth of testing ability. Instrumented indentation differs from typical hardness tests in both the fact that the load and depth are measured during the test as well as the fact that the indents are extremely small, thus optical observation of the contact area is difficult so contact area must be calibrated to indentation depth by indenting a standard material, typically fused quartz or polycarbonate, at various depths. Based on contact mechanics equations [47], material hardness and modulus values can be determined from the load-depth curve. The initial portion of the unloading segment is purely elastic, with the slope $S$ representing the stiffness of the material, where $S = dP/dh$, and therefore can be used to calculate the elastic modulus of the material. The stiffness however is indicative of both the elastic response of the material and the machine response, therefore a combination of the material of interest and the tip material yields a reduced modulus, $E_r$, where:
This reduced modulus is a combination of the sample modulus, $E_s$, as well as the indenter tip modulus, $E_i$, and is related through the contact mechanics equation:

$$E_r = \frac{1}{E_i} + \frac{1}{E_s}$$

where $\nu_i$ is the Poison’s ratio of the indenter material and $\nu_s$ is the Poison’s ratio of the sample. Typical nanoindentation probes use a diamond tip, with $E_i=1140$ GPa and $\nu_i=0.07$. The hardness of the material can be calculated by the relationship: $H=P_{\text{max}}/A$, where $P_{\text{max}}$ is the maximum load and $A$ is the contact area.

The projected contact area of the indent is calculated using a standard material (with known modulus) to calibrate a tip area function based on specific depths. Although this allows the mechanical values to be quickly calculated from the indentation depth, it is also problematic if the area function does not accurately depict the actual contact area to depth calibration. A large number of materials exhibit either a sink in or pile up effect during nanoindentation [48] which can change the actual contact area and thus the calculated reduced modulus and hardness of the tested material. A material which exhibits perfectly plastic deformation would deform freely as opposed to elastically deforming underneath the tip, this results in significant pile-up around the indenter, as is depicted by the blue dashed line in Figure 1-4. This results in a much higher contact area than is assumed from the tip area function calibrations, which in turn will depict a larger calculated reduced modulus and, to a greater extent, the hardness values. Similarly, sink-in will have a smaller actual contact area and calculate artificially small values for both the modulus and hardness.
Not only can material modulus and hardness values be determined, but depending on the tip geometry the strain-hardening behavior can also be inferred. Based on the included angle of a conical indenter tip, different local strains are created in the material immediately beneath the contact [49]. Using this approximation, a Berkovich ($\theta=65.35^\circ$) and cube-corner ($\theta=45^\circ$) indenter geometry correspond to an effective strain of approximately 8% and 22%, respectively [50]. Using these effective strains the strain-hardening response of a material can be investigated, where a material that exhibits strain-hardening will have a higher hardness when tested with a cube-corner tip.

Another technique for investigating the strain-hardening response of a material regards the relative pile-up around the indenter. For if a material exhibits significant strain-hardening, it will harden with increasing deformation and thus reduces the amount of pile-up occurring around the indenter. Bower developed a relationship between the amount of pile up and the strain-hardening response of the material [51]:

\[
\frac{h}{a} = \frac{(\kappa - 1)}{\kappa \tan \theta}
\]  

(1-3)

where $h$ is the height of the pile-up region, $a$ is the contact radius, $\theta$ is the included angle of the indenter and $\kappa$ is related to the strain-hardening ability of the material. Figure 1-4 shows a schematic for a material that exhibits pile-up (blue line), sink-in (black dashed line), and neutral deformation (red dashed line). As is annotated in the figure, the pile-up height drastically changes the contact area at the same depth whereas sink-in reduces the contact area. Using a combination of these two techniques, the strain-hardening response of the sample can be inferred, though the specific strain-hardening exponent cannot be absolutely determined due to the complicated stress state that exists under the indenter tip. To determine a value for the strain-hardening response of
the material, a uniaxial condition is required, leading to either micro-pillar or micro-tensile testing techniques.

Figure 1-4. Schematic of pile-up and sink-in effects on the contact radius during indentation. Pile-up (blue line) occurs in materials which readily plastically deform whereas sink-in occurs when the material can elastically account for the material being displaced by the indenter.

Traditionally high temperature testing of materials has been limited to tensile testing of macro-scale samples or static indentation, with elevated temperature instrumented indentation (ETI) only increasing in popularity over the past few years. One of the main complications with ETI is thermal drift [51-53] which occurs as a result of the temperature difference in the sample as well as between the sample and the indenter tip. To overcome the internal temperature difference the sample is typically allowed to come into thermal equilibrium typically for a minimum of one hour, though the thermal gradient from the bottom of the sample contacting the heating stage to the surface still exists. Another option is to heat the tip as well as the sample, which has been shown to reduce the drift to less than 1 nm/s in some cases [53]. Even with the issues surrounding ETI, this technique is quick, easy to use and provides reliable comparisons between samples and different testing conditions even if the strain state is non-linear.
1.4.2. **Micro-pillar Compression**

Micro-pillar compression experiments provide an essentially uniaxial stress state, which allows for more accurate determination of the strain-hardening ability in materials. This technique has been widely used to investigate size effect properties in both bulk materials and thin films as well as deformation mechanisms in multilayer films. The presence of a nearly uniaxial stress state is highly appealing when trying to understand material properties and fundamental relationships. Traditionally, these pillars are fabricated using focused-ion beam (FIB) milling which has two major complications: development of an ion damage layer and a significant tapered geometry. The damage caused by the ion beam can cause the material to show uncharacteristic properties, depending on the material, significantly altering the measured modulus and strength. The taper produced from traditional milling is another concern since the smaller top section of the pillar will start to yield and plastically deform before the bottom section, strictly due to the smaller cross-sectional area. This leads to an artificial strain-hardening effect. However, this effect can be removed to some extent by using a first-order correction assuming elastic-perfectly plastic deformation behavior. This technique has been used previously by Mara et.al. by dividing the tapered pillar into small trapezoid segments which are deformed, one by one until the segment reaches the same diameter as the base diameter [55]. A simple schematic of this process is shown in Figure 1-5.
Figure 1-5. Pre-deformed micro-pillar showing taper of approximately 3.25° resulting from FIB milling (left). Schematic of the assumptions behind taper correction calculations used in data analysis, which assumes elastic-perfectly plastic deformation behavior (right).

The relative load, corrected based on the original diameter of the trapezoid and the displacement difference (Figure 1-6, left) is calculated assuming conservation of volume, with the different variables labeled in Figure 1-5. Since this correction assumes elastic-perfectly plastic behavior, the resulting stress-strain curve will be an over correction for materials that exhibit strain-hardening, so results will be slightly skewed in showing less strain-hardening that is likely occurring in the system. From the first-order approximations of the relative load and displacement correction, a general equation can be curve fit to subtract the artificial hardening effect, which would be strictly due to the geometry of the pillar (Figure 1-6, right).
Figure 1-6. Example of load correction curve fit based on a tapered pillar used in the current investigations.

Not only does this taper produce an artificial hardening effect but it also inherently creates different stress states along the length of one pillar, and allows for a qualitative examination of deformation at different stresses/strains using one test, an example of which will be seen later in Chapter 4. Overall, this technique allows for a more accurate determination of properties such as maximum stress and hardening exponent under compressive loading than the nanoindentation technique and is an important contribution to the current investigation.

1.4.3. Micro-tensile testing

Tensile testing is the most widely used and straightforward way to determine hardening relationships and strength properties in bulk materials because of the uniaxial stress state that occurs in the sample. Typical uniaxial stresses in materials will yield the well-known relationship between stress and strain [56]:

\[ \sigma = K \varepsilon^n \]  

(1-6)
Where $n$ is the strain-hardening exponent of the true stress-strain curves. From these curves the ultimate tensile strength, ductility, toughness, and yield strength of the material can be determined.

Micro-tensile testing of free-standing thin films has several challenges, mostly due to sample preparation and machine alignment. In general, sample preparation is less expensive and time consuming than creating FIB micro-pillars but if any defects are present on the edges of the gage section (common if cutting or grinding is used to create the samples), it can lead to premature failure. For films manufactured by sputter coating or evaporation, a simple metal lift-off technique is enough to create smooth, defect free edges. However, releasing these dog-bone shaped films from the substrate adds an additional challenge, especially for films that have significant residual stresses from deposition. If the films have a large residual tensile stress they can break just after being released from the substrate, so deposition conditions have to be closely monitored. Poor alignment of the machine is also a potential obstacle that can occur in this testing method and can lead to stress concentrations in the filet region and premature failure. However, this can generally be avoided if enough time is taken to properly align the sample. In general, this technique is difficult to perform but the data is much easier to interpret whereas nanoindentation is an easy test to perform with more difficult data analysis.

The main goals of the research are to investigate the nanoscale strengthening mechanisms and their effect on thermal stability of two different types of thin film systems. Chapters 2 through 7 focus on nano-scale metallic multilayer films and the behavior of these films past the initial yield point (strain-hardening ability) and impact of elevated temperature on the structure and properties, both deformation at temperature as well as response after annealing. The microstructural, thermal, and electrical stability of oxide dispersion strengthened Au films was also investigated to examine
the extent at which particles can stabilize the microstructure under mechanical and thermal stresses.
CHAPTER 2: Strain-hardening of Nanoscale Metallic Multilayers

Abstract

Strain-hardening in tri-component nano-scale metallic multilayers (NMMs) was experimentally investigated using nanoindentation and micro-pillar compression testing. Cu/Ni/Nb films were made in tri-layer structures as well as a bi-layer consisting of an alloy of Cu-Ni/Nb. Results from both techniques show strain-hardening increases as the layer thickness decreases in the tri-layer system, with 5 nm layers of Cu/Ni/Nb exhibiting higher strengths and hardening coefficients than 30 nm layers. The experimental evidence is described in light of the confined layer slip model for three metal systems and previously proposed dislocation cross slip mechanisms unique to tri-layer structures.

2.1. Introduction

Computational simulations of tri-layer nano-scale metallic multilayer (NMM) systems, those having a combination of both coherent and incoherent interfaces, have suggested that tri-layer systems that have both types of interfaces will possess significant strain-hardening ability above that of their bi-layer counterparts [25]–[28]. However, previous experimental validation of the strain-hardening behavior [2] has only been carried out at a single tri-layer thickness period. With significant evidence in bi-layer NMMs that layer thickness plays a substantial role in controlling the deformation processes in these exceptionally strong materials [57]–[59], the effect of layer thickness on tri-layer systems needs to be evaluated.

Multiple experimental techniques can be used to investigate a material’s relative strain-hardening ability including tensile, compression, and nanoindentation testing. Two different nanoindentation techniques can be used to compare strain-hardening in a given system. The first
compares the hardness measured using tips with different included angles which create different local strains in the material directly beneath the contact [49]. The Berkovich and cube-corner indenter geometries, corresponding to equivalent cone angles of 70.3° and 42.3°, result in effective strains of approximately 8% and 22% [29], respectively. A material that exhibits strain-hardening between 8% and 22% strain will show larger hardness values with the cube-corner tip, whereas an elastic-perfectly plastic material should have the same hardness values regardless of indenter geometry. The second technique inspects the pile-up formation from the nanoindentation experiments. Typically, a material that is highly ductile will develop a pile-up around the indentation as a result of the constraint of a stiffer substrate [60]. When a strain-hardening material is deformed, the material continues to harden during indentation and thus reduces the amount of pile-up; the pile up to contact ratio can be related to the strain-hardening coefficient in some cases, where more pile up suggests a lower strain-hardening coefficient [51]. Using a combination of these two techniques, the strain-hardening response of the sample can be inferred, though the specific strain-hardening exponent cannot be absolutely determined due to the complicated stress state that exists under the indenter tip.

Micro-pillar compression testing provides an essentially uniaxial stress state which allows for more accurate determination of the strain-hardening coefficient of these NMMs. The limitation of the comparative hardening coefficients from examining indentations is that for most commercially available self-similar indenters the low strain behavior is unavailable. Micro-pillar compression tests can access the strain regime from initial yield to the 8% value probed by a Berkovich tip. Traditionally, these pillars are fabricated using focused-ion beam (FIB) milling which has the tendency to create pillars with a slight taper. As the tapered pillar begins to deform, the smaller diameter top section deforms before the thicker bottom section leading to an artificial
strain-hardening effect. This artificial hardening can be removed by a first-order correction factor used by Mara et.al. [55], in which the tapered pillar is divided into small trapezoid segments which are deformed assuming elastic-perfectly plastic behavior until all pillars have the same diameter. This assumption would cause an over correction for strain-hardening materials, resulting in corrected stress-strain curves which will exhibit less strain-hardening that is likely occurring in the system. A limitation of micro-pillar compression testing is that shear often is initiated at the edge of the punch/pillar contact, leading to the inability to generated uniaxial stress strain conditions past 10% in many materials. Therefore, the combination of indentation and compression testing will allow a more complete study of strain-hardening in these novel multi-component multilayers.

2.2. Sample Preparation and Experimental Procedure

Tri-component films consisting of Cu, Ni, and Nb are the basis of this study. First, Cu/Ni/Nb NMM films used in this study were deposited using magnetron sputtering on (100) oriented Si, starting with the Nb layer and ending with the Cu layer, to a total thickness of 3 μm with equal individual layer thicknesses of 5 and 30 nm. A second set of samples was fabricated to investigate any possible interdiffusion or intermixing at the Cu/Ni interface; these samples began with a 5 or 30 nm Nb layer and then used co-deposition sputtering to create a 10 or 20 nm thick FCC alloy layer. The alloy system was deposited to a total thickness of 1.5 μm, the repeating period of layers was constant between the alloy and tri-layer system. These structures will be referred to as Cu/Ni/Nb for the FCC/FCC/BCC tri-layer and Cu-Ni/Nb for the FCC alloy/BCC bi-layer.

Micro-pillars with diameters of 1 μm with aspect ratios of 1:3 were fabricated using a Ga ion beam at an accelerating voltage of 30 keV in Tescan Vela FIB instrument. Initially, high currents of 4 nA were used to mill rough pillar shapes with exact dimensions achieved after low
current polishing to help minimize irradiation damage with lower currents ranging from 1 nA to 100 pA. The micro-pillars were imaged using a Hitachi S4800 high-resolution scanning electron microscope (HRSEM) to determine the taper due to FIB milling. These particular milling conditions resulted in a taper angle of 3.25°, the effects of which were subtracted from initial load-displacement curves using the technique previously described.

Nanoindentation was conducted using a Hysitron UBI indenter on the films to indentation depths less than 10% of the total film thickness to ensure substrate effects were minimized. Hardness values were determined from similar contact areas to reduce differences due to indentation size effects and no less than 20 indents were obtained to ensure statistical reliability. To gain an accurate measurement of the strain-hardening exponent at lower strains micro-pillar compression tests were conducted in a Zeiss DSM 962 SEM with a modified Alemnis \textit{in situ} indenter first developed by Rabe et al. [61], modified and improved by Wheeler and Michler [62], using displacement control loading and conducted at strain rates of approximately 1e-3/s.

2.3. Strain-hardening Behavior From Nanoindentation

Figure 2-1 shows the nanoindentation results obtained from the two different tips on all four multilayers. The substantial increase in hardness for the 5 nm sample indicates a significant strain-hardening ability in the tri-layer, with little strain-hardening present in the bi-layer alloy. The 30 nm sample shows a small increase in hardness for both the tri-layer and alloy film, which indicates some strain-hardening has occurred but is significantly less than the 5 nm sample.
Figure 2-1. Hardness measurements from nanoindentation experiments conducted using a Berkovich tip (effective strain 8%) and cube-corner tip (effective strain 22%), approximating the hardening response of multilayer films with mixed interfaces (tri-layer) and incoherent interfaces (alloy).

After indentation, scanning probe microscopy images of indentations made from the cube-corner tip were collected and pile-up height and contact radius were measured (Figure 2-2). There was no statistically significant difference between the calculated pile up to contact radius values; all ranged from 0.138 to 0.194, but the standard deviation was on the order of 0.08 for all samples. Since previous studies have shown residual stresses in thin films can have an effect on the amount of pile-up occurring during indentation [63], [64], the results of these pile-up measurements may
indicate that a difference in residual stresses as a result of the deposition conditions lead to the inconclusive results using the pile-up assessment.

Figure 2-2. (a) Characteristic SPM image of cube-corner indent showing significant pile-up around the edges of the tip for both 5 nm films (top) and 30 nm films (bottom). (b) Line scan across pile-up and through bottom of indents for both layer thicknesses, showing indistinguishable difference from the different layer thicknesses.

2.4. Determination of Hardening Exponent From Micro-pillar Compression Tests

The taper corrections previously described were applied to the load-depth curves and resulted in the true stress-true strain curves shown in Figure 2-3. In this case, the substrate stiffness is sufficiently higher than the tri-layer films, so the effect of pillar sink-in into the substrate compliance was found to be negligible [65]. The beginning of each curve is slightly non-linear due to rounding of the top of the pillar from FIB milling, therefore, the curves were offset so that the extrapolated elastic portion crosses the origin. Additionally, a line corresponding to 8% strain (analogous to the strain produced during nanoindentation with a Berkovich tip) is added to act as a guide for comparisons made to nanoindentation experiments.
Figure 2-3. Example of stress-strain curves from micro-pillar compression testing of mixed interface (left) and incoherent interface (right) films.

Uniaxial strain-hardening behavior follows the well-known Holloman relationship between stress and strain [56]:

\[ \sigma_{S-H} = K \varepsilon^n \]  \hspace{1cm} (2-1)

where \( n \) is the strain-hardening coefficient and \( K \) is the strength index. By curve fitting the portion of the stress-strain curves after yielding up to the maximum stress (\( \sigma_{\text{max}} \)), the strain-hardening coefficient can be determined. The portion of each curve used in curve fitting is emphasized in red diamonds and overlaid over the stress-strain curve with the curve fits shown as dashed lines. All curve fits have R-values of at least 0.95, suggesting these are reasonable fits describing the strain-hardening relationship of the films. A summary of the mechanical properties from micro-pillar compression tests is listed in Table 2-1.
Table 2-1. Strength summary for tri-layer and alloy films tested using micro-pillar compression and nanoindentation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micro-pillar Compression</th>
<th>Nanoindentation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>True Yield Strength (GPa)</td>
<td>σ_{max} (GPa)</td>
</tr>
<tr>
<td>5 nm Tri-layer</td>
<td>1.48</td>
<td>2.167</td>
</tr>
<tr>
<td>P1</td>
<td>1.565</td>
<td>2.315</td>
</tr>
<tr>
<td>P2*</td>
<td>1.444</td>
<td>1.849</td>
</tr>
<tr>
<td>30 nm Tri-layer</td>
<td>1.183</td>
<td>1.534</td>
</tr>
<tr>
<td>P1</td>
<td>1.64</td>
<td>2.60</td>
</tr>
<tr>
<td>P2*</td>
<td>1.82</td>
<td>2.24</td>
</tr>
<tr>
<td>5 nm Alloy</td>
<td>1.32</td>
<td>1.75</td>
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<tr>
<td>P1</td>
<td>1.36</td>
<td>1.68</td>
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<tr>
<td>P2*</td>
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<tr>
<td>30 nm Alloy</td>
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<td>P1</td>
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<tr>
<td>P2*</td>
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</table>

SEM images of the pillars before and after testing, shown in Figure 2-4, show an obvious shear band in the deformed 5 nm layers whereas the 30 nm layers show much more gradual yielding with no global shear. The \( \sigma_{\text{max}} \) of the two different films follows the expected strength trend with the 5 nm films showing higher strengths than the 30 nm films [25]. The yield strength of the films are more similar between samples, with the average strength of the 5 nm tri-layers only slightly higher than the 30 nm layers. Since the initial yield of the composite signifies the strength required to initiate dislocation motion in the softest layer (Cu in this material system), and thus is an inherent material property, it is not surprising that the yield strength is not as strongly affected by the layered structure. This was also seen by Abdolrahim et. al. [66]. The strain-hardening curve fits indicate the strain-hardening coefficient of the 5 nm films to be twice that of the 30 nm films before full plasticity occurs.
Figure 2-4. Post mortem pillars of mixed interface tri-layer films (left) and incoherent interface alloy films (right) showing difference in deformation as a result of interface type and layer thickness.
2.5. Discussion

The stress-strain curves in Figure 2-3 indicate that by 8% strain, the 30 nm tri-layer film has reached the flow stress while the 5 nm tri-layer film continues to harden until the pillar shears at approximately 11% strain. This explains why the 30 nm film does not show a significant increase in hardness when indented using Berkovich and cube-corner tip geometries. Likewise, the 5 nm film continues to harden up until the pillar shears at 11% strain, this hardening is reflected in the nanoindentation results. Comparing the strength of the micro-pillars at 8% strain to Berkovich tip indentation results show that the nanoindentation hardness values are slightly lower, but similar to, the strength determined from the stress-strain curve.

Strain-hardening in multilayers has been shown to be a result of increased dislocation content that is deposited along the interface as dislocations propagate through an individual layer [21]. These deposited dislocations act as barriers to further deformation and also can act as nucleation sources for more dislocations, leading to an increase in the dislocation density of the films. Furthermore, a previous study conducted by Abdolrahim et al. indicates decreasing layer thickness results in an increase in the number of interfacial interactions and dislocation nucleation sites [66], which would increase the strain-hardening rate as the dislocations interact with one another and delay further deformation. For this specific tri-layer system, deformation is driven by “super threader” dislocations that have penetrated the coherent interface and propagate through the Cu and Ni layers [30]. Due to the different moduli of the two FCC materials, a coherency stress is created at the boundary that causes the threading dislocation to lag at this interface. Additionally, the portions of the dislocation in each of the two layers propagate at different speeds as a result of the different moduli. This causes instability in the dislocation at the coherent boundary. The BCC layer adds additional strength to the system as a whole, which provides enough internal shear stress
to allow for cross slip of the super threader at the coherent interface. This in turn can act as dislocation pinning sites or a dislocation source, both of which lead to strain-hardening in this tri-layer NMM. The defects produced from cross-slip debris have a minimum stable size and so will act as a larger relative barrier to dislocation motion in thinner layers, since there is less room to allow for dislocation bowing around the defect. Additionally, as the layer thickness decreases, the interface density increases alloying this mechanism to occur more often in the same volume. Thereby, in a tri-layer system when the individual layer thickness is reduced there are more dislocation interactions and an increased strain-hardening ability.

There are few published studies of the strain-hardening behavior of multilayer films. One recent study by Lei and co-workers [67] describes the Cu/Zr system strain-hardening behavior as a function of layer thickness using micropillar compression, and has determined that thinner layers lead to lower strain-hardening in this bi-layer system. They posit that the decreased strain-hardening in thinner layers is a result of the balance between interfaces acting as sources and sinks for dislocations in layer thicknesses in the 5-100 nm regime. In our current study, the bi-layer alloy multilayer appears to show less ability to strain harden than the tri-layer films. Therefore, the dislocation dynamics simulations of a tri-layer film, which indicate that the elastic mismatch in the FCC layers will lead to more cross slip and more dislocation content and storage over a bi-layer system, are supported by the current experimental study.

2.6. Conclusions

In summary, complementary experimental measurement techniques have that tri-layer NMM films with smaller layer thicknesses show a greater strain-hardening ability and a greater hardness than those with larger layer thicknesses. The tri-layer structure adds a unique capability
that is not observed in the more conventional bi-layer multilayers. The experimental data presented here supports the hypothesis that a unique structure of FCC layers with differing elastic modulus values provides a cross slip and subsequent dislocation storage mechanism not possible in bi-layer structures.

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CHAPTER 3 : Elevated Temperature Dependence of Hardness in Tri-Metallic Nano-Scale Metallic Multilayer Systems

Abstract

A tri-layer nano-scale metallic multilayer (Cu/Ni/Nb) system with a mixture of incoherent and coherent interfaces was investigated to determine the effect of elevated temperature conditions on the strength at temperature and after annealing. Elevated temperature nanoindentation showed a reduction in temperature sensitivity of hardness as individual layer thickness decreases (i.e. thinner layers retain strength better at elevated temperatures). This is explained using the confined layer slip model that suggests the drop in stress is due to both changes in the shear modulus of the film as well as dislocation/interface interactions. Molecular dynamic simulations of Cu/Nb bi-layers are presented in support of the concept that dislocation interactions at incoherent interfaces are less temperature sensitive than dislocation-dislocation interactions within the layers, supporting the experimental results.

3.1. Introduction

Nano-scale metallic multilayers (NMM) exhibit exceptional mechanical properties and a resistance to harsh environments due to the nature of their interfaces, with strengths far exceeding those of the corresponding bulk constituents [19]. The strengthening mechanism of multilayers is dependent on the interface morphology, which can be separated into two categories: coherent and incoherent. Coherent interfaces are constructed of layers with similar crystallographic structures (i.e. Cu/Ni), which grow epitaxially to create continuous slip systems. The increased strength of this interface is derived from the elastic modulus mismatch (resulting in image forces across the
interface [68]) and lattice spacing mismatch (resulting in coherency stresses [69]), both of which make slip transmission more difficult. Slip systems are continuous and therefore allow dislocation transmission across the interface, leading to reasonable ductility in addition to increased strength. Conversely, incoherent interfaces consist of layers with different crystallographic structures (i.e. Cu/Nb), with no continuous slip plane and thus are strong barriers to slip transmission [70]. Tri-layer NMM systems, having a combination of coherent and incoherent interfaces, have been shown, through both experimental tests and molecular-dynamics (MD) simulations, to possess properties of both types of interfaces [26]–[28]. This produces a material with high strength and ductility, as well as increased strain-hardening over the bi-layer systems (Cu/Ni and Cu/Nb).

Unless NMMs are thermally stable and maintain their layered structure in elevated temperature operating conditions, they will only be used at near ambient temperature conditions, limiting their ability to be used as hard coatings for technical applications. There have been studies conducted on the thermal stability of NMMs, mostly focusing on incoherent interfaces [31]–[42]. When compared to thin film materials without a layered structure, NMMs have shown reduced temperature sensitivity, retaining hardness as temperatures increase. An elevated temperature nanoindentation study on thin film Cu [43] showed a 60% reduction in hardness as the temperature increases by 100°C, coupled with a pronounced drop in modulus. Other Cu/Nb multilayer studies conducted at elevated temperatures only showed a 40% drop in yield strength after a 200°C temperature increase [40]. This suggests the addition of a layered structure decreases the temperature sensitivity of thin film systems. However, since the layered structure is a metastable state, once enough energy is introduced into the system, the layers will rearrange to minimize the total energy, either by interfacial mixing and alloying [45], spherodization [21] or layer breakdown due to triple joint formation [44].
Several detailed studies have been conducted on the thermal stability of Cu/Nb bi-layers [21], [26], [36], [57], [70]–[72], examining both mechanical and structural changes for different interface structures. The Cu/Nb system shows remarkable resistance to thermal degradation, maintaining the layered structure to temperatures over 900K, however this is dependent on layer thickness with thinner layers breaking down at lower temperatures [21]. This change in microstructure corresponded to a hardness drop in thinner layer systems due to the degradation of the layered structure, which shows that thinner layered films are more sensitive to mechanical degradation at high temperatures as a result of the structural change, but does not probe the strength at temperature. Other annealing studies conducted in different atmospheres showed little to no oxidation in the system, but did see a significant hardness drop after annealing at temperatures less than 900K [36]. The authors contribute this decrease in strength to a change in the internal stress of the films as a result of annealing. Elevated temperature micro-tensile tests of freestanding Cu/Nb films showed a significant drop in tensile strength and elastic modulus coupled with an increase in ductility as the testing temperature increased [40]. Post-mortem microscopy showed triple-joint formation in the unstrained portions, whereas the deformed region showed grain elongation in Cu layers, suggesting diffusional or power-law creep, and grain rotation of the Nb layers, suggesting grain boundary sliding. Elevated temperature nanoindentation on Cu/Nb multilayers fabricated using two different techniques (physical vapor deposition (PVD) and accumulative roll bonding (ARB)) showed a critical layer thickness that results in optimal thermal stability [73], with sputtered films having a critical thickness of 5 nm while ARB had a thickness of 18 nm.

Elevated temperature testing of coherent interfaces (Cu/Ni) is less common than for incoherent systems since they are often miscible and can readily alloy at elevated temperatures [20], [45], [46]. If this were to occur, it would eliminate the strengthening benefit of the layered
structure. Previous studies of Cu/Ni bi-layers annealed and deposited at high temperatures showed significant alloying when the deposition temperature exceeded 625°C and for samples annealed above 600°C, but did not determine the alloying effect on hardness and yield strength [20]. For layer thicknesses above 100 nm, elevated temperature tensile testing shows that thinner layers have a larger drop in yield strength than for thicker layers [46].

To this date, no studies have been conducted on the thermal stability and performance at temperature of a mixed interface system at elevated temperature, which is the principle interest of this investigation, specifically focusing on the Cu/Ni/Nb tri-layer system.

3.2. Experimental Details

The films in this study were synthesized using magnetron sputtering on (100) oriented Si with a silicon dioxide barrier layer, starting with the Nb layer and ended with the Cu layer to a total thickness of 2 μm with equal layer thicknesses, 5, 10 or 30 nm. These films were tested using the Hysitron TI950 equipped with a 400°C xSol temperature control stage which has a heating element architecture that consists of both top and bottom heated plates creating a thermal chamber, allowing for passive tip heating to create an isothermal tip-sample contact and reducing thermal drift of the system (generally less than ±0.8 nm/s). Elevated temperature nanoindentation was then conducted with a Berkovich diamond tip at four temperatures: 298K, 400K, 500K, and 600K, tested from highest to lowest to limit the influence of possible changes in microstructure due to annealing. For each sample, the tip was brought into contact with the sample for one hour and remained in contact throughout the test to maintain thermal equilibrium between the sample and the tip, reducing thermal drift. The films were indented using a load controlled partial unload technique to a maximum load of 5000 μN. After performing at least 10 indentations at each
temperature, the temperature was lowered and the process repeated for each testing temperature until the sample was again at room temperature. Hardness values reported here are from similar indentation depths (about 100 nm), deep enough to eliminate roughness effects and less than 10% of the thickness of the films to minimize substrate effects [47]. The reduced modulus for all three films is consistent and independent of indentation temperature, around 160 ± 10 GPa.

Molecular dynamics (MD) simulations were conducted on Cu/Nb bi-layers with layer thicknesses of 5 and 14 nm and two different temperatures (1K and 300K) in uniaxial tension at a strain rate of 3e8 s⁻¹ using LAMMPS with potentials based on the embedded atom method. The structure created is based on the Kurdjumov–Sachs (KS1) [74] crystallographic orientation such that (111)₁₁₁[_(110)ₙₙ] and <110>₃₃₃₁₁₁ with periodic boundary conditions on all directions to simulate the configuration of the multilayers in bulk. The layer thickness of each element was varied between 1 and 14 nm (total bi-layer thickness between 2 and 28 nm) with lateral dimensions of 49.6×9.7 nm in x and z directions. Additional MD simulations were conducted at 300K and 500K with Cu/Nb bi-layers under uniaxial tension with layer thicknesses between 5 nm and 20 nm. Simulations were conducted using a strain rate of 3e8 s⁻¹ on a bi-layer of Cu/Nb with lateral dimensions of 42 nm in the x and z directions. Before loading, the structure is brought to minimal energy followed by dynamics relaxation for 50 ps at the desired temperature and 0 bar pressure, using an NPT ensemble. The boundary conditions had 2D periodicity along x and z directions, with free surfaces in the y direction.

3.3. Results and Discussion

3.3.1. Elevated Temperature Nanoindentation
A typical experimental load-depth curve for indentations into the 30 nm thick layered system is shown in Figure 3-1 at two different indentation temperatures (298K and 600K) exhibiting an obvious decrease in hardness at elevated temperatures. The inset highlights the increased creep seen at 600K which could be a result of power-law or diffusion-based creep, as was seen in a uniaxial tensile study on Cu/Nb bi-layers [36], though is not the focus of this study. As was seen in prior bi-layer studies [21], [36], [40], [42], [44], the hardness of all three tri-layer films decreases as the temperature increases (Figure 3-1b). However, by comparing the relative drop in hardness, it is clear that thinner layers are more resistant to mechanical degradation than thicker layers. Across a 300K temperature range, the hardness of the 30 nm sample drops 35% while the 5 nm sample only drops 15%. Since this system includes two sets of miscible systems (Cu-Ni and Ni-Nb) and may have some interface broadening, CuNi alloying and the formation of NbNi precipitates can occur. This has the potential to either weaken the system through layer degradation, or possibly add additional strengthening from dislocation interactions with the new solid solution layer or precipitates and will be the focus of future investigations.
Figure 3-1. (a) Typical load-depth curves at two different temperatures 298K (solid) and 600K (dashed) in 30 nm Cu/Ni/Nb tri-layers. As can be seen from the inset, creep increases at 600K, possibly due to power-law or diffusional-based creep. (b) Summary of elevated temperature indentation for the three different layer thicknesses at four different temperatures. The room temperature data reported here is from the after annealed condition.

Since the layer thicknesses investigated here are in the confined layer slip (CLS) regime [21], and the temperature range is low enough to suspect there is not significant degradation in the layered structure, the same dislocation mechanisms should be active. The CLS model suggests the yield or flow strength is

$$\sigma_{cls} = \frac{M \mu b}{8\pi h'} \left( \frac{4-v}{1-v} \right) \left[ \ln \left( \frac{\alpha h'}{b} \right) \right] - \frac{f}{h'} + \frac{C}{\lambda}$$

(3-1)

where $C=\mu b(1-v)$, $h'$ is the layer thickness measured parallel to the glide plane, $\alpha$ represents the core cut off parameter where low (high) values represent a wide (compact) dislocation core, $v$ is
the Poisson ratio, $\mu$ is the shear modulus, $b$ is the length of the Burgers vector, $f$ is the interface stress arising from elastic deformation, $M$ is the Taylor factor, and $\lambda$ is the spacing between misfit dislocations deposited from gliding loops.

Since we assume the difference in temperature sensitivity for different layer thicknesses is not a result of a different mechanism, there must be a balance of increased dislocation mobility, possible activation of additional slip planes, and maintained strength from decreasing layer thickness (CLS model). There are three significant contributions to strength in the CLS model: (1) the stress required for Orowan bowing confined in between two interfaces, (2) the interfacial stress from elastic lattice mismatch, and (3) stresses arising from dislocation/dislocation interactions. Both the first and third terms are linearly dependent on the shear modulus of the films. Since this material property is temperature dependent, both of these sections would drop as shear modulus ($\mu$) drops at elevated temperatures. According to the study conducted by Nadal and Le Poac, the shear modulus of Cu should drop by 20% from room temperature when testing at a temperature of 600K [75], causing (1) and (3) to decrease by an equivalent amount. If the reduction in strength is only due to the reduced shear modulus, there would be no differences in reduction for the different layer thicknesses. As was stated earlier, the 5 nm layer thickness drops by only 15% whereas the 30 nm sample drops 35%, suggesting that the reduced shear modulus is not the only effect on the change in hardness. The interfacial stress is a function of the materials that comprise the interface, in this study it is assumed that these are not changing, therefore (2) is likely temperature independent. The third term is dependent on stresses arising from arrays of dislocation/dislocation interactions, of which the morphology should be controlled by the layer thickness and is the focus of the MD simulation study.
When the as-deposited (prior to annealing) hardness was compared to the hardness after annealing, it was found that all samples exhibited no measurable decrease in hardness or, in some cases, an increase in hardness. This is in marked contrast to the results of Economy and co-workers where annealing at moderate temperatures caused a decrease in strength with no significant change in microstructure. Figure 3-2 shows an XRD scan for the 10 nm and 30 nm samples after elevated temperature indentation. There are three distinct peaks for Cu, Ni and Nb for all annealing conditions inferring there is minimal alloying of the Cu and Ni layers and no significant formation of NbNi intermetallics (or extremely small precipitates which are difficult to detect using XRD). Admittedly, the Cu-Ni alloy (111) diffraction peak falls in the middle of the Cu (111) and Ni (111) and a small amount of alloying would be difficult to discern; however, there are still two distinct peaks suggesting that even if the layers have started alloying, they are not fully alloyed and a significant amount of the layered structure remains. Furthermore, each layer remains highly textured with the preferred orientation typical from magnetron sputtering (100) for BCC systems and (111) for FCC systems, likely following the KS structure. The extent of alloying and precipitate formation will be the focus of future investigations.
Figure 3-2. X-Ray diffraction scan of 10 nm and 30 nm post annealed films. The Cu, Ni, and Nb elemental peak positions are shown and corresponding peaks in the tested film are labeled. For both films, distinct Cu and Ni peaks are still seen after annealing, indicating there is still some layered structure remaining.

3.3.1. Molecular Dynamics Simulations

Results from the Cu/Nb bilayer MD simulations at 1K and 300K are shown in Figure 3-3. Representative stress-strain curves at 1K (Figure 3-3a) show two distinct yield points. The first yield point corresponds to the nucleation of dislocations in the FCC layer while the second yield point relates to the nucleation of dislocations in the BCC layer. The first yield point is constant with increasing thickness, which is not surprising since this corresponds to the nucleation of the first dislocation from a defect free structure that is purely dependent on material properties. The second yield point, however, shows the yield values increasing with decreasing layer thickness up to a critical thickness of 4 nm [31]. The trends are similar at 300K up to a critical thickness of 5 nm, indicating similar deformation mechanisms at both temperatures. In smaller layer thicknesses, more dislocations are nucleated at the interface from the increased interface density, causing more
individual slip systems to activate and resulting in increased dislocation-dislocation interactions. This makes it harder to shear the interface, delaying dislocation nucleation in the Nb layer and increasing the hardness. This trend is seen for both temperatures, showing there is no change in deformation mechanism in this temperature regime. Since the second yield strengths correspond to dislocation nucleation in the Nb layer, and nucleation of dislocations is temperature sensitive phenomena [66], higher temperatures lead to a decrease in nucleation stresses in all layer thickness ranges, resulting in overall lower yield stresses at 300K.

![Figure 3-3. Results from MD simulation of Cu/Nb bi-layer film in uniaxial tensile deformation at two different temperatures, 1K and 300K. (a) Stress-strain curves of the films at 1K show the response of the system at different layer thicknesses, 5 nm, 10 nm, and 14 nm. Two distinct yield points are highlighted in the figure, with only the second yield showing any thickness dependence. (b) Summary of simulation results indicating the effect of temperature on the second yield point as a function of layer thickness for thicknesses ranging from 1 nm to 14 nm. Details of this simulation can be found in [66].](image)

Another interesting phenomenon that is apparent from these results is the temperature sensitivity as a result of different layer thicknesses. As the individual layer thickness decreases
from 14 to 5 nm, the relative drop in hardness also decreases from 26% to about 15% (highlighted in Figure 3-3b), the same trend as was seen in the nanoindentation results described in Section 3.1. At larger layer thicknesses, fewer slip systems are activated (Figure 3-4) and dislocations can propagate easily on the activated slip systems confined in the FCC layer with fewer interactions. As the dislocations shear the interface, dislocation nucleation in the Nb layer is easier, leading to the decreased yield strength for thicker layers. Increasing the temperature to 300K activates additional slip planes, increasing shearing of the interface and leading to large drops in strength values. Due to limited thickness in the smaller layers, there is less room for dislocation glides leading to more dislocation interactions and less shearing at the interface is observed. Since increasing the temperature does not affect the sheared regions at the interface, the nucleation stress of thinner layers is less sensitive to temperature.

Figure 3-4. Snapshots of Cu layer deformation as a result of MD simulations at 1K for the 4 nm (a) and 10 nm (b) layer thicknesses. Blue arrows indicate intersections of dislocations which result in increased hardening. Deformation in the structure with smaller layer thickness leads to more dislocation interactions within the film. Atoms are colored according to the centro-symmetry parameter [76] See reference [66] for greater detail.
MD simulations conducted at 300K and 500K show additional slip planes being activated at larger layer thicknesses and the highest temperature. Figure 3-5 shows snapshots from the two different layer thicknesses (5 nm and 20 nm) at the two different temperatures with atoms colored according to the centro-symmetry parameter [76]. The 5 nm layer thickness shows similar dislocation mechanisms at both temperatures, with no change in the active slip systems and similar dislocation nucleation in the Nb layer. However, the 20 nm sample shows an additional active slip system at 500K leading to intersections of dislocations at the interface. Dislocation nucleation in the Nb layer initiates at this intersection (Figure 3-5d) leading to an overall decrease in the yield strength of the multilayer. This also could be a possible explanation for the higher temperature sensitivity of the larger layer thicknesses.

Figure 3-5. MD simulations of 5 nm layer thicknesses at 300K (a) and 500K (b) and 20 nm layer thickness at 300K (c) and 500K (d) show the activation of additional slip planes at larger layer thicknesses and higher temperatures (d). The interaction of both slip planes at the interface allows for easier dislocation nucleation in the Nb layer. Atoms are colored according to the centro-symmetry parameter [76].
Using both elevated temperature nanoindentation as well as MD simulations, it has been shown that the strength of multilayers is less temperature sensitive as the layer thickness decreases in the thickness and temperature range investigated here. A summary of nanoindentation and MD simulations as normalized strength versus change in temperature (Figure 3-6) shows excellent agreement at $\Delta T = 300^\circ C$ with the normalized strength from simulations of the 5 nm layers overlapping exactly with the results from nanoindentation.

![Figure 3-6. Summary of elevated temperature results showing excellent agreement between nanoindentation and simulation results. Normalized hardness for both experimental and simulation results shows a smaller relative drop in hardness as the layer thickness decreases when tested at 600K.](image)

### 3.4. Conclusions

The mechanical response of tri-layer NMMs has been measured at elevated temperatures using nanoindentation and compared to MD simulations of Cu/Nb bi-layers. Both results show decreasing temperature sensitivity as the layer thickness decreases for multilayer films within the
range in which strength is dominated by the confined layer slip model. Since these layer thicknesses are all in the range in which the CLS model describes the deformation mechanism, it appears that the change in temperature sensitivity is not a result of a different dislocation process but rather the interaction of dislocations with the interface. Simulations conducted at 500K further show that at larger layer thicknesses additional slip planes are activated, leading to the decreased strength observed in both the simulation and experimental results. Post annealing indentation shows that the tri-layer system is resistant to significant degradation in strength when annealed to 600K for 4 hours. Additional evidence of strengthening after annealing suggests the possibility of local interfacial changes, either from small amounts of Cu/Ni intermixing at the interface or the addition of very small NbNi precipitates at the Nb/Ni interface, both of which could enhance strength in these systems.

3.5. Acknowledgements

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CHAPTER 4: Elevated Temperature Response of Mixed and Incoherent Interface Systems

Abstract

Nano-scale metallic multilayers exhibit superior mechanical properties and a resistance to harsh environments due to the nature of their interfaces. Incoherent interfaces are generally stronger, acting as barriers to slip transmission, and are dislocation and radiation-induced defect sinks. Coherent interfaces, however, show more ductility from the continuous slip system across the boundary but tend to be less resistant to thermal degradation due to the similarity of their crystal structures. A Cu/Ni/Nb tri-layer system, having a mixture of incoherent and coherent interfaces, shows decreasing temperature sensitivity as individual layer thicknesses decrease. To determine if this was a result of Cu-Ni alloying, a bi-layer system of CuNi/Nb was tested to simulate fully alloying of the Cu and Ni layers. Results showed a similar layer thickness dependence on elevated temperature strength. Additionally, annealing of both systems shows an increase in room temperature strength, which has not been seen in other multilayer systems. By choosing the layer thickness and material selection of the multilayer films, mechanical properties can be specifically tailored.

4.1. Introduction

Investigating the thermal stability of nanoscale metallic multilayers (NMM) is vital for understanding their response in practical applications. The layered structure, which is crucial to the strengthening benefit of these materials, is also a metastable state due to the high energy of the interfaces. Therefore, thermal energy introduced into the system will allow the layers to rearrange in a way that minimizes the total energy, either by spherodization [21], alloying [45], triple-joint...
formation [33], [44], or complete layer degradation [36], [42], all of which would result in reduced strength. Numerous studies have been conducted specifically on the annealing behavior of multilayer consisting of both incoherent [31]–[42] and coherent interface structures. The Cu/Nb multilayer system has been the focus of numerous studies over the past decade, examining deformation mechanisms at room temperature and elevated temperatures as well as annealing effects on microstructure. Generally, this system can withstand temperatures upwards of 800°C with minimal effect on microstructure and maintains the majority of its strength; however, has been shown to be highly dependent on the individual layer thickness. Films with thinner individual layer thicknesses cannot withstand the more extreme temperatures and result in a breakdown of the layered structure while thicker individual layers can retain the basic layered structure but form triple-joints at grain boundary and interface junctions [21], [33], [36]. A recent elevated temperature nanoindentation study show the existence of a critical layer thickness for optional thermal stability which is also dependent on the interface morphology [73]. Limited elevated temperature testing of coherent interfaces has occurred because they are more often miscible, alloying and eliminating the strengthening benefit of the layered structure [20], [45], [46]. Previous studies conducted on Cu/Ni multilayers showed significant alloying when annealed above 600°C, though the resulting effect on strength was not investigated [20]. For layer thicknesses above 100 nm, elevated temperature tensile testing have shown that thinner layers have a larger drop in yield strength than for thicker layers [46], in contrast to the increasing resistance to the strength at temperature at small layer thicknesses as has been seen in other studies [73], [77].

A limited number of studies have been conducted on multilayers that are constructed with mixed interfaces [26], [28], [30], [77], [78], including simulation studies as well as room temperature and elevated temperature nanoindentation. Results have shown that this tri-layer
system has unique characteristics as a result of the combined incoherent and coherent interfaces which allow cross-slip to occur, resulting in additional obstacles to dislocation propagation. Elevated temperature nanoindentation of Cu/Ni/Nb films with individual layer thicknesses of 5, 10, and 30 nm layers showed a smaller relative drop in strength at elevated temperatures as the layer thickness decreased. This result is attributed to the fact that the temperature sensitive portions of the deformation mechanism model are not the major contributing factors to the strength, leaving the majority of the strengthening benefits still intact. The results also show the room temperature hardness of both films increases after annealing, a phenomenon not seen in other multilayer films. Since this system is comprised of Cu, Ni, and Nb alternating layers, the potential for alloying and precipitate formation is likely. To determine the effect full annealing of the Cu/Ni layers has on the elevated temperature response of the material, both Cu/Ni/Nb tri-layers as well as Cu-Ni (alloy)/Nb bi-layers were studied using the micro-pillar compression technique at temperatures up to 325°C.

Elevated temperature micro-pillar compression of multilayers is a relatively untouched field of research. However this technique allows for investigation of deformation mechanisms of multilayers at elevated temperatures in a relatively uniaxial stress state, as opposed to the complicated stress states that occur in nanoindentation. Additionally, a more complete picture of the deformation mechanisms that take place in the multilayer films is presented from both the stress-strain curve as well as examination of the deformed pillars after testing.
4.2. Experimental Details

Films used in this study were deposited using magnetron sputtering on (100) oriented Si starting with the Nb layer. Tri-layer films had equal individual layer thicknesses of 5 and 30 nm while the alloy Cu-Ni in the bi-layer films was twice the thickness of the Nb layer in an attempt to simulate the complete alloying condition for the tri-layers. Micro-pillars with aspect ratios of 1:3 were fabricated using a Ga ion beam at an accelerating voltage of 30 keV in Tescan Vela FIB instrument. Initially, high currents of 4 nA were used to mill rough pillar shapes followed by low current (ranging from 1 nA to 100 pA) polishing to help minimize irradiation damage. The micro-pillars were imaged using a Hitachi S4800 high-resolution scanning electron microscope (HRSEM) to determine the taper (3.25°) due to FIB processing. The artificial hardening effect resulting from the pillar taper was subtracted from initial load-displacement curves using the technique previously described by Mara et. al. [55]. This causes an over correction for materials that exhibit strain-hardening since the technique assumes elastic-perfectly plastic behavior. However, since the same correction is used for all materials in the present study, the comparison is valid. Ten pillars were tested on each film, aiming for two tests per condition. In some cases misalignment or testing complications led to some conditions that only had one data point.

Elevated temperature micro-pillar compression tests were conducted in a Zeiss DSM 962 SEM with a modified Alemnis in situ indenter [61], [62], using displacement controlled loading and conducted at strain rates of approximately 1e-3/s. This new system incorporates both substrate heating as well as tip heating to create thermal equilibrium between the sample and the tip, alleviating the majority of thermal drift in the measurements. Initial room temperature tests were conducted followed by elevated temperature testing at 325°C, 225°C, 125°C and then again back at room temperature to determine the annealing effect on the films. All samples were held at 325°C
for two hours before testing commenced to allow any microstructural changes to occur in the system. In all of these cases the substrate stiffness is sufficiently higher than the tri-layer films so the additional compliance due to pillar sink-in was determined to be negligible [65].

Additionally, the top edges of each pillar has more local damage as a result of FIB milling as can be seen from the slight rounding at the top of the pillar. This, along with any slight misalignment or roughness of the contacting surface results in a small non-linear portion of the initial loading curve, therefore, all curves were offset so that the extrapolated elastic portion crosses the origin. Elevated temperature nanoindentation was also conducted on both CuNi/Nb bi-layer films using the method described in [77], and compared to the results found in the previous study, providing valuable statistical verification of the micro-pillar compression results.

4.3. Micro-pillar Compression Result of Cu/Ni/Nb Mixed Interface System

The mixed interface tri-layer samples with individual layer thicknesses of 5 nm and 30 nm were compressed up until the first failure event, or at least 10% strain if no load drop was observed. A comparison of HRSEM images of deformed tri-layer pillars (both thicknesses) at all testing temperatures is shown in Figure 4-1. The most distinct difference between the two layer thicknesses is the absence of any macro shear event in the 30 nm layers, whereas each of the 5 nm tri-layer pillars show unstable shear, regardless of temperature. Typically, increased testing temperature leads to an increase in dislocation glide, diffusion, ductility, and interface sliding [79], evidence of which should be visible in the deformation of the pillars where an increase in any of these mechanisms should, generally, reduce the likelihood of shear events. Therefore, these mechanisms are suppressed in the 5 nm films due to the extremely high strengths and robust nature of these films.
Figure 4-1. Post mortem images of micro-pillars for 5 nm (left column) and 30 nm (right column) tri-layer films. Unstable shear is seen at all temperatures for the 5 nm films, however this is not seen in the 30 nm sample.
Some pillars show a small amount of bending which could indicate slight misalignment during testing or a shift of the loading axis off center due to gradual shear of the pillar. Since the majority of the pillars which show bending also show gradual or unstable shear, the latter is most likely. The change from unstable shear at small layer thicknesses to barreling and layer thinning at larger layer thicknesses has been seen in many previous studies [80], [81] and is attributed to a change in deformation from uniform thinning of the soft layer caused by stable plastic flow in thicker layers, to transmission of dislocations across the interface when the interface barrier strength is lower than the maximum strength of the multilayer (as is the case for thinner layers).

**4.3.1. 5 nm Tri-layer Deformation**

Generally, the 5 nm tri-layer films are more brittle than the 30 nm films, which is apparent by the presence of drastic shear events in each of the testing conditions. The initial as-deposited room temperature test shows shear initiating from the top of the corner of the pillar and angled approximately 45º from the loading direction. The top corner of the pillar is a typical starting point for plastic deformation in many micro-pillar compression experiments due to the stress concentration caused by the pillar geometry and the presence of the stiff diamond punch [79], [82]. Since the shear is occurring at 45º from the loading direction, rather than along the layer direction, it indicates the main deformation mechanism is not by interface sliding but is rather controlled by overcoming the interface barrier strength and therefore the max shear strength of the pillar. This has been seen previously in other systems both Cu/Nb and Cu/Zr multilayers, with unstable shear occurring after a certain strain [83]. Other studies have attributed the unstable shear to a combination of dislocation mechanisms in the soft layer accompanied by grain rotation via boundary sliding in the stronger layer [80], [84]. However, this mechanism requires the grain size in the stronger layer to be significantly smaller than the layer thickness since the grains must rotate...
into the proper configuration for shear propagation across the layer by shearing of the grain boundaries. In these small layer thicknesses, it is highly unlikely that the individual grains are on the order of a few nanometers. Therefore, the likelihood of this deformation mechanism is unlikely and overcoming the interface barrier strength is the more probable scenario. The interface barrier strength (IBS) (Equation 4-1) is a characteristic of interface structure, shear modulus, dislocation density, and lattice mismatch, and is thus highly dependent on the layer material.

\[
σ_{IBS} = M \left[ ξμ^*(ζ - \frac{b}{λ}) + \frac{Rμ_{hard} \sin φ}{8π} \right]
\]  

(4-1)

Where \( M \) is the Taylor factor, \( ξ \) is Saada’s constant, \( μ^* = (μ_{soft} \cdot μ_{hard})/(V_{hard}μ_{soft} + V_{soft}μ_{Nb}) \) is the effective shear modulus of the system, \( ζ \) is the lattice mismatch, \( λ \) is a parallel array of spaced glide loops, \( b \) is the magnitude of the Burgers vector, \( R = (μ_{soft} - μ_{hard})/(μ_{soft} + μ_{hard}) \), and \( φ \) is the angle between the slip plane and the interface [80]. Assumingly, the interface barrier strength should be layer thickness independent and therefore, as the strength in the multilayer system as a whole overcomes the strength of the interface, dislocations can propagate across the interface and lead to the drastic shear observed in this experiment.

Suppressed extrusion of the softer layer is common in thinner multilayers since the strength of the soft layer increases with the decreasing thickness, closing the strength discrepancy between the two layers and leading to co-deformation of the layers [80], [83]. In this case, the 5 nm film is reaching the maximum strength that can be obtained for this system; therefore, co-deformation (even though it is impossible to see at SEM resolutions) is likely occurring. Reduced interface sliding and plastic flow of the soft layer also lead to a decrease in ductility of the film, which
results in limited barreling of the top portion of the pillar, apparent in the lower temperature testing conditions.

When the testing temperature is increased to 325°C, slip once again initiates from the top corner of the pillar, but after closer examination of the shear band (Figure 4-2) some segments slip perpendicular to loading direction (along the interface), resulting in a slightly more jagged appearance than that which is expected by strictly cutting of the interface. This observation suggests some interface sliding is also occurring in addition to through layer fracture. As the testing temperature increases, diffusion and interfacial energies increase, providing an easier path for dislocations and shear propagation. The general trend is also observed in the other testing temperatures and may imply that decreasing amounts of interface sliding deformation occurs at lower testing temperatures. Additionally, a small amount of barreling prior to the shear event occurs in pillars tested at higher temperatures (above room temperature) further indicating the presence of an additional deformation mechanism and increased ductility in the system as testing temperatures increase. However, complete suppression of shear is not seen at any of the temperatures investigated in the current study indicating the main deformation mechanism leading to failure is still from overcoming the interface barrier strength.
Figure 4-2. High magnification image of shear event in 5 nm Cu/Ni/Nb tri-layers tested at 25°C (left) and 325°C (right), showing slightly more barreling and jagged shear face as testing temperature increases, indicating an increase in interface sliding.

The engineering stress-strain curves correlating to the pillars shown in Figure 4-1 are depicted in Figure 4-3. Measured load was corrected to remove artificial hardening from the tapered geometry using the method described in the Experimental Details section (and more thoroughly in Chapter 1). Since the amount of plasticity that is occurring in the 5 nm layers is less than what is assumed in the taper correction calculation it overcompensates for hardening effects, which would lead to lower calculated strength values. When comparing elevated temperature tests to the annealed room temperature test, $\sigma_{\text{max}}$ decreases as testing temperature increases, as was seen in previous nanoindentation experiments (Chapter 3) and is expected based on increased diffusion, dislocation motion, and grain-boundary/interface sliding [40], [77], [85].

A distinct load drop occurs at similar strains during each testing temperature, which correlates to the shear events observed in the SEM images, indicating minimal change in ductility as temperature increases. While increased ductility is often seen at elevated temperatures in most other systems, if the increase in dislocation motion, grain boundary sliding, and diffusion are not
enough to weaken the film below the IBS, then failure will still occur as unstable shear, which is seen in the present study. After initial shear, the stress-strain curve begins to show large serrations, which only occur during elevated temperature testing. While serrations are seen in some elevated temperature micro-pillar compression tests and are a result of dislocation build-up and release, ones of this magnitude are not typically observed. This suggests either a different deformation mechanism is occurring in these pillars as temperature increases or is possibly a result of the sheared faces sticking back together due to the elevated testing temperature. As will be discussed later, these large serrations are only seen in the pillars that exhibit distinct shear events, suggesting this is indeed an artifact of the sheared faces interacting at elevated temperatures.

Finally, room temperature maximum strength increased after annealing at 325°C for 4 hours which is atypical for most other multilayer systems. Annealing usually results in a decrease in strength as the layered structure is compromised, especially at these small layer thicknesses. However, since this effect has been reported in previous nanoindentation experiments conducted on similar tri-layer films [77], it is apparent that this is not merely a fluke or as a result of a small sample size. In the previous study, precipitation of NbNi particles at the Nb/Ni interface or initial alloying of the Cu/Ni interface was hypothesized as being the source of the increased strength after annealing. In either of these cases, both precipitates as well as a small solid solution layer would act as additional barriers to dislocation motion that would not occur in typical bi-layer laminate systems.
4.3.2. 30 nm Tri-layer Deformation

When the individual layer thickness increases to 30 nm, the observed deformation behavior is much different. For this system, there is no evidence of a catastrophic shear event in either the SEM images (Figure 4-1) or the stress-strain curves (Figure 4-5) regardless of temperature. Instead, deformation is much more uniform with the main mechanism being deformation of the most compliant layer, which would be the entire Cu/Ni bi-layer for this system due to the coherency of the interface. This mechanism is highly apparent in the elevated temperature tests, and subtly observed in the annealed room temperature test (Figure 4-4). For these thicker layers only the as-deposited 25°C condition shows any sort of shear occurring in the pillar. The shear is gradual as opposed to catastrophic and corresponds to softening at higher strains as seen in the...
stress-strain curve (Figure 4-5). At these length scales, the softer layer (effectively the Cu-Ni bi-layer) is sufficiently large enough that the strength does not exceed the interface barrier strength, therefore slip is confined in the layers and allows this layer to undergo uniform thinning [81], [86]. The absence of unstable shear indicates that the strength in the layers is not exceeding the interface strength; therefore, dislocations are free to move through the layer as opposed to crossing the interface. In this case, interface sliding, layer thinning, and/or grain rotation are likely the dominating deformation mechanisms, as has been seen in other multilayer systems [23], [79], [80], [83]. A small amount of grain extrusion is also seen in these room temperature tests, resulting from plastic deformation of the soft layer (likely following the CLS mechanism). The extrusion is more prominent along the shear band where the most deformation has occurred, with only a small amount observed in other portions of the pillar (Figure 4-4).

Since barreling is a result of the friction constraint of the indenter, it will hinder plastic deformation of the sample at the contacting surface; therefore, the more ductile a sample is, the more barreling will occur in the system. Ductility in the film could be a result of the films interfacial sliding or layer thinning (either of an individual layer or co-deformation); however, as has been seen in other micro-pillar compression testing of multilayer systems, if interface sliding were the dominant mechanism, grains from the ductile layer would show obvious extrusion out from the sides of the pillar as was seen in the case of Cu/Zr and Al/SiC [79], [87]. Since this isn’t the case for these samples tested at room temperature, it is safe to say this is not the dominant mechanism for this system at this temperature. Rather, the most likely mechanism is uniform thinning of the layers, with the possibility of co-deformation since there is no obvious extrusion at this strain level excepting what was observed in the shear band.
When the testing temperature is increased to 325ºC, the deformation mechanism changes significantly with substantial amounts of material extruding out of the sides of the pillar. However, due to the initial taper of the pillar the amount of extrusion is not uniform along the length of the pillar, with a larger amount occurring at the top where there is a higher stress concentration and at the bottom where the rigid Si substrate creates a region of stress concentration [79], [87], [88]. This taper therefore gives us an idea of the response of the material at different stress/strain states during one test. At higher stresses (near the top of the pillar) more material extrudes out of the sides of the pillars than towards the middle of the pillar where no extrusion is observed, indicating a threshold for the maximum stress the structure can withstand at a certain temperature. The high magnification SEM image shown in Figure 4.4 shows the top section of the pillars that are subjected to the highest stresses and thus the most amount of deformation. Close examination of the extruded layer(s) of the film tested at 325ºC suggests only part of the Cu and/or Ni layers are extruding. Since the amount of extruded material is significantly less than 2/3 of the repeating layer thickness, only part of the Cu/Ni layers are extruding, rather than the entire bi-layer, which would have signified interface sliding at the incoherent interface as the deformation mechanism as was seen in elevated temperature Al/SiC micropillar testing [79]. Instead, this deformation is very similar to room temperature micropillar compression results from Cu/Zr bi-layer samples examined by Zhang et. al. [88] and ultrafine-grained alloys [89] where grain-boundary sliding controlled the deformation. As the testing temperature increases, the amount of layer extrusion also increases due to the increase in grain-boundary diffusion and dislocation mobility, making grain boundary sliding and CLS easier thus resulting in larger layer thinning and thereby extrusion from the sides of the pillars.
Figure 4-4. High magnification image of 30 nm Cu/Ni/Nb tri-layer film tested at 25°C and 325°C, showing increased amount of grain extrusion as a result of the higher testing temperatures. Extrusion is concentrated to the top of the pillar where the taper creates a higher stress state than is seen in the bottom portion of the pillar.

Typical engineering stress-strain curves for the 30 nm tri-layers at all testing temperatures (Figure 4-5) shows the same trend for $\sigma_{\text{max}}$ as was seen in the 5 nm layers where strength decreases with increasing testing temperature. However, there is no distinct load drop as a result of a shear event as was seen in the 5 nm layers. Even without this shear event serrated flow is observed in the higher temperature testing conditions. The serrations are much smaller in these films and are more gradual than in the 5 nm layers, which would indicate they are a result of dislocation build-up or pinning and either dislocation avalanche (in the case of build-up) or release, if they have been pinned as a result of dislocation-dislocation, dislocation-particle, or dislocation-interface interactions. The tri-layer system allows for cross-slip of dislocations at the coherent interface, which provides pinning sites for dislocations. When the dislocation is pinned, more stress is required to move the dislocation and leads to the increasing portion of serration. As the stress required to overcome the pinning site and dislocation motion can once again commence, there is a load drop once that obstacle is overcome. As the temperature increases, it becomes easier for
cross-slip to occur which provides additional pinning sites, however it is equally easier for the dislocations to overcome the obstacle as the temperature increases, leading to both an increase in serrations as well as a decrease in the height of each occurrence.

Both room temperature tests show some indication of softening at higher strains, though it is minimal and could be a result of over compensation of the taper correction. The as-deposited softening is likely due to the gradual shear which is occurring in the system, as was discussed previously. However, the softening in the annealed pillar (which doesn’t show an obvious shear band) could be due to the propagation of a small crack somewhere in the pillar. Very close examination of the annealed pillar suggests there could be a small, thin crack on the right side of the pillar, which is travelling perpendicular to the layer direction. However, the resolution of this image is not high enough to unequivocally verify this theory.
Figure 4-5. Engineering stress-strain curves for 30 nm Cu/Ni/Nb tri-layer films conducted at 25°C (as-deposited: black, annealed: blue), 125°C (green), 225°C (orange), and 325°C (red). Significantly smaller serrations are seen at elevated testing temperatures when compared to the 5 nm film thickness.

4.4. Cu-Ni/Nb Incoherent Interface System

From first glance, the deformation mechanisms in the alloyed Cu-Ni/Nb incoherent bi-layer system is much different from the mixed interface system, showing significantly more ductility and a higher tolerance to catastrophic shear in most cases. All conditions show barreling in the upper portion of the deformed pillars, previously associated to the relative ductility of the material, with only two shear events in the 5 nm layer thicknesses, one at 25°C after annealing and the second during 225°C. The 30 nm layers show similar behavior to the tri-layer samples with similar amounts of barreling and material extrusion of the softer Cu-Ni alloy layer at higher temperatures.
Figure 4-5. Post mortem Cu-Ni/Nb alloy micropillars with individual layer thicknesses of 5 nm (left) and 30 nm (right). Deformation for 30 nm layers is similar to tri-layer samples while 5 nm layers show more barreling and less unstable shear than the tri-layer counterpart.
4.4.1. 5 nm Alloy Bi-layer Deformation

The most noticeable difference between the tri-layer and alloy bi-layer system occurs in the 5 nm layer thickness samples. While the tri-layer system exhibits catastrophic shear events in all testing conditions, the 5 nm Cu-Ni alloy bi-layer system only shows shear after annealing. The second pillar tested at 25°C did actually end up shearing but after such a high strain that the layered structure was likely compromised. The post anneal room temperature shear event could be explained if annealing creates an additional strengthening component which increases the strength of the soft layer to above the strength required to shear the interface boundary. Or conversely, if the interface boundary strength changes after annealing so that $\sigma_{\text{max}} > \sigma_{\text{IBS}}$. The last shear event seen in these samples occurred in the second pillar tested at 125°C, which showed double shear but was not included in the data set because debris on the surface skewed the stress-strain curves, making it unreliable. It can be conclude that annealing seems to change the behavior of the interface or the soft layer, allowing it to overcome the IBS at lower strains and shear across the interfaces. Therefore, shear does occur in the 5 nm alloy system at very high strains, which indicates that there is an increase in ductility when compared to 5 nm tri-layer films. As testing temperature increases above 225°C it is easier for dislocations to propagate in the CuNi layer as opposed to crossing the interface, thus suppressing shear and likely leading to increased layer thinning and grain boundary/interface sliding. Since the intrinsic size of these pillars is too small for the resolution of the SEM, this mechanism cannot be verified at this time. High-resolution images of pillars tested at the pre-annealed 25°C and 325°C temperature show very similar deformation, suggesting similar deformation mechanisms are occurring. The pillar tested at 325°C shows roughening at the surface of the pillar, which could be due to local melting from the tip-
pillar contact surface, adhesion to the tip from the increased temperature, or a result of debris on the tip leaving an imprint on the surface.

Figure 4-6. High magnification SEM images of 5 nm Cu-Ni/Nb alloy bi-layers tested at 25°C for the pre-annealed condition (left) and 325°C (right) showing very similar deformation mechanisms at this length scale and imaging resolution.

Figure 4-7 shows the stress-strain data for the 5 nm Cu-Ni/Nb sample, following a similar trend as the tri-layer system where $\sigma_{\text{max}}$ decreases as testing temperature increases; however, both shear events in this system are more gradual as opposed to the sudden stress drop as was seen in all testing temperatures in the tri-layer films. The non-linearity seen in the loading of the 325°C test is likely due to the debris between the tip and the sample surface, as was previously discussed. While this wouldn’t necessarily affect the maximum strength observed in the pillar, it would affect the initial loading, as the debris would yield before the pillar leading to the small amount of plasticity events observed in the elastic portion of the curve. For these films, the maximum stress in the as-deposited room temperature test is larger than the annealed film; however, the yield stress is lower. Since the as-deposited film shows significantly more strain-hardening than the annealed film, it results in a higher maximum stress.
Figure 4-7. Engineering stress-strain curves for 5 nm Cu-Ni/Nb alloy bi-layer at 25°C (annealed: blue; as-deposited: black), 125°C (green), 225°C (orange), and 325°C (red). The large strain-hardening in the as-deposited room temperature test results in a higher maximum stress than the annealed film, contrary to the trend observed in all other samples.

4.4.2. 30 nm Alloy Bi-layer Deformation

The 30 nm Cu-Ni/Nb alloy bi-layer films show similar deformations as the 30 nm tri-layer films, indicating similar deformation mechanisms. All temperature conditions show layer extrusion, likely coming from layer thinning or possibly even interface sliding. However, since the deformation doesn’t show a “pancake effect” (where one layer is completely extruded while the other layer is mostly intact), as is seen in other Al/SiC elevated temperature tests, it is more likely the deformation is not a result of purely interface sliding. A higher magnification image of the top of the pillar tested at 25°C and 325°C (Figure 4-8) once again shows more extrusion at the top of the pillars where stresses are highest. The extruded grains in the bottom portion of the pillar are
initiating from the center of the layer rather than extrusion of full grains originating at the top and bottom interfaces. This observation suggests the interface between the Cu-Ni alloy and Nb layer is strong enough to withstand shear at all temperature ranges tested here, leaving deformation confined in the layers, likely via confined layer slip. Towards the top of the pillar where more of the material is extruded, the amount of extruded material is about 1/2 of the total layer period. If interface sliding were dominant at this temperature, the proportion would be much closer to 2/3 since the entire Cu-Ni layer would shear from both interfaces. The pillar tested at 25°C shows much more uniform deformation with grain “pop-out” occurring in both layers, indicating co-deformation of the layers and grain boundary sliding.

Figure 4-8. High magnification image of 30 nm Cu-Ni/Nb alloy bi-layer film tested at 25°C (left) and 325°C (right), showing grain extrusion as a result of the higher testing temperature. Extrusion is once again concentrated to the top of the pillar where the taper creates a higher stress state than is seen in the bottom portion of the pillar. The pillar tested at 25°C shows co-deformation of the layers.
The stress-strain curves for this system are shown in Figure 4-9, once again following the expected trend of decreased strength with increasing testing temperature. The annealed film is again stronger than the as-deposited film, confirming this trend for multilayer with Cu, Ni, and Nb constituents. Serrated flow is once again observed in the elevated temperature testing conditions though not to the extent as is seen in the 5 nm tri-layer film. This serrated flow can be a result of dislocation avalanches as was suggested previously. There could also be cracks that are propagating inside the pillar as opposed to on the edges, which would lead to the observed small load drops.

Figure 4-9. Engineering stress-strain curves for 30 nm Cu-Ni/Nb alloy bi-layer at 25°C (annealed: blue; as-deposited: black), 125°C (green), 225°C (orange), 325°C (red). Once again, strength increases after annealing, suggesting a change in microstructure.
4.5. Annealing Effect on Strength

One observation which was brought up several times is the increase in $\sigma_{\text{max}}$ at room temperature after annealing, which is not typically observed in multilayer systems. Figure 4-10 summarizes the room temperature strength values for the as deposited and annealed conditions in all four films with error bars showing the spread between the two tests performed. The majority of multilayer systems show a breakdown of the layered structure resulting in an overall softening of the film after annealing, whereas in the current study only the 5 nm Cu-Ni/Nb alloy incoherent interface film showed a decrease in the room temperature strength as a result of the current annealing conditions. This increase in strength as a result from annealing was also seen during elevated temperature nanoindentation [77] and was suggested as being a result of precipitation of NbNi particles along the interface, adding to the strength of the multilayer system as a whole. There are a few different possible reasons why the 5 nm sample does not show this same trend. Either the Ni in the alloy prefers to stay in the alloy rather than diffuse into the Ni and create precipitates, in which case there would not be that additional strengthening mechanism, or annealing has caused a breakdown in the layered structure likely resulting in spherodization, which has been seen to occur in other bi-layer systems. Since the 30 nm film still shows increased strength after annealing, it is more likely that layer breakdown is occurring in the 5 nm sample.
Figure 4-10. Room temperature $\sigma_{\text{max}}$ values for as-deposited and annealed conditions. Error bars represent spread between two micro-pillar compression tests; values without error bars only had one compression test.

4.6. Elevated Temperature Indentation of Mixed and Incoherent Interface Systems

Elevated temperature nanoindentation investigations that were previously conducted on the same Cu/Ni/Nb tri-layer system showed similar temperature response as was seen in the current micropillar investigations [77]. Additional experiments were carried out on CuNi/Nb alloy incoherent interface multilayers (Figure 4-11) to verify temperature sensitivity trends observed in the alloy system. All nanoindentation results show that the 5 nm films have a smaller relative drop in hardness when compared to the larger layer thicknesses, independent of the alloying condition of the Cu and Ni, mirroring the micropillar compression results.
Figure 4-11. Elevated temperature nanoindentation of Cu-Ni/Nb alloy films. While the general trend for decreasing temperature dependence as layer thickness decreases still holds, the 5 nm film exhibits a hardness drop after annealing, different from both tri-layer films and the 30 nm alloy film.

Similar to micropillar compression, room temperature hardness of 5 nm thick films before and after annealing is seen to decrease by approximately 12%, similar to the drop seen in the micropillar tests. The hardness of the 30 nm film increases by 22%, once again mirroring the micropillar compression results. Since nanoindentation can provide significant statistics due to high throughput, these results help to validate the trends seen in the limited number micropillar tests that were conducted. The relative temperature sensitivity determined from the slope of the hardness-temperature trend and normalized by the predicted room temperature hardness is
summarized in Table 4-1, including results from the previous study on the tri-layer films. The observed trend between the two different interface systems and between the two different testing techniques is remarkably consistent, indicating this is a legitimate mechanism occurring in the incoherent interface multilayers.

Table 4-1. Relative temperature sensitivity (°C⁻¹) of Cu/Ni/Nb and CuNi/Nb multilayers tested via elevated temperature nanoindentation.

<table>
<thead>
<tr>
<th>Layer Thickness (nm)</th>
<th>Cu/Ni/Nb [77]</th>
<th>CuNi/Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.23</td>
<td>3.17*</td>
</tr>
<tr>
<td>10</td>
<td>6.15</td>
<td>N/A</td>
</tr>
<tr>
<td>30</td>
<td>11.56</td>
<td>11.67</td>
</tr>
</tbody>
</table>

*compared to as-deposited instead of annealed condition

The actual hardness drop at 325°C for each of the films is reported in Table 4-2 to determine if the same mechanism is causing the drop in hardness, and if it is layer thickness independent. The hardness drop in the tri-layer film system is lower for the 5 nm and 10 nm layer thicknesses; however, all are very close to the same value. The drop in the alloy film when compared to the as-deposited sample is about 1/4 as was seen in the 30 nm alloy sample. Since the 5 nm films showed a decrease in hardness after annealing, the hardness when tested at 325°C is actually larger than the post annealed film. Since that is physically improbable, the comparison was made to the as deposited condition instead. The relatively constant drop in hardness for the tri-layer films suggests the same mechanism is occurring and is independent of layer thickness. Additionally, since the 30 nm tri-layer and alloy films have a similar drop in hardness in this case, the mechanism is also likely to be only dependent on the incoherent interface.
Table 4-2. Actual hardness drop when tested at annealed room temperature and 325°C (GPa).

<table>
<thead>
<tr>
<th>Layer Thickness (nm)</th>
<th>Cu/Ni/Nb [77]</th>
<th>CuNi/Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.78</td>
<td>0.58*</td>
</tr>
<tr>
<td>10</td>
<td>1.39</td>
<td>N/A</td>
</tr>
<tr>
<td>30</td>
<td>2.14</td>
<td>2.27</td>
</tr>
</tbody>
</table>

*used as-deposited condition

4.7. Discussion

4.7.1. Strength at temperature dependence on layer thickness

The temperature tolerance of the films follows a similar trend as has been seen in previous elevated temperature nanoindentation experiments [73], [77], where NMM films with smaller layer thicknesses can withstand increases in temperature with smaller drops in strength when compared to the same sample with larger individual layer thicknesses. A compilation of all maximum stress values for the elevated temperature micro-pillar compression tests are summarized in Figure 4-11. The data is curve fit using the post-annealed room temperature data to compare values from similar microstructures. Concentrating on the Cu-Ni/Nb bi-layer film, the 5 nm layer thickness stress-temperature slope is significantly less than the 30 nm film. This was previously thought to be from increased dislocation nucleation at the interface in the thinner layer samples as was seen in molecular dynamic simulations [66]. Since this trend is seen in both the Cu/Ni/Nb tri-layer mixed interface system as well as the Cu-Ni/Nb alloy bi-layer system, it is apparent that the increased temperature tolerance as layer thickness decreases is a characteristic of the incoherent interface and not a result of alloying the Cu/Ni layers from annealing.
From the figure, it also seems as though the 30 nm tri-layer system maintains its strength more than the 30 nm alloy since the slope for the tri-layer film is shallower than the slope for the alloy. Deformation in the tri-layer films follows the confined layer slip model with dislocation propagation occurring as super threaders in both the Cu/Ni layers, as was previously described in Chapter 2. The unique ability of the tri-layer to exhibit cross-slip across the coherent interface, something that is not easily achieved in incoherent interface multilayer systems, could provide a possible explanation for this phenomenon. Since cross-slip will occur more readily at higher temperatures, this could lead to additional strengthening and reduce the total loss of strength in the system. Since the CuNi alloy layer does not have the coherency stress from the additional interface nor the lagged slip front in one of the layers, it has no ability for cross-slip and thus the potential strengthening benefit of this mechanism is removed. Since the 30 nm CuNi alloy film is more affected by temperature than the tri-layer films, it provides validation for the proposed super threader and cross-slip mechanism of the mixed interface system observed in previous simulation studies.
Figure 4-12. Summary of $\sigma_{\text{max}}$ of all films as a function of testing temperature. Extraneous data points were removed where applicable, and curve fits of the temperature trend are shown.

The relative temperature sensitivity was determined from the slope of the strength dependence lines normalized by the point at which they cross room temperature (25°C) and summarized in Table 4-3. The trend seen in previous nanoindentation experiments is once again validated, where 5 nm layer thicknesses have less sensitivity than 30 nm layers. While there isn’t as large of a difference in the tri-layer films as was seen in nanoindentation and is observed in the alloys, this could be due to the smaller sample size and slightly different barreling or loading conditions skewing the results.
Table 4-3. Relative temperature sensitivity of Cu/Ni/Nb and CuNi/Nb multilayers (°C⁻¹) from micropillar compression testing.

<table>
<thead>
<tr>
<th>Layer thickness (nm)</th>
<th>Cu/Ni/Nb</th>
<th>CuNi/Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm</td>
<td>3.99</td>
<td>3.83</td>
</tr>
<tr>
<td>30 nm</td>
<td>5.40</td>
<td>9.12</td>
</tr>
</tbody>
</table>

According to the confined layer slip (CLS) model (Equation 4-2), dislocations propagate along an individual layer and the stress required to do this is based on three different contributions: (1) the stress required for Orowan bowing confined in between two interfaces, (2) the interfacial stress from elastic lattice mismatch, and (3) stresses arising from dislocation/dislocation interactions.

\[
\sigma_{cls} = \frac{M \mu b}{8\pi h'} \left( \frac{4 - \nu}{1 - \nu} \right) \ln \left( \frac{\alpha h'}{b} \right) - \frac{f}{h'} + \frac{C}{\lambda}
\]

(4-2)

where \(C=\mu b/(1-\nu)\), \(h'\) is the layer thickness measured parallel to the glide plane, \(\alpha\) represents the core cut off parameter where low (high) values represent a wide (compact) dislocation core, \(\nu\) is the Poisson ratio, \(\mu\) is the shear modulus, \(b\) is the length of the Burgers vector, \(f\) is the interface stress arising from elastic deformation, \(M\) is the Taylor factor, and \(\lambda\) is the spacing between misfit dislocations deposited from gliding loops.

The first and third terms are dependent on the shear modulus of the film, which generally tends to drop as temperature increases. Closer examination of the stress-strain curves from these
experiments shows that the modulus of all films remains approximately constant within this temperature range, suggesting this factor is likely minimal. The second term, which is affected by the interfacial stress, is likely different between the Cu/Ni/Nb tri-layers and CuNi/Nb alloy bi-layers due to the difference in moduli and lattice constants. Theoretically, if the Cu-Ni-Nb tri-layer interface energy doesn’t respond as strongly as the CuNi-Nb to changes in temperature, it could be another explanation for the different reactions of the 30 nm alloy layers; however, has not been the focus of this investigation. Furthermore, since the third term is dependent on stresses arising from arrays of dislocation/dislocation interactions, and MD simulations have shown an increase in dislocation nucleation at incoherent interfaces as layer thickness decreases [66], the larger number of interface dislocations hinder deformation and thereby resisting the drop in strength. This mechanism is the most likely of the three in the CLS model to explain why the 5 nm layer thicknesses have a smaller relative drop in strength at higher temperatures.

4.7.2. Strength Increase From Annealing

The room temperature strength increase after the annealing conditions is uncommon, with most multilayers decreasing in strength due to a layer structure breakdown. This behavior was seen in previous results for the same tri-layer system as was used in this study [77] as well as one Cu/Nb bi-layer study [36]. In the Cu/Ni/Nb investigation it was hypothesized that the Ni-Nb interface could be creating intermetallic precipitates along the boundary due to subtle diffusion from annealing. These precipitates can act as an additional strengthening mechanism as well as help stabilize the microstructure. The decrease in the 5 nm CuNi/Nb alloy system suggests that the strengthening effect in the tri-layer system is more robust than in the alloy system. This could be due to the fact that Ni is already in a solid solution with Cu and thus would make it harder to diffuse into the Nb layer which is necessary to create the precipitates. Alternatively, the 5 nm
CuNi/Nb alloy system could be more susceptible to spherodization and subsequent layer breakdown, leading to the softening of the film. More extensive testing and microstructural characterization is required to determine the exact mechanisms.

4.8. Conclusions

Elevated temperature micropillar compression tests were conducted to investigate the trend observed in previous nanoindentation results with decreasing temperature dependence as individual layer thicknesses decreases for the Cu/Ni/Nb tri-layer system. In order to determine if this trend was a result of Cu-Ni alloying, both Cu/Ni/Nb mixed interface and CuNi/Nb incoherent interface samples were investigated. The tests conducted in this study validate the results found in the elevated temperature indentation study, although the actual temperature sensitivity value calculated for the 30 nm tri-layer system did not match that seen in nanoindentation. Additionally, the tri-layer films seem to be even less temperature sensitive when compared to the alloy film, potentially due to the propensity for dislocations in the tri-layer film to cross-slip leading to additional hardening. However, this particular trend is not seen in the indentation experiments indicating a more thorough investigation would be needed to validate this observation. In general, the temperature sensitivity trend seen in both films signifies this mechanism is dependent on the incoherent interface structure and not a result of alloying in the Cu/Ni layers.

Deformation behavior changes in both films as layer thickness increases, showing significantly more material extrusion and layer thinning in the 30 nm systems while unstable shear and co-deformation of the layers is seen in the 5 nm tri-layer and alloy films, respectively. Additionally, the alloy films show significantly more barreling in the top portion of the pillar due to increased ductility of the film. Both interface types show significantly less extrusion than what was seen in the Al/SiC system, which is the only other multilayer film that has been tested at
elevated temperatures so far. Since there still exists semi-coherency in the Cu/Ni/Nb incoherent interfaces, complete interface shearing and entire layer extrusion is not seen. Instead only about 1/3 – 1/2 of the soft layer is extruding at any of the temperature conditions.

Finally, three of the four samples tested here showed significant strengthening after elevated temperature testing, which is indicative of a change in the microstructure. This trend was also seen in the indentation studies conducted previously and was thought to be a result of alloying of the Cu/Ni layers or possibly the development of small NbNi precipitates at the Nb/Ni interface. Since the trend is seen in both the tri-layer and bi-layer films, precipitation of intermetallic particles is a more likely scenario. The 5 nm alloy film did not follow the same trend as the other samples, which suggest layer breakdown has started to occur leading to decreased strength.
CHAPTER 5: Microstructural Changes in Multilayers from Annealing

Abstract

Room temperature nanoindentation showed an increase in hardness of the tri-layer film after elevated temperature testing had been conducted, indicating the likelihood of a change in the microstructure. X-ray diffraction measurements were conducted on pristine and annealed (in two different controlled atmospheres) films and compared to determine if the increased hardness was a result of alloying or oxide formation. Slight changes in intensity peak-valley ratios could indicate a small degree of Cu-Ni alloying in the 10 nm and 30 nm layer thicknesses, or could be a result of peak shifting from a change in internal stress. Post annealing nanoindentation results showed slightly different results as was seen in the elevated temperature investigations, though not to a significant extent. Both XRD and nanoindentation results show that alloying is not a major contributing factor to the annealing behavior of the films.

5.1. Introduction

X-ray diffraction is a quick, non-destructive technique often used to identify elements in a given sample and determine any residual stresses that might exist in the film. In this technique, the x-rays that penetrate the sample get reflected off at specific angles, unique to the crystal orientation and lattice spacing following the relationship known as Bragg’s Law:

\[ 2d \sin \theta = n\lambda \]  

(5-1)

Where \( d \) is the lattice parameter, \( \theta \) is the incidence angle, \( n \) is an integer, and \( \lambda \) is the wavelength of the x-ray beam. Each material has a unique pattern that can be used to determine the chemistry of an alloy or powder. When a material is highly textured, or single crystalline, there
will only be one peak which corresponds to the crystallographic plane which is normal to the surface. For example, a Cu (111) crystal will have a single peak at \(2\theta = 43.3^\circ\).

For fine powders or polycrystalline samples, specifically ones with very small grain sizes, the crystallite size can be determined from the full-width half-max (FWHM) of the peak of interest where smaller crystallites result in significant broadening of the diffracted peak. Although the crystallite size is not necessarily the grain size, it is often a close approximation. While this is a very useful characteristic of XRD, it leads to some complications in multilayer measurements as was seen in the current study. Additionally, the broadening of the peak makes it more difficult to pinpoint the diffraction angle and thus makes it more difficult to determine residual stresses and exact chemistry. The residual stress in the film can actually be inferred from the lattice spacing if the chemistry is already known. Elastic strains in the lattice will cause either a smaller (for compressive stress) or larger (tensile stress) lattice spacing when compared to films without intrinsic strains. First order residual stresses can then be calculated from these elastic strains using the known elastic modulus and the well-known Hooke’s Law \(\sigma = E \cdot \varepsilon\).

Since the nanolaminate systems investigated here are created using sputter deposition each layer is highly textured, making them ideal for XRD characterization. Both intrinsic stresses which develop from deposition as well as any alloy resulting from deposition or annealing can be determined from the scans. XRD scans from each of the samples are compared to reference peaks of pure materials to identify composition and determine the relative shift due to internal stresses. After annealing, the films were once again examined using XRD, comparing peak to valley ratios to determine the relative amount of alloying from annealing.
5.2. As-deposited Microstructure Determined from XRD Measurements

XRD scans on as-deposited Cu/Ni/Nb tri-layer and Cu-Ni/Nb bi-layer films that were used in micropillar compression tests indicate the starting microstructure for the different layer thicknesses. The XRD scans were compared to known standard JCPDS files from the International Centre for Diffraction Data for Cu, Ni, and Nb diffraction peaks for determination of their pre- and post-anneal structure. Figure 5-1 shows the difference in 5 nm (left) and 30 nm (right) tri-layer films. The 30 nm films show very discrete peaks from each of the layers, corresponding to Nb (green- 38.5), Cu, (orange- 43.3), and Ni (grey- 44.5). All three peaks are slightly shifted to the right of the reference peaks indicating a compressive strain in the film. While mismatched lattice constants can create their own strains across a coherent interface, if this were the only source of strain in the multilayers then there would be a shortening of the lattice constant in one layer (Cu) and a lengthening in the other (Ni). However, both the Cu and Ni peaks are shifted to the right of the standard peaks, indicating there are additional stresses from the deposition process causing this shift.
Figure 5-1. X-ray diffraction experiments showing structure of Cu/Ni/Nb tri-layer films with 5 nm (left) and 30 nm (right) layer thicknesses. Peak merging from two different materials that exhibit large peak broadening can result in a shoulder, as is seen on the 5 nm scan (emphasized by red dashed circle).

The 5 nm sample shows a significantly different XRD structure, which at first glance seems to be a result of alloying of the Cu and Ni layers. However, as the layer thickness decreases, the crystallite size also decreases and thus causes significant peak broadening, as is seen in the Nb peak. When there is broadening of two peaks that are very close together, the signals can overlap and the total intensities would add, schematically depicted in Figure 5-2. When this happens there will be shoulders on the combined peak from the portions of the individual peaks that were not overlapping. This is seen on both sides of the 5 nm Cu/Ni combined peak, more noticeably on the Cu side of the peak that is circled in the Figure. While this doesn’t necessarily guarantee the layers are completely discrete, it does show that the layers are not fully alloyed from the beginning. Once again, the Nb peak is shifted slightly to the right, indicating a tensile stress exists in the as deposited film.
Figure 5-2. Schematic of how merging XRD elemental peaks can combine to create a merged peak with a shoulder as was seen in the 5 nm tri-layer sample.

As-deposited Cu-Ni/Nb alloy films were also inspected using XRD to compare structure and intrinsic stress to the tri-layer films. The 30 nm film shows two distinct peaks, one from the Nb layer and the other from the Cu-Ni alloy. The third peak in the scan is the second diffraction peak belonging to the Nb (200), which is often seen in highly textured samples. The Cu-Ni alloy peak is also shifted slightly to the right of the reference peaks, once again indicating a slight tensile stress in the film. Once again there is significant peak broadening in the Nb layer while only a slight broadening in the Cu-Ni alloy. Since the CuNi alloy layer is twice the thickness of the Cu or Ni layers in the tri-layer film, the observed crystallite size can also be twice that of the tri-layer films leading to less peak broadening. The 5 nm film also shows some additional fringe peaks on either side of the main Nb peak, which are a result of additional interference resulting from the repeating Nb layers being close together.
5.3. Annealing Tri-layer Films in Various Atmospheres

An annealing study was conducted to mimic the temperature conditions encountered during elevated temperature indentation and determine the effect of potential oxidation or alloying. If a significant amount of oxide formed during annealing, the increased room temperature hardness which was observed after annealing (described in Chapter 4) could be a result of a hard surface oxide layer rather than an intrinsic property of the multilayers. Therefore, XRD characterization of annealed films is a crucial step in understanding the nanoindentation results. All tri-layer films were annealed in ambient laboratory conditions at 325°C for 4 hours and then allowed to furnace cool for approximately 6 hours. To examine the effect of decreasing oxygen content, the samples were also annealed in a furnace with flowing Argon (reduced oxygen atmosphere). Both annealing atmospheres were compared to the as-deposited films to determine changes in both the XRD scans as well as nanoindentation hardness.
The films used in this study are the same as were used in the elevated temperature indentation experiment. The as deposited condition for the 30 nm film is as expected, with distinct peaks for Nb (110), Cu (111), and Ni (111) at \(2\theta = 38.5, 43.3,\) and 44.5 respectively. The 10 nm sample shows similar peaks but with more broadening, suggesting smaller grains [90], which is expected since the grain size should scale with the individual layer thickness. The broadening is similar to that seen in the as deposited 5 nm films described in the previous section with merged Cu and Ni peaks as indicated by the slight shoulder on the Cu side of the peak.

X-ray diffraction (XRD) was then performed on the post-annealed films to determine the effect on the structure of the multilayers. The films were removed from the silicon substrate and attached to a glass slide prior to testing using double-sided tape. Using a Bruker D8 Focus X-Ray Diffractometer with Cu K\(\alpha\) source and high speed 1D Lynxeye detector, scans were run between \(2\theta = 20^\circ\) to 80\(^\circ\), at 40 kV and 40 mA at a step size of 4 deg/min.

Figure 5-4. XRD scans of ex situ annealing of (a) 5 nm, (b) 10 nm and (c) 30 nm layers for as deposited, reduced oxygen atmosphere (ROA), and air anneal.
Figure 5-4 shows the XRD analysis for the 5, 10, and 30 nm samples. The 30 nm layers show a very slight change in peak ratio, but with a significant shift in the peaks as a result of annealing. The Nb peak shifts to the left of the original peak whereas the Cu and Ni peaks shift slightly to the right, indicating a developing compressive stress in the Nb layer and tensile stresses in the Cu and Ni layers. The 10 nm sample also shows significant peak shifts, which could explain the increased intensity where CuNi alloy should be. Since the Ni peak shift is nearly nonexistent and the Cu shifts to the right, closer to the Ni peak, the amount of overlap between increases and the resulting total intensity increases. However, with this technique it is impossible to determine if the increase in intensity between the two primary peaks is strictly due to the peak shift or if there is a small amount of alloying occurring between the two layers. The 5 nm film shows a completely different story than expected. In this case, the Nb peak which should be occurring around $\theta=38.5$ is extremely broad in the as-deposited condition and essentially non-existent in the annealed conditions. The broad peak suggest an extremely small crystallite size, either signifying a small grain size or a much smaller layer thickness than what was expected. Considering the 5 nm films were deposited at a different facility than the other two films, this is not a surprising result. The disappearance of the Nb peak with annealing suggests it could have possibly combined to create intermetallic precipitates, ones that are too small to resolve with this system. Additionally, while the other films show an increase in the intensity between the Cu and Ni peak, this 5 nm films actually shows a sharpening which is most likely a result of peak narrowing due to grain growth from annealing.

After annealing, quasi-static nanoindentation using a Berkovich tip on a Hysitron Triboscope was conducted to determine the resulting change in hardness. Load controlled quasi-
static partial unload indentation (to determine the variation of hardness with depth) was conducted to a maximum of 10% of the film thickness in order to reduce the substrate effect.

Figure 5-5. Hardness of annealed films in different atmospheres shows little effect of atmosphere, signifying minimal oxidation of the films.

As shown in Figure 5-5 there is a minimal change in hardness regardless of the annealing atmosphere for the larger layer thicknesses, suggesting any potential oxidation that has occurred is limited to a very thin top layer. Therefore, oxidation would have little effect on the temperature sensitivity trend seen in nanoindentation results and is also not the cause of the increased hardness seen in both nanoindentation and micropillar experiments. The 5 nm films do show a significant drop in hardness after annealing and seem to be slightly dependent on the atmosphere, with a larger drop occurring in the ambient annealed condition, which could be a result of the disappearance of
the Nb layer (suggested from the disappearance of the elemental peak), which would remove the hardening mechanism from the incoherent interface. A change in residual stresses in the film (apparent from the peak shifts in the XRD scans) could also affect these hardness results if the relative pile-up changes.

5.4. Conclusions

X-ray diffraction examination of thin films is a quick, non-destructive way to investigate the microstructure including texture and internal stresses that exist in the NMM films. Scans of the as-deposited tri-layer and alloy films used in micropillar compression testing show highly textured films with internal stresses created during deposition. Some intrinsic stresses would occur in the films as a result of different lattice constants and coherency across the interface; however, if this were the only cause of stress the Cu ad Ni peaks would shift in opposite directions, as one layer would be in compression while the other is in tension. Instead, all peaks in all samples are shifted to the right of the standard peaks, indicating tensile stress in the entire film.

An annealing study aimed at mimicking the annealing conditions occurring in the elevated temperature nanoindentation but in different atmospheres did not show significant layer degradation nor oxide formation in any of the annealed conditions. Slight peak shifts occur in the annealed condition for the 10 nm and 30 nm films in both atmospheres, which in turn causes an increased diffraction intensity in between the Cu and Ni peaks. Since this is where the CuNi alloy peak would reside, it is impossible to distinguish if the peak developing there is a result of Cu and Ni alloying from annealing conditions or is merely a result of the changing stresses in the film from annealing. The 5 nm films show a sharpening of the Cu and Ni peaks along with a complete disappearance of the small Nb peak, suggesting grain growth in the Cu and Ni layers and possible intermetallic formation of the Nb. No conditions resulted in distinguishable crystalline oxide
formation. Nanoindentation on these annealed films showed stable hardness for the 10 nm and 30 nm films, regardless of annealing atmosphere. The 5 nm film does show a drop in hardness, opposite to the trend seen in the elevated temperature nanoindentation study, which is suggested to be the result of a change in the internal stress of the film or the disappearance of the Nb peak.
CHAPTER 6 : Design and Development of Micro-tensile Machine

Abstract

A custom designed machine was built to use for investigating the strain-hardening behavior of the Cu/Ni/Nb tri-layer thin films. Freestanding thin films are patterned using a metal lift-off technique to eliminate surface defects along the gage section, which helps avoid premature failure due to stress concentrations. The machine utilizes digital image correlation technique to calculate actual strain on the film surface, eliminating the effect of internal machine compliance on this measurement. Precision and accuracy of the machine is verified on thin film Au samples, which are well documented in current literature.

6.1. Machine Design

Due to the complicated stress states involved and the difficulty in obtaining true strain-hardening behavior of a material during nanoindentation, a micro-tensile testing apparatus was designed and built (Figure 6-1). The machine utilizes a nano-stepper motor with a 10 N load cell with a 5 axis positioning stage and equipped with a 20x objective lens and CMOS monochrome USB camera for strain measurements. Custom sample grips use a recessed cutout to aid in alignment of the sample and proper load application. These grips do not require super glue or epoxy as the method to secure the samples, leading to high sample throughput and the ability to adjust slight misalignments before testing. Instead, the ends of the grips have a raised ledge that transfers the force to the sample paddles during testing. The clamps on the top help to provide stability when cutting the support bars on the sample frame as well as stop the sample from lifting at the ends during testing. This does not require an excessive amount of force and therefore does
not create a point of stress concentration on the films, which would lead to premature failure of the specimen.

Figure 6-1. Custom designed and built micro-tensile testing apparatus utilizing digital image correlation for strain measurement.

A 5x objective lens is used as a way to align the grips and 5 axis stage to the camera and nano-stepper motor, while a 20x objective lens provides higher resolution during measurements. Initially, the camera is aligned to the fixed grip on the left side of the machine with the specimen only in this left grip, to avoid any misalignment from the rest of the system. This grip is attached
to the load cell and a linear stage, which helps position the specimen in the center of the camera. Using the USB camera program, guides are overlaid onto the image to mark where the sample is aligned while still in the left grips. From there, the sample is transferred to the right grips where the different axes are adjusted until the sample is within the bounds of the previous overlaid marks. Additionally, the stepper motor is extended and retracted to ensure the linear motion during testing is in line with the sample axis and will not go out of focus while testing. Once the system is initially aligned, there should be little to no adjustments required after a sample change, however slight misalignments can occur due to the small amount of extra space around the sample in the recessed groove.

The machine is programmed and controlled in LabVIEW in either a straight, single partial unload, multiple partial unload, or fatigue cycle option. The displacement rate can be controlled with the maximum displacement rate being 1 mm/s with no technical minimum. Therefore, the minimum displacement rate is determined by the user and the user’s preference on the extent of smooth travel during testing.

6.2. Sample Preparation

All films are prepped using DC magnetron sputtering on top of patterned silicon wafers. Wafers were patterned using a bi-layer liftoff technique developed by MicroChem and patterned into dogbone-shapes. Original attempts at making freestanding dogbone shaped films by deep reactive ion etching (DRIE) of the silicon wafer did not prove fruitful, regardless of the conditions. Instead, frames were laser cut from thin Delrin sheets (see Figure 6-2) to provide both support for the thin films as well as providing the “paddle” that fits inside the recess in the grips to transfer the load into the film. From there, the frames are glued to the patterned dogbone samples using a
two-part epoxy that is resistant to acetone and allowed to cure overnight under a heavy weight to help adhesion. To ensure proper alignment, the frames are positioned under a stereomicroscope and aligned at approximately 5x magnification. After the epoxy is fully cured, the samples are released from the substrate by soaking or sonicating in acetone, creating a freestanding dog-bone shaped specimen attached to a support frame for easy handling.

Figure 6-2. Laser cut Delrin frames (left) are used as a rigid frame to transport and grip fragile thin film samples. Dogbone shaped thin films glued to the frames (right) are aligned in a stereomicroscope to ensure proper alignment and load application during testing.

6.3. Digital Image Correlation (DIC) for Strain Calculation

The strain measurement technique was designed to minimizing extraneous compliance issues by utilizing digital image correlation (DIC), a technique which tracks markers on the surface of the film and compares consecutive images in a series to the original starting image to determine the strain occurring in the sample. The markers are deposited onto the surface of the film using a
device created to spray very fine particles from the bottom of the contraption up through an interchangeable fine mesh grating and then onto the surface of the film, schematically shown in Figure 6-3. For most films fine silicon particles a few hundred nanometers in diameter adhere well enough to the surface strictly from static forces. However, for Cu/Ni/Nb films, fine nickel particles work better than silicon fines due to the slightly magnetic nature of the films. In general, this technique creates a well dispersed fine particle speckle pattern ideal for DIC particle tracking and strain determination. The pattern can be optimized depending on the magnification and resolution required simply by changing the initial particle size or the mesh grating size to alter the particle density and size.

Figure 6-3. Schematic of technique used to pattern topside of dogbone free-standing thin films for DIC measurement. Any fine disperse powder can be used in this method, so long as it sticks on the sample surface.
Once patterned, the films are placed in the machine grips and secured with clamps to hold the sample while the support bars are melted with a soldering iron, releasing the film without any large lateral forces from cutting or grinding of the support beams. The film is then brought into focus and tested under a constant displacement rate with several load-unload options: no unload (straight), single unload, multiple unload, and fatigue (number of cycles is input by the user). A one-dimensional strain calculation is incorporated into the program, which calculates the true strain in the film based on the following equation:

$$\varepsilon = \ln \left( 1 + \frac{\Delta l}{l} \right)$$

The original gage length \((l)\) is determined by the number of pixels between two markers, chosen by the user, in the speckle pattern. Figure 6-4 shows a typical speckle pattern used in DIC strain measurements captured at the beginning (left) and at 45 seconds into one test (right). The red line overlaid on the image shows the distance between two speckle points at the start of the test and is used as a guide in the second image to show the amount of strain that has occurred in the film. Although there is significant lateral movement as well as strain in the film, the tracking feature accounts for this lateral movement and merely compares the relative pixel distance between two speckle features. Ideally the speckles will be large enough as to be correctly recognized as the same speckle in subsequent frames however not too large (like the larger circles in Figure 6-4) as to lose resolution. The tracking feature function used in the LabView program tracks the features based on a change in contrast across a distance of 10 pixels. The number of pixels over which the program looks for a change in contrast is important in determining the particle of interest since it can easily lose track of the object if the correct parameters are not chosen. This value can be altered until proper tracking is observed and will be dependent on the size of the particles being tracked.
and the chosen magnification. In general, at the 20x magnification and the silicon fines used in the preliminary study, excellent tracking is achieved as long as the sample does not go out of focus during the test.

![Figure 6-4](image)

**Figure 6-4.** Frames captured during a test run for the 10 nm Cu/Ni/Nb film system at two different times: the very beginning of the test (left) and at 45 seconds into the test (right). The red overlaid line marks the distance between two choice particles in the initial image and is copied into the right image to use as a guide to see the amount of strain that has occurred in the film after 45 seconds.

### 6.4. Reliability of Machine Design by Comparison to Pure Au Thin Films

Thin Au films were manufactured and tested to evaluate the accuracy and precision of the machine by comparing the modulus and maximum stress of six freestanding Au films (Figure 6-5). Since modulus is a known value and is not size dependent, this value is most important in determining accuracy of the current testing method. Modulus values are summarized from linear fits of the elastic portion of the stress-strain curves from the six different Au tests (Figure 6-4b),
and compared to literature values in Table 6-1. The calculated modulus values using this machine design is remarkably similar to other modulus values from other micro-tensile testing results. Additionally, across six different tests the elastic modulus values do not vary greatly, with one standard deviation being approximately 15% of the average value. That small discrepancy is mainly due to the one outlier (red circles in Figure 6-5), which when excluded would drop the average to 59.7 GPa with a standard deviation less than 10%. Since the initial portion of this outlying test begins to decrease in strain (making no logical sense), it is likely the particles were not tracked properly due to initial sample misalignment. Both of these checks verify the testing technique and DIC measurements are both precise and accurate when comparing to a sample with known mechanical properties, such as gold.

![Stress-strain curves from six thin film Au specimens showing excellent reproducibility of modulus and strength values. (b) Linear curve fits of the initial elastic portions of the curves show quite consistent modulus values.](image)

Figure 6-5. (a) Stress-strain curves from six thin film Au specimens showing excellent reproducibility of modulus and strength values. (b) Linear curve fits of the initial elastic portions of the curves show quite consistent modulus values.
The maximum stress of these thin film Au specimens is also reported in Table 6-1. These films have a grain size of approximately 200-500 nm, which leads to a strength of approximately 400 MPa [1]. The average strength from the six films tested using this system show a maximum strength of 424 MPa with a standard deviation less than 10%. Some of the films seem to show premature failure, with strains less than 2%, which for Au is highly unusual. Since slight misalignment or surface defects can cause stress concentrations and lead to premature failure, these tests could be excluded from analysis, further decreasing the standard deviation. Therefore, the maximum stress values also prove to be precise and accurate.

Table 6-1. Reliability measurements of six 2 μm thick Au films using custom micro-tensile machine

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Standard Deviation</th>
<th>Range</th>
<th>Literature Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>62.57</td>
<td>8.742</td>
<td>27.05</td>
<td>66 ± 4.5 [91]</td>
</tr>
<tr>
<td>Maximum Stress (MPa)</td>
<td>424.37</td>
<td>41.23</td>
<td>125.3</td>
<td>~400 [1]</td>
</tr>
</tbody>
</table>

One Au film was tested using the multiple unload program function, Figure 6-6. This option is incorporated into the program as a way to get multiple modulus values without testing multiple samples. The unloading portion of the curve is an even better determination of elastic modulus since the only recovery that would occur would be purely elastic. Since there could be microplasticity and some straightening of the film in the initial portions of the stress-strain curves, the modulus values from these unloading segments could be more accurate. This particular test seems to have some tracking issues half way through the test, as can be seen from the jump
backwards in the strain measurement. Since this does not affect the stress calculation, the values obtained from this test are still valid even if there appears to be premature fracture due to the relatively low elongation for Au.

![Stress-Strain Curve](image)

**Figure 6-6.** Example of the multiple unload option for 2um thick Au film. This film has undergone three unloading segments before failure. Unloading and reloading have approximately the same slope and thus elastic modulus.

Due to sample preparation complications and machine alignment issues, to this date, successful stress-strain data for the Cu/Ni/Nb tri-layers have not been obtained using this system. An example of one attempt on a 10 nm tri-layer sample is shown in Figure 6-7, clearly portraying some complications in the strain calculation due to misalignment and poor tracking of the chosen markers. The general shape of the stress-strain curve is as to be expected with a relatively straight elastic portion followed by significant hardening during plastic deformation before final fracture.
Further alterations to the machine and sample preparation process are required to get reliable stress-strain data to determine tensile strength and strain-hardening measurements.

Figure 6-7. 10 nm Cu/Ni/Nb tri-layer film tested slightly off axis. The non-linear motion is due to misalignment, causing the film to drift out of focus and thus resulting in poor tracking.

6.5. Conclusions

Micro-tensile testing of thin films is a challenging test to perform both as a result of machine and sample preparation obstacles. The machine designed and built for the purpose of determining the strain-hardening behavior of multilayer films has shown significant promise when testing an ideal system such as Au, having both remarkable precision and accuracy in these thin films. Tests conducted on tri-layer films have not been successful to this date due to misalignment of the sample. In order to obtain stress-strain data for these films, micro-tensile tests were conducted using other systems and are the topic of the following Chapter.
CHAPTER 7: Tensile Deformation of Tri-layer Cu/Ni/Nb Films

Abstract

Micro-tensile tests on Cu/Ni/Nb tri-layer films with different layer thicknesses were conducted to determine deformation mechanisms under tensile. Room temperature tensile tests on films with 2 nm and 5 nm individual layer thickness show decent reproducibility with ultimate strengths closely matching those found in both nanoindentation and micropillar compression tests. The ductility of these films in tension is extremely small, and any strain-hardening that might have been observed in these films is very difficult to curve fit. Elevated temperature micro-tensile tests were conducted on tri-layer films with 2 nm, 5 nm, and 10 nm layer thickness at room temperature and then again at 150°C, after which the fracture surface was examined to determine a change in deformation mechanisms after this modest increase in testing temperature. Increasing the testing temperature in these films showed an increase in relative ductile behavior, though the failure is still controlled by crack propagation along the grain-boundaries.

7.1. Room Temperature Tensile Testing of 2 nm and 5 nm Tri-layers

Other micro-tensile experiments were conducted on tri-layer films with 2 nm and 5 nm individual layer thicknesses at Johns Hopkins University in Baltimore, MD. Sample preparation for these samples was similar to the process described previously with the speckle pattern created using fine ceramic powder in an aqueous solution rather than via air deposition. This technique results in a less controllable speckle pattern with a mixture of large clumps and finer dispersions (Figure 7-1). Strain is determined using a two-dimensional DIC MatLab script developed by Christoph Eberl, Robert Thompson, Daniel Gianola at Johns Hopkins University, though only one-dimensional measurements are reported here. The machine set up is remarkably similar to the one
described above however uses a UV-curable epoxy to fix the samples to a stationary stage and linear actuator. A small initial load is imposed on the film as a result of the curing process and thus could possibly induce some micro-plasticity in the films before testing even begins. The preload is removed before testing actually commences, but whatever damage has already occurred in the films will remain.

Figure 7-1. Speckle pattern for films conducted at Johns Hopkins University. This particular film is a 5nm Cu/Ni/Nb sample.

Figure 7-2 shows stress-strain data from two different tests conducted on tri-layer films with layer thicknesses of 2 nm and 5 nm. Both films show remarkably similar strength properties with a maximum strength of approximately 1.3 GPa though the 5 nm films are more repeatable than the 2nm films. Both films have limited ductility, fracturing at less than 1.8% strain and showing only micro-plasticity. Additionally, since the uniaxial tensile stress allows for interface and grain-boundary sliding/fracture while indentation suppresses this mechanism (strictly by being in a compressive stress state), it is understandable that these films show minimal plasticity if those
mechanisms are prominent. Due to the extremely high strength of these films, the significantly reduced plasticity is not surprising, though makes determining a strain-hardening relationship impossible from these measurements. Nanoindentation and micropillar compression results from similar 5 nm tri-layer films have shown a strength of about 1.6 GPa, showing remarkable repeatability across the different tests.

In general, the modulus of the 2 nm films is lower than the 5 nm films, even when considering the film with the highest modulus. The modulus value of the 5 nm tri-layer film is similar to modulus values determined by nanoindentation (about 160 GPa). Since these films have highly preferential orientations (111) for Cu and Ni layers and (110) for the Nb layer, a difference in the modulus values would be expected when tested along (compression testing) and perpendicular to (tensile testing) the preferred direction. While compression testing mostly tests a single preferred direction, tensile testing would test all other directions, making it much closer to a homogeneous sample. According to the rule of mixtures for these three components, the expected modulus for a homogeneous sample would be about 165 GPa, assuming equal volume fractions of each element and based on individual elastic modulus values of $E_{Cu}=115$ GPa, $E_{Ni}=200$ GPa, and $E_{Nb}=180$ GPa. Considering the broad assumptions, the measured modulus is quite similar to the expected composite modulus.
7.2. Deformation Behavior in Elevated Temperature Micro-tensile Testing

In an attempt to examine the change in deformation behavior of different layer thicknesses during elevated temperature uniaxial tension, micro-tensile testing of 2 nm, 5 nm, and 10 nm tri-layer films was conducted at room temperature and 150°C. Due to machine constraints, additional compliance in the system made obtaining reliable stress-strain data too difficult. Therefore, stress-strain curves and strength values are not reported. However, the fracture surfaces of the films after testing can still provide insight into any changed in the deformation processes that are occurring as a result of the higher testing temperature.

Images of the fracture surfaces (Figure 7-3) from the three different samples tested at room temperature (left column) and 150°C (right column) show a subtle change in the deformation mechanisms depending on both the layer thickness and temperature. These images also give use some idea as to the structure of the films even if the individual layers cannot be resolved. Somehow, the 2 nm sample seems to have an unknown bi-layer on the top and in the center which
is much thicker than any of the individual layers. Since the smallest intrinsic length scale is the controlling factor for strength, and these layers will not affect the observed deformation mechanism drastically, they can essentially be disregarded for the present interpretation. Another interesting observation from the 2 nm tri-layer deformation is the apparent layered structure that the room temperature fracture surface seems to possess. This is surprising since the layered structure should be too small to resolve in the SEM. Additionally, these “layers” are on the order of several tens of nanometers thick, which is much larger than the projected layer thickness or even the modulation period of these samples. Since these films were sputtered in 6 layer intervals, which would deposit approximately 12 nm of material during one run, it is likely that the pause between deposition sets allowed imperfections to occur in the layers and lead to preferential interface sliding at these interfaces. The film tested at 150°C seems much closer to what was expected, where the fracture surface more closely resembles a bulk ductile fracture surface with the characteristic dimples from void nucleation and growth before fracture. At these layer thicknesses, deformation is no longer dominated by the interface structure as dislocations will cross the interface and propagate through consecutive layers. This allows a more uniform deformation closely resembling bulk deformation, while still maintaining the strengthening benefit of interfaces.

As expected, the 5 nm film does not show a distinct layered structure at this resolution since the individual layer thicknesses are too small. The fracture surface of the room temperature test shows deformation occurred by grain separation likely due to grain boundary sliding as is indicated by the lack of dimple formations. Furthermore, the relief seen in this test could be additional evidence of grain boundary or interface sliding, which was also seen in testing of Cu/Nb layers [41]. When the testing temperature increases to 150°C, the fracture surface once again shows a
more typical ductile fracture surface, with small void nucleation and coalescence, opposite to the trend seen in the Cu/Nb work referenced previously where increased testing temperature lead to an increase in grain boundary/interface sliding. Another interesting observation is the change in deformation pattern from the top to bottom of the fractures surface, where the top of the fracture surface appears to fail via ductile fracture from relatively large voids whereas the bottom third of the film looks much closer to brittle fracture or at least the coalescence of smaller voids. Although the film is presumably in uniaxial tension throughout the thickness of the film, the film was attached to the grips on one side instead of sandwiched in between clamps, this could cause a small difference in the stress state across the thickness of the sample. Additionally, the film could have not been centered in the heater causing a thermal gradient in the film that would change the ductility and thus the size of void growth.

The 10 nm film fracture surface seems to show deformation similar to those seen in the study conducted on Cu/Nb films where the room temperature fracture shows void coalescence and the 150°C shows evidence of grain pullout and some interface sliding. Since this is the opposite trend as was seen in the 5 nm films, there is likely a layer thickness threshold for the different mechanisms.
Figure 7-3. Elevated temperature micro-tensile test fracture surfaces at room temperature (left column) and 150°C (right column) for layer thicknesses of 2 nm (a and b), 5 nm (c and d), and 10 nm (e and f). A change in deformation mechanisms is seen when testing temperatures increase to 150°C leading, in general, to more ductile fracture behavior than that seen in the room temperature tests.
Figure 7-4 shows the top of each film close to the fracture surface at both testing temperatures, except 10 nm at 150°C. It is immediately apparent that there are a significant number of crack propagation along the grain boundaries, though not all cracks proceed to failure. Therefore, deformation begins by void formation at triple joint grain boundaries followed by coalescence and crack propagation along the high-energy grain-boundaries. This is observed in each of the testing conditions, regardless of temperature and layer thickness.

The top surface of these 2 nm films shows signs of ductility in the form of micro-necking in the different “layers” observed in the cross-sectional images, in both testing temperatures. From this viewpoint, there is very little difference in the observed deformation behavior at these temperatures, whereas the cross-sectional images indicated an increase in the void formation at the higher temperature. Since individual grains cannot be resolved for this sample, the presence of grain pull out can neither be proved nor disproved using this technique.

As is observed in Figure 7-4, void formation begins at the triple joint grain boundaries and then coalesce to create intergranular microcracks. This general mechanism is observed for both the 5 nm and 10 nm films, though elevated temperature testing did show a slight difference in the micro-ductility in the 5 nm film. The 5 nm film tested at 150°C shows increased necking of the individual grains, similar to that seen in the 2 nm films.
Figure 7-4. Surface of films near the fracture surface at room temperature (left column) and 150°C (right column) or layer thicknesses of 2 nm (a and b), 5 nm (c and d), and 10 nm (e). The surface of the 10 nm film tested at 150°C is not shown, however likely shows similar grain boundary cracks as is seen in the other films.
7.3. Conclusions

Elevated temperature micro-tensile experiments conducted on tri-layer nanolaminate Cu/Ni/Nb films with individual layer thicknesses of 2 nm, 5 nm and 10 nm showed a slight change in deformation behavior and fracture surface characteristics. The two samples with thinner individual layer thicknesses (2 nm and 5 nm) show increased micro-plasticity as the temperature increases whereas the 10 nm film shows increased grain pullout and interface sliding. This change in behavior could indicate a change in deformation mechanism as layer thickness decreases but is difficult to determine strictly from the present experiments.
CHAPTER 8 : Wear Resistance of Oxide Dispersion Strengthened Au-ZnO Thin Films

Abstract

Electrical contact switches require low contact resistance for efficient passage of signals while withstanding repetitive cycling. Hard gold with alloy additions of Ni, Co or Ag can increase the wear resistance of Au films, however this causes a significant decrease in conductivity and alloying elements can segregate during long-term aging leading to property evolution. The current work demonstrates that Au-ZnO nanocomposites can create a hard Au coating with a uniform, stable structure under frictional loading. Addition of ZnO particles decreases the grain size and texture of the film by 35% and 40-75% respectively, indicating a change in growth behavior of the film. The nanoindentation hardness increased directly with increasing ZnO concentration. Atomic force microscopy examination of wear-tested films demonstrated morphological stability after frictional contact and thus show the potential for these films to replace current hard Au used on contact terminals.

8.1. Introduction

Gold is an ideal material for electrical contacts due to its high electrical conductivity and resistance to harsh environments. However, repetitive cyclic contact can cause mechanical degradation and stress-induced grain growth [1–5]. Additionally, high currents passing through the switch can lead to micro-welding and further deformation when the contact is broken [96]–[99]. In order to increase the lifetime of the contacts, “hard Au” is used to enhance wear resistance by increasing the hardness of the films. There are numerous ways in which the hardness can be
increased: control of grain size [1]–[4], deposition of nanolaminate structures [5]–[7], addition of solid solution impurities [3], [8]–[11], or using an oxide dispersion strengthened (ODS) material [9], [12], [13], all of which have been demonstrated previously. However, all of these strengthening techniques can substantially increase the resistivity of the host metal. Therefore, a material that shows increased wear resistance without appreciably decreasing conductivity is required for optimal performance.

Decreasing the grain size of a metal is a widely used strengthening technique and has been studied for decades on a variety of different materials. The strength follows a relationship that was first observed by Hall [4] and Petch [2], increasing with the inverse square of the grain size. This relationship breaks down for grain sizes on the order of tens of nanometers, leading to an upper bound for this type of strengthening. However, grain refinement strengthening is only temporary under wear conditions if the material can undergo stress-induced grain growth that would then lead to a decrease in strength and wear resistance. Modeling studies [14], [15] suggest the grain growth is attributed to grain-boundary sliding, diffusion, and grain rotation. Therefore, if these elements are suppressed grain growth should be slowed or even stopped. Numerous studies have been conducted using impurities to stabilize nanocrystalline microstructures by reducing grain boundary mobility, thus stopping grain growth [11], [16], [17]. In samples with lower impurity concentrations, the deformed region can exhibit significant grain growth while the grain size in the un-deformed regions remains the same as the as-deposited condition [18]. In contrast, stress-enhanced grain growth in the deformed region is not seen at high impurity concentrations. This suggests that impurities are effective ways to decrease stress-induced grain growth by pinning grain boundaries, thus reducing grain boundary sliding, rotation, and diffusion.
Hard Au films can also be formed via oxide dispersion strengthening (ODS), where small oxide particles are used to increase strength [30]. The ODS technique shows great promise for increasing hardness without greatly affecting conductivity [12]. Comparing the effect of a Au-V alloy versus Au-V$_2$O$_5$ to the strength and conductivity benefits for the system, the ODS Au showed both a larger increase in hardness as well as a smaller increase in resistivity as a function of V content in the film, suggesting ODS films are more effective in strengthening a film when high conductivity is still desired. If the oxide used in the ODS film is also conducting or semi-conducting, the increase in resistivity could be minimized while still gaining the benefits of particle strengthening. ZnO has recently become the subject of many studies due to the potential use as a semiconductor material [100]–[102], and it’s easy availability makes it a promising oxide to increase strength without drastically increasing the resistivity of the film, making the Au-ZnO ODS a likely candidate for creating a hard, wear-resistant Au film that still exhibits high conductivity.

8.2. Experimental Details

Composite thin films of gold and zinc oxide (ZnO) were synthesized by the same method as described by Argibay and coworkers [103], co-deposition using a 10 kV Triad e-beam evaporation system. The source materials were Au pellets with 99.999% purity and ZnO tablets with 99.9% purity, both from Materion Advanced Chemicals. Each material deposition rate was controlled independently via feedback from quartz crystal microbalances (QCM). Films were deposited on single crystal silicon wafers with 250 nm of both Ti and Pt which act as adhesion/barrier layers. Four concentrations were deposited: 0.1, 0.5, 1.0 and 2.0 vol% ZnO up to a thickness of 2µm and compared to pure Au deposited under the same conditions. Electron backscatter diffraction (EBSD) on a Zeiss SEM (LEO 1525) equipped with an EDAX EBSD
system and TSL OIM Analysis 5 software was used to determine the starting microstructure of each of the films. Data was collected using an accelerating voltage of 20 kV, and scan resolution of 0.02 µm/point. Texture and grain size analysis were conducted on 4 scans containing a total of approximately 20,000 grains to ensure the analysis is representative of the whole structure. Confidence index standardization was utilized in determining grain size and orientation. Nanoindentation and nanowear studies were conducted using a Hysitron Triboindenter 900 and UBI respectively to determine the hardness and wear behavior of the films at different concentrations of ZnO. Nanoindentation was performed using a Berkovich diamond tip at a constant load of 1250 µN and loading rate of 200 µN/s with a hold segment of 30 seconds to reduce effects of creep. The wear study was conducted in laboratory conditions with relative humidity less than 40% using a 1µm conical diamond tip utilizing the scanning probe microscopy (SPM) ability of the Hysitron system. Five different normal loads (25 µN, 50 µN, 100 µN, 200 µN, and 400 µN) were applied to the sample surface for four different number of passes (1, 2, 5 and 10), creating 20 different wear conditions. A wear box was created using a raster scanning of the tip with 256 lines per side (forward and reverse, resulting in 512 total line scans per “pass”). There is no obvious indication of material transfer onto the counter face as a result of these wear conditions. Characterization of the wear-track topography was determined using atomic force microscopy (AFM) tapping mode for each wear condition and ZnO concentration. The AFM scans were performed at a rate of 1 Hz, with scanner head scanning in the direction perpendicular to the wear lines. Image size of 1024x1024 pixels and scan area size of 1 x 1 µm² were selected to show details of the surface topography. The scanning probe microscopy (SPM) feature in the Hysitron system was repeated on the 400 µN 10 pass wear box at 1 Hz and a scan size of 80 x 80 µm² to determine wear volume, comparing the average depth of wear from 10 different line scans from the 400 µN
10 pass condition. The nanoscratch technique using the Hysitron 2D transducer and the same 1 µm conical diamond tip used in the nanowear study was also utilized to determine any change in the coefficient of friction (COF) as a result of ZnO concentration. Ten scratch tests were conducted under a constant load of 50 µN and averaged to detect any change in the COF as a result of the addition of ZnO particles. Higher load scratch tests showed similar COF results, but were not exhaustively analyzed within this current study.

8.3. Results

8.3.1. Microstructural Characterization

The as-deposited film structure was investigated using EBSD to determine the effect ZnO particles had on the growth of the film (Figure 8-1). All films are nanograin with a predominately (111) out of plane orientation, which is typical for face-centered cubic physical vapor deposited thin film growth [104]. Since systems tend toward the lowest energy configuration, as the film grows thicker grains with orientations that have the lowest surface energy will overcome the less preferred orientations, leading to the strong texture seen in the pure Au film. Grain size was determined from four EBSD scans placed randomly across a given sample to ensure statistical reliability and random sampling. The most probable grain size for each concentration is presented in Table 8-1 and shows a 35% decrease as a result of the addition of ZnO particles.
Figure 8-1. As Deposited EBSD scans of pure Au (a), 0.1%ZnO (b), 0.5%ZnO (c), 1.0%ZnO (d), and 2.0%ZnO films. Inset shows the (111) pole figures of each scan to show the change in texture of the films as a result of the addition of ZnO, including maximum values. Intensity of (111) normally oriented grains decreases as ZnO particles are introduced into the system.

Table 8-1. Most probable grain size of as deposited Au-ZnO films from EBSD measurements.

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>0.1% ZnO</th>
<th>0.5% ZnO</th>
<th>1.0% ZnO</th>
<th>2.0% ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>204</td>
<td>144</td>
<td>124</td>
<td>133</td>
<td>163</td>
</tr>
</tbody>
</table>

8.4. Effect of ZnO Concentration on Strength of Films

Nanoindentation conducted on the as-deposited pristine films shows an increase in hardness as the ZnO concentration increases (Figure 8-2). Since there is significant pile up in Au systems and some roughness due to sample preparation, the P/S² [105] value (which is comparable to hardness) is also included as a comparison to ensure that this trend is not a result of different roughness or pile up effects. Both analysis techniques show the same trend, increasing strength with increasing ZnO concentration. There is only a slight increase in hardness with the addition of 0.1% ZnO which may or may not be strictly a result of the smaller grain size. However, as the ZnO
concentration continues to increase the hardness also increases without a corresponding decrease in grain size, indicating the presence of other strengthening mechanisms.

![Graph showing the relationship between P/S² and hardness with ZnO concentration.](image)

**Figure 8-2.** Strength increase as a result of different ZnO concentrations determined from nanoindentation with a Berkovich diamond tip. Both P/S² (solid circles) and hardness (open squares) values are provided to show increase in strength is not dependent on roughness or pile-up effects.

8.5. Effect of ZnO Concentration on Wear Behavior

8.5.1. Topographical Response to Different Wear Conditions

Identical wear testing conditions were conducted on each of the samples, followed by AFM scans to determine if there is a marked difference between samples. Examination of these scans focused on observing any reduction in stress-induced grain growth, a problem with current hard Au films. The test conditions resulted in a minimal difference in the wear topography between the pure Au and 0.1% ZnO films. However, the higher concentrations do show a significant change in
their response. Figure 8-3 shows the full matrix of wear tests for pure Au and 2.0% ZnO films. For pure Au, changes in the topography are immediately apparent in even the lowest wear condition. Before the evolution of wear tracks, there seems to be possible grain coalescence in the lower loads and number of passes. The topography of the 2.0% ZnO film, however, is very different. There is less evidence of wear tracks forming at the lower loads and the possibility of grain refinement instead of the grain coalescence seen in the pure Au film.
Figure 8-3. Full wear matrix of pure nanograined Au (a) and 2.0%ZnO (b) with the wear direction indicated on the side of each matrix. Largest difference between the two wear responses is for the low pass and low load conditions, with markedly less wear track formation in the composite film.
A closer comparison of the 50 µN 10 pass wear behavior of each of the films (Figure 8-4) shows a significant increase in wear resistance at ZnO concentrations above 0.1%. Both pure Au and 0.1% ZnO show a similar wear behavior with highly deformed grains while 0.5%, 1.0% and 2.0% not only show reduced wear tracks, but also likely grain refinement. To determine the potential amount of grain refinement, a point count was conducted on the worn film scans (Table 8-2) to determine a rough estimate of the reduction in grain size. Although the resolution of the images makes it hard to distinguish sharp grain boundaries, a distinct difference between the pristine and worn films is apparent. There is not a large difference in the wear behavior between 0.5%, 1.0% and 2.0% ZnO at this condition, indicating there is likely a concentration threshold that allows for the observed stress-induced grain reduction. Of importance to note here is that under no circumstances was any stress-assisted grain growth identified in the higher concentration ZnO containing composite films.

![Figure 8-4. Change in film topography from pristine, as-deposited films (top row) to the 50 µN 10 pass wear condition (bottom row) for each all ZnO concentration films. Note the change in wear behavior once the ZnO concentration gets above 0.5% ZnO, with potential grain refinement occurring as a result of the wear test.](Image)
Table 8-2. Point count of pristine and 50 µN 10 pass AFM scans to approximate grain refinement.

<table>
<thead>
<tr>
<th>Wear Condition</th>
<th>Au</th>
<th>0.1% ZnO</th>
<th>0.5% ZnO</th>
<th>1.0% ZnO</th>
<th>2.0% ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>135</td>
<td>112</td>
<td>112</td>
<td>112</td>
<td>116</td>
</tr>
<tr>
<td>50 µN 10 pass</td>
<td>N/A</td>
<td>N/A</td>
<td>76</td>
<td>85</td>
<td>79</td>
</tr>
</tbody>
</table>

Since actual contact forces for small electrical switches would be in the low load regime, the wear behavior of pure Au and 2.0% ZnO at the lowest load conducted in this study (25 µN), is highlighted in Figure 8-5. Pure Au shows deformation even after the first pass at the lowest loads, with the potential onset of grain coalescence. In contrast, the 2.0% ZnO film shows little to no change in topography at this low load condition, regardless of the number of passes. The 2 pass and 5 pass images are less defined than the other conditions, but this is merely an imaging phenomenon and not an indication of a change in the film.

Figure 8-5. Low load (25 µN) wear behavior of pure Au (top row) and 2.0%ZnO (bottom row) for different number of passes. Pure Au shows significant wear track formation after only one pass whereas the 2.0%ZnO film does not show wear tracks for all number of passes.
According to Johnson’s theory of elastic contact [106], the mean pressure \((p_m)\) produced by a spherical contact with radius \(R\) and load \(P\) on a nominally flat surface is:

\[
p_m = \frac{P}{\pi \left( \frac{3PR}{4E^*} \right)^{2/3}}
\]  

Where \(E^*\) is taken to be 80 GPa, as is typical for Au films. Table 8-3 shows the pressure at which plasticity initiates according to this theory as well as the condition, elastic (E) or plastic (P), at which each film is expected to be in relative to the hardness values determined from nanoindentation. This explains why no plasticity is seen in the 25 μN normal load condition for the 2.0% ZnO film where as significant plasticity is seen in the pure Au film.

<table>
<thead>
<tr>
<th>Normal Load (μN)</th>
<th>Mean Pressure (GPa)</th>
<th>0.1% ZnO</th>
<th>0.5% ZnO</th>
<th>1.0% ZnO</th>
<th>2.0% ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.09</td>
<td>P</td>
<td>P</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>50</td>
<td>2.64</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>E</td>
</tr>
<tr>
<td>100</td>
<td>3.32</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>200</td>
<td>4.19</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>400</td>
<td>5.28</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
</tbody>
</table>

**8.5.2. Changes in Wear Depth as a Result of ZnO Concentration**

SEM images focusing on the edge of the 400 μN 5 pass wear boxes (Figure 8-6) show a reduction in the amount of plastic deformation as the ZnO concentration increases. The Au and 0.1% ZnO show significant plastic deformation at the edge of the wear box with most of the wear
deformation piled up at the sides of the box without flaking. This indicates that these films are much more ductile than the films with a 0.5% ZnO concentration or more. Once the film has a concentration over 0.5%, there seems to be a switch to more brittle behavior as indicated by the evolution of wear debris caused by brittle surface fracture.

![Figure 8-6. SEM images of wear debris produced as a result of the 400 µN 5 pass condition for all compositions. More plastic deformation (and less debris) is seen for the pure Au and 0.1% compositions when compared to higher concentration films.](image)

The wear depth of each film was determined from SPM scans by averaging the depth of material removed from ten different line profiles of the 400 µN 10 pass wear condition. A certain amount of material is pushed to the sides of each wear box, either plastically (as is seen in the Au and 0.1% ZnO films) or as wear debris (as is seen in the higher ZnO concentration films) with additional plastic deformation underneath the wear track [107], [108]. According to the Johnson’s cavity model for indentation plastic zone size, the total depth of the plastic zone is dependent on the normal load applied to the surface and the hardness of the pristine material [106]:

\[
c = \sqrt{\frac{3P}{2\pi\sigma_{ys}}} \tag{8-2}
\]
where \( c \) is the plastic zone size, \( P \) is the indentation load, and \( \sigma_{ys} = H/2.7 \) according to the Tabor relationship [49]. These plastic zone sizes (Table 8-4) are much larger than the wear depths determined from SPM scans of the wear boxes, the difference of which can be seen in Table 8-6, indicating the majority of the plastic deformation occurs underneath the wear track and is not removed as wear debris.

**Table 8-4. Plastic zone size according to the Tabor relationship at different loads**

<table>
<thead>
<tr>
<th>Load (μN)</th>
<th>Au</th>
<th>0.1% ZnO</th>
<th>0.5% ZnO</th>
<th>1.0% ZnO</th>
<th>2.0% ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Plastic Zone Depth (nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>123</td>
<td>121</td>
<td>106</td>
<td>97</td>
<td>96</td>
</tr>
<tr>
<td>50</td>
<td>174</td>
<td>171</td>
<td>151</td>
<td>138</td>
<td>136</td>
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<td>100</td>
<td>246</td>
<td>242</td>
<td>213</td>
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<tr>
<td>400</td>
<td>493</td>
<td>484</td>
<td>426</td>
<td>390</td>
<td>385</td>
</tr>
</tbody>
</table>

Nanoscratch tests conducted at a constant load of 50 μN indicates no change in the coefficient of friction from the addition of ZnO particles (Table 8-5). This shows introducing ZnO particles to the Au film increases the wear resistance due to the increased hardness of the composite films rather than from any change in the coefficient of friction.
Table 8-5. Wear properties of Au-ZnO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>50 μN COF</th>
<th>400 μN Wear Depth (nm)</th>
<th>Plastic Deformation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0.29 ± 0.05</td>
<td>77.3 ±8.5</td>
<td>415</td>
</tr>
<tr>
<td>0.1% ZnO</td>
<td>0.27 ± 0.04</td>
<td>56.8 ± 6.3</td>
<td>427</td>
</tr>
<tr>
<td>0.5% ZnO</td>
<td>0.29 ± 0.04</td>
<td>48.9 ± 6.3</td>
<td>377</td>
</tr>
<tr>
<td>1.0% ZnO</td>
<td>0.27 ± 0.04</td>
<td>29.4 ± 6.3</td>
<td>360</td>
</tr>
<tr>
<td>2.0% ZnO</td>
<td>0.28 ± 0.05</td>
<td>30.5 ± 4.1</td>
<td>355</td>
</tr>
</tbody>
</table>

8.5.3. Mechanical Property Changes From Wear Test

To investigate strength changes as a result of wear testing due to either stress-induced grain growth (resulting in local softening), or storage of dislocations (resulting in local hardening), nanoindentation was conducted on the regions of material subjected to the wear conditions. The same indentation conditions used on the pristine films were used on all wear conditions for each of the samples. The different wear conditions show no significant change in hardness for any of the tested ZnO concentrations (Figure 8-7), indicating there is little to no dislocation storage which would have resulted in hardening, nor any indication of stress-induced grain growth which would have shown film softening. However, as the plastic zone under the indentations made in this study is larger than the depth that would plastically deform during wear, it is possible that the pristine material below the worn material convolutes the effects.
Figure 8-7. Hardness change as a result of different wear conditions for (a) Au, (b) 0.1% ZnO, (c) 0.5% ZnO, (d) 1.0% ZnO, and (e) 2.0% ZnO. Different colors and shapes refer to different number of passes, where the columns refer to normal load applied during testing. Lines refer to the pristine film condition, with one standard deviation on either side indicated by the dashed lines.

8.6. Discussion

The addition of ZnO particles significantly alters the microstructure and mechanical properties of Au films, creating a more robust film that resists morphological changes from sliding wear contact more so than pure nanograined Au films. E-beam co-evaporation of Au and ZnO produces a microstructure with reduced texture and grain size (refer to Figure 8-1), suggesting there is either a change in the through-thickness structure from traditional columnar to more equiaxed grain growth, or the particles are pinning grain boundaries which would result in a more random final orientation. If the ZnO particles act as barriers to grain growth by hindering grain boundary motion as has been seen to occur with other impurities [10], [11], [16], the initial nucleation, likely randomly oriented, will continue to grow without being absorbed by the faster growing (111) grains, resulting in smaller, randomly distributed columnar grains. The increase in brittle behavior (likely from grain boundary embrittlement) seen in SEM micrographs of wear boxes suggests ZnO segregation to the grain boundaries is likely in films with ZnO concentrations
of 0.5% or greater. Either change in growth method can only be verified by cross-sectional microscopy or EBSD examination, which has not yet been conducted for these films.

Reduction in the grain size of the films would lead to a certain amount of additional hardness which is independent of ZnO particles and would following the traditional Hall-Petch relationship [2], [4]:

\[
\sigma_{HP} = \sigma_o + Kd^{-\frac{1}{2}}
\]  

(8-3)

Where \(\sigma_o\) is the intrinsic strength required to move a dislocation, \(K_{HP}\) is the strengthening coefficient (7.9 GPa√nm [1]), and \(d\) is the grain size. According to the grain sizes determined from the EBSD scans, this would lead to an increased hardness (Assuming \(H=2.7\sigma_y\) [49]) for each concentration of ZnO as summarized in Table 8-6.

**Table 8-6. Potential increase in hardness (compared to pure Au film) as a result of observed decreased grain size.**

<table>
<thead>
<tr>
<th>Strengthening Mechanism</th>
<th>ZnO Concentration (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>(\Delta H_{HP})</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Hardness values calculated strictly from the reduction in grain size is significantly less than the increase seen in the composite films, except in the case of the 0.1% ZnO sample, which appears to be hardened primarily by the change in grain size. Therefore, there must be an additional
hardening mechanism due to the ZnO particles creating a precipitation hardening effect which can be described using the Ashby-Orowan model [109]:

$$\tau = \frac{Gb}{2\pi L} \ln \frac{x}{2b}$$  \hspace{1cm} (8-4)

Where $x$ is the average precipitate diameter, $L$ is the surface to surface spacing between particles ($L \propto f^{1/3}$), where $f$ is the volume fraction of ZnO in the grains, $G$ is shear modulus, and $b$ is the burgers vector. Assuming the ZnO particles for each sample are the same diameter, all variables will be constant, with the exception of the spacing between particles. Examination of Figure 8-2 shows a cube-root fit of the P/S$^2$ values as a function of ZnO volume fraction (i.e. proportional to the spacing $L$ assuming spherical particles in a cubic matrix) describes the data well.

The increase in hardness of the nanocomposite films results in a similar increase in wear resistance as was seen from the AFM scans of the worn film topography (Figures 8-4, 8-5, and 8-6) and verified from wear depth determination. Once the ZnO concentration increased beyond 0.1%, additional grain refinement was clearly seen in the 50 μN 10 pass wear condition. Similar behavior has been observed in plastically deformed Cu and Ni reaching grains on the order of 100 nm, albeit starting with a larger grain size, and this behavior has been ascribed to dislocation processes [110], [111].

Nanoindentation experiments showed no apparent change in hardness, indicating no significant strain-hardening or softening from stress-induced grain growth. However, this is not necessarily surprising. Even though apparent grain refinement is seen in some of the wear conditions, the change in grain size is relatively minor and likely to not add significantly to a Hall-
Petch type mechanism. A micro-contact mechanical cycling study conducted on Au thin films showed only a very slight increase in hardness as a result of a half-million cold switching cycles [99], which suggests the wear conditions used in this study could not be enough to produce significant differences in local hardness. The observed consistency in hardness could also be due strictly to the ratio of worn material versus unworn material sampled during indentation. The plastic zone radius during indentation is about 2.12 to 3.5 times the contact radius [48], [112] (in this case a contact radius of 350-500 nm, depending on ZnO concentration), leading to a sample volume several times larger than the expected damage zone caused by wear testing. This leads to a significant amount of the plastically sampled volume coming from the unworn material underneath the damaged layer, and therefore the current experiments cannot unequivocally determine if these films show no hardening due to wear.

8.7. Conclusions

Co-deposition using e-beam evaporation of Au with ZnO particles provides significant hardening over a pure Au film. These particles change the structure of the films during deposition by refining the grain size by approximately 35% and at the same time reducing the (111) preferred orientation of the films by 40-70%. The hardness of ZnO-containing films increased beyond that expected solely from a reduction in grain size, this additional strength is likely due to precipitation strengthening. A wear study was conducted to determine the effect of adding ZnO particles on both topographical changes and the wear depth. The increase wear resistance of films with ZnO concentrations over 0.1% is evident from a reduced wear track, as well as a continuously decreasing wear depth at a given condition. Possible grain refinement during wear was also observed in some of the lower load and pass number wear conditions; no stress assisted grain growth was observed in these films. Nanoindentation of the wear-tested films showed no
significant difference in hardness as a result of the different wear conditions applied in this study, further proving the reliability of these films as a robust material for hard Au coatings in light of the previously reported small changes in electrical resistance observed in these films [103], [113].

8.8. Acknowledgements

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CHAPTER 9: Thermal and Electrical Stability of Au-ZnO films

Abstract

The addition of ZnO particles to Au films deposited using physical vapor deposition leads to a significant grain refinement; the addition of only 0.1 vol% of ZnO reduces the as-grown grain size by over 30%. The hardness of the as-grown films doubles with 2% ZnO additions, from 1.8 to 3.6 GPa as measured by nanoindentation. Upon annealing at 350 °C, films with ZnO additions greater than 0.5% show no significant grain growth while pure gold and smaller additions do exhibit grain growth and subsequent mechanical softening. Films with 1% and 2% ZnO show a decrease in electrical resistivity and no change in hardness after annealing. The ZnO is co-deposited with Au, and a model accounting for both changes in the interface structure between the dispersed particles and the Au matrix appears to capture both the mechanical and electrical resistivity. The addition 1-2% ZnO provide a method to create mechanically hard and thermally stable films with a resistivity less than 80 nΩ-m.

9.1. Introduction

Electrical contacts typically undergo numerous loading cycles in the course of their effective life. This cyclic loading can cause considerable degradation of mechanical and electrical properties from grain growth [1–5] and micro-welding [6–8]. Traditionally gold is used for electrical contacts due to its high electrical conductivity and resistance to corrosion, oxidation and other environmental effects. However, pure gold is a low strength material that often is not able to withstand contact loading for the number of cycles required of these devices. Additionally, the high currents that are passed through the switch can lead to micro-welding, followed by detrimental deformation when the contact is broken [114], [115]. In order to increase the lifetime
of these contacts, numerous different techniques are used to increase the wear resistance by increasing the hardness of Au: grain size reduction [1]–[4], addition of solid solution impurities [3], [8]–[11], deposition of nanolaminate structures [5]–[7], or the introduction of small oxide particles [9], [12], [13]. However, all of these strengthening techniques can substantially increase the resistivity of Au.

One of the most common ways to increase the strength of a material is to reduce the grain size. However, many materials have shown evidence of undergoing stress-induced grain growth, which leads to a decrease in strength, making this strengthening mechanism temporary. Studies conducted on nanocrystalline materials [21-22] suggest this type of grain growth can be attributed to grain-boundary sliding, diffusion, and grain rotation; therefore, if these are reduced, grain growth should be slowed or even stopped. Impurities introduced into the system can stabilize nanocrystalline microstructures by reducing grain boundary mobility and thereby stopping grain growth [11], [16]–[18]. Therefore, solid-solution strengthening, which has been used as a strengthening technique in gold systems, [3], [116], [117], could also potentially reduce stress-induced grain growth. In these types of systems, strength increases with the square root of impurity concentration, but is highly dependent on the type of impurity and its solubility in the host material [56], [109].

Another way to increase the strength of gold films is via oxide dispersion strengthening (ODS), where small oxide particles act as precipitates to block dislocation motion [30]. One aspect of the ODS technique that shows great promise is the ability to increase hardness without greatly affecting conductivity [12]. ODS material, Au-V$_2$O$_5$, showed both a larger increase in hardness coupled with a smaller increase in resistivity as a function of V content when compared to Au-V solid-solution. This suggests that the ODS films are more effective in strengthening a film when
high conductivity is still desired, which should lead to increased wear resistance, grain boundary
pinning, and a comparatively smaller reduction in electrical conductivity.

The drawback to adding any impurities to pure materials is the disruption of the electrical
pathway. All three strengthening mechanisms (grain size reduction, solid-solution strengthening,
and oxide dispersion strengthening) lead to an increase in resistivity by the same general
mechanism, electron scattering at the defect site [119], [120]. Electrical conductivity in metals
relates directly to the mean free path, \( \lambda \), of the electron. For the case of grain boundary scattering
in very small grains, \( \lambda \) is approximately equal to the size of the grain; therefore, small-grained
materials have higher resistivity. Similarly, a disruption in the regular crystal structure of the metal
leads to local strain fields that also disrupt the path of electrons, causing the resistivity to increase.
This is seen in both solid solution and precipitation strengthened metals. The study conducted by
Bannuru et. al on Au-V and Au-V\(_2\)O\(_5\) show that the solid-solution Au-V has an electrical
resistivity four times that of the ODS film with the same V content, suggesting solid-solution
atoms cause more electron scattering than oxide dispersion strengthened material with the same
volume percentage [12]. Additional causes of increased resistivity include temperature, vacancies,
and dislocations. Since resistivity is an additive property [119], a combination of different types
of strengthening mechanisms will continuously increase the resistivity of the material. The ODS
system used in this investigation has shown in previous studies to lead to a reduced grain size over
pure gold films as well as particle strengthening when compared to a pure Au film [121], leading
to scattering from both grain boundaries as well as oxide particles.
9.2. Experimental Details

Au-ZnO ODS thin films were deposited on single crystal silicon wafers (t = 550µm and biaxial elastic modulus, $M = 180.5$ GPa) using dual source e-beam evaporation to a thickness of approximately 2 µm as was previously described by Argibay and coworkers [103]. Titanium and platinum (250 nm each) were used as adhesion/diffusion barrier layers. Four concentrations were investigated in this study: 0.1, 0.5, 1.0 and 2.0 vol% ZnO and compared to pure Au deposited under the same conditions. XRD data were collected with a PANalytical Empyrean X-ray diffractometer equipped with a PIXcel3D detector and operated at 45 kV and 40 kA using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The patterns were collected in the 2θ range of 10 to 90°, with a step size of 0.026°, and exposure time of 300 seconds. Diffraction pattern processing was performed using the software package HighScore Plus®. Rietveld refinement analysis of the patterns show lattice compressive percent strains to be 0.00, 0.081, 0.052, 0.065, and 0.058 for pure Au, 0.1%ZnO, 0.5%ZnO, 1.0%ZnO, and 2.0%ZnO respectively.

Wafer curvature experiments were conducted on a custom machine designed and built at the Erich Schmidt Institute in Leoben, Austria. The wafer curvature chamber was put under vacuum and allowed to come to pressure for at least 20 minutes, which results in a base pressure of approximately $10^{-4}$-$10^{-5}$ Torr. Initial curvature readings were taken at room temperature (25°C), and the stresses calculated from curvature results were offset by the initial internal stress calculated from lattice strain measurements determined by the Rietveld refinement of the XRD scans. Each sample was cycled up to a temperature of 350°C and back to room temperature at a rate of 0.17°C/s for one cycle, after which electron backscatter diffraction (EBSD) using a Zeiss SEM (LEO 1525) system was conducted to determine microstructural changes. To determine the stability of the microstructure, three concentrations (pure Au, 0.5%ZnO, and 2.0%ZnO) were then cycled an
additional four times and examined once again using EBSD. All changes in microstructure due to annealing were determined using EBSD with an accelerating voltage of 20 kV, and scan resolution of 0.02 µm/point and analyzed using TSL OIM Analysis 5 software. Confidence index standardization was utilized in determining grain size and orientation.

Nanoindentation with a Hysitron TI 950 Triboindenter was performed on as-deposited and annealed samples using a Berkovich diamond tip at a constant load of 1250 µN and loading rate of 200 µN/s with a hold segment of 30 seconds to reduce effects of creep. Fifteen indents were performed at a spacing of 15 µm. Four-point probe resistance measurements were conducted before and after annealing using a Jandel multi height, inline probe with a probe spacing of 1 mm. A 10 mV voltage was applied to the outer probes and the resulting current recorded from at least 3 different measurements. The resulting resistivity values were calculated using thickness measurements determined from scanning electron microscope (SEM) scans and using geometry modified sheet resistance to account for edge effects due to the small sample size [122].

9.3. Wafer Curvature

Wafer curvature experiments were conducted on each of the films to determine the stability of this ODS system under high stress and temperature conditions. The films were cycled under the delamination temperature (≈400 °C), insuring that any plasticity is a result of microstructural changes or typical yielding expected in metallic films and not a result of delamination. Stress-temperature curves were calculated using:

$$\sigma_f = \frac{E_s t_s^2}{6(1 - \nu)t_f R}$$  \hspace{1cm} (9-1)
Where \( E_s \) is the substrate biaxial modulus, \( t_s \) is the substrate thickness, \( \nu \) is the film Poisson’s ratio, \( t_f \) the film thickness, and \( R \) is the measured curvature. All substrates were approximately 550 \( \mu \text{m} \) thick, though exact substrate and film thicknesses were determined using SEM images for accurate stress measurements.

### 9.4. Stress-Temperature Relationship

Stress-temperature results from the first 350°C wafer curvature cycles are shown in Figure 9-1. Initial as-deposited stress measurements calculated from XRD lattice strain measurements are used as initial film stress and have values of 0 MPa, 64.0 MPa, 41.1 MPa, 51.4 MPa and 45.8 MPa for pure Au, 0.1\%ZnO, 0.5\%ZnO, 1.0\%ZnO and 2.0\%ZnO respectively. The heating segment of all the curves follow approximately the same slope (\( M_{\text{heating}} \)) until initial yielding, indicating the elastic modulus is independent of ZnO concentration. After the initial elastic portion of the heating curve, the stress slowly levels out as the temperature increases, indicating the start of stress relaxation brought on by diffusion-based creep, dislocation motion, grain growth, or phase transformations [123]–[125], most likely a mixture of multiple mechanisms depending on the stress and temperature state [126]–[128]. The stress at the onset of plasticity (\( \sigma_{\text{min}} \)) is unique for each film and is indicative of the strength of the film, with increasing strength for increasing ZnO content. However, since the yield strength is a temperature sensitive property these strengths cannot be directly compared to the room temperature nanoindentation results. As the temperature increases it is easier to activate thermally controlled deformation processes; therefore, the onset of plasticity is a coupled stress-temperature response with stronger films yielding at both higher stresses as well as higher temperatures. After the onset of plasticity, all of the films undergo a similar amount of stress relaxation (\( \Delta \sigma_p \)) (within 5\%) indicating the same deformation mechanisms are active in all systems and independent of ZnO concentration. As cooling begins, the stress rises
at approximately the same rate, once again indicating the same thermally activated deformation processes are occurring. As the temperature drops further, the slopes ($M_{\text{cooling}}$) begin to deviate with Au, 0.1%ZnO and 0.5%ZnO following similar paths and 1.0% and 2.0%ZnO following another. The change in the cooling profile suggests a change in the microstructure of the film is occurring. Specifically, if significant grain growth occurred in the Au, 0.1%ZnO, and 0.5%ZnO films, the strength and strain-hardening ability would be reduced, leading to a shallower slope. Table 9-1 summarizes the differences between all the five curves, with specific changes in bold.

![Figure 9-1](image)

**Figure 9-1.** Stress-temperature profiles for Au-ZnO films obtained using wafer curvature technique. Dotted lines refer to single cycle run on as deposited films of Pure Au (red), 0.1%ZnO (orange), 0.5%ZnO (green), 1.0%ZnO (blue), and 2.0%ZnO (black). Solid lines are additional cycles conducted on pure Au, 0.5% ZnO, and 2.0%ZnO samples to determine microstructural stability. Additionally, portions of the curves corresponding to values referred to in Table 1 are labeled.

Three of the films were thermally cycled for an additional 4 times to determine the stability of the microstructure after one thermal cycle. Pure Au, 0.5%ZnO, and 2.0%ZnO were chosen since
these three concentrations showed characteristics of all films, with 0.1%ZnO and 1.0%ZnO performing similarly to pure Au and 2.0%ZnO, respectively. The curves were offset so that the starting stress in the films is the same as the ending stress from the first cycle. Figure 9-3 shows the stress-temperature response from multiple thermal cycles to 350°C. Pure Au undergoes one additional 60 MPa increase in tensile stress after the second cycle, however, the overlapping loops seen in the last three cycles indicates a stable microstructure. The 0.5%ZnO film also undergoes an additional 60 MPa stress increase after the second cycle; this film continues to raster after each additional cycle suggesting continued grain growth. This evolving stress-temperature profile suggests that the microstructure is also evolving with each additional cycle. The 2.0%ZnO more or less exhibits an elastic response through the entire temperature regime, with each additional cycle overlapped on the previous one, indicating a stable microstructure.

Table 9-1. Summary of wafer curvature results for all film concentrations

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>0.1%ZnO</th>
<th>0.5%ZnO</th>
<th>1.0%ZnO</th>
<th>2.0%ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>171.02</td>
<td>143.65</td>
<td>159.80</td>
<td>189.76</td>
<td>240.61</td>
</tr>
<tr>
<td>Minimum</td>
<td>-143.79</td>
<td>-209.04</td>
<td>-221.55</td>
<td>-255.08</td>
<td>-255.31</td>
</tr>
<tr>
<td>σ at 350°C</td>
<td>-92.54</td>
<td>-146.14</td>
<td>-161.75</td>
<td>-199.59</td>
<td>-196.08</td>
</tr>
<tr>
<td>Δσ_p</td>
<td>-51.25</td>
<td>-62.90</td>
<td>-59.80</td>
<td>-55.49</td>
<td>-59.22</td>
</tr>
<tr>
<td>M Heating</td>
<td>-1.27</td>
<td>-1.55</td>
<td>-1.43</td>
<td>-1.37</td>
<td>-1.30</td>
</tr>
<tr>
<td>M Cooling (E)</td>
<td>-1.74</td>
<td>-1.98</td>
<td>-1.70</td>
<td>-1.80</td>
<td>-1.94</td>
</tr>
<tr>
<td>M Cooling (P)</td>
<td>-0.83</td>
<td>-0.67</td>
<td>-0.73</td>
<td>-1.15</td>
<td>-1.27</td>
</tr>
<tr>
<td>Δσ_anneal</td>
<td>231.82</td>
<td>207.83</td>
<td>285.19</td>
<td>265.26</td>
<td>314.41</td>
</tr>
</tbody>
</table>
9.4.1. Microstructural Evolution

To examine microstructural changes as a result of the wafer curvature experiment, EBSD was used to investigate the grain size distribution and texture of the films in their as-deposited condition and after thermal cycling (Figure 9-2). The starting microstructure for each film (top row) shows predominantly (111) textured, nanocrystalline grains; however as ZnO particles are introduced into the system, both the texture strength and grain size decrease significantly with grain size reducing by 35% and texture strength dropping by 40-70%. After one thermal cycle to 350°C (bottom row), drastic grain growth is seen for the pure Au and 0.1%ZnO conditions, with grain sizes increasing by over an order of magnitude. Additionally, both films develop a significant number of annealing twins, doubling the number of Σ3 boundaries. Both 1.0%ZnO and 2.0%ZnO show little to no grain growth as a result of this particular annealing condition. The 0.5%ZnO sample develops a bimodal distribution with approximately 60% of the original nanocrystalline grains along with a few larger grains that also show signs of twinning. Twinning as a mode of strain reduction is commonly found in materials with low stacking fault energy [129], [130] with the potential to compensate for up to 16.7% in-plane strain by creating a set of orthogonal twins [130]. This twinning mechanism could provide one explanation for the change in cooling slope seen in the pure Au, 0.1%ZnO, and 0.5%ZnO stress-temperature curves.
Figure 9-2. EBSD texture map of as-deposited (a) pure Au, (b) 0.1%ZnO, (c) 0.5%ZnO, (d) 1.0%ZnO, and (e) 2.0%ZnO and annealed (f) pure Au, (g) 0.1%ZnO, (h) 0.5%ZnO, (i) 1.0%ZnO, and (j) 2.0%ZnO. Microstructures of films with higher concentrations of ZnO are significantly more stable than the lower concentration films.

After repetitive cycling of the pure Au, 0.5%ZnO, and 2.0%ZnO film, the microstructures were once again examined using EBSD. Figure 9-3 highlights the evolution of the grain size distribution from the as-deposited condition (solid line), after undergoing one thermal cycle (dashed line), and after five thermal cycles (dotted line) for pure Au, 0.5%ZnO, and 2.0%ZnO. Pure Au shows an order of magnitude increase in grain size after only one thermal cycle, but only a very slight additional increase after five thermal cycles, indicating grain growth is complete after the initial 350°C anneal. After the first cycle of the 0.5%ZnO film, an obvious bimodal distribution develops consisting of one mode with the original grain size and the second mode with diameters approximately 10 times larger (with approximately a 3:1 ratio of small grains to large grains).
However, there is additional grain growth during the five thermal cycle where the fraction of small grains is drastically reduced and the ratio of small grains to larger grains is closer to 1:1. This continually evolving grain size indicates that this concentration of ZnO is not sufficient to completely pin the grain boundaries. Finally, there is virtually no change in grain size distribution for the 2.0%ZnO films regardless of the number of cycles in this study, which shows a concentration of 2.0 vol% ZnO is enough to successfully pin the grain boundaries to stop grain growth. Therefore, it is apparent that there is a minimum concentration of ZnO required in the nanocomposite to successfully prohibit grain growth, somewhere between 0.5%ZnO and 2.0%ZnO.

Figure 9-3. Evolution of grain size distribution of pure Au (top), 0.5%ZnO (middle), and 2.0%ZnO films (bottom) as a result of one (dashed line) and five (dotted line) thermal cycles showing significant grain growth in pure Au sample and a stable grain size in 2.0%ZnO sample, with accompanying EBSD scans (right).
9.5. Mechanical and Electrical Response of As-Deposited and Annealed Films

9.5.1. Annealing Effect on Hardness

Nanoindentation of both the as-deposited and annealed conditions (Figure 9-4) was conducted to determine the change in hardness as a result of ZnO concentration and their reaction to a coupled stress-thermal cycling. As-deposited films show a non-linear increase in hardness with the addition of ZnO particles likely due to a combination of strengthening methods. As was discussed previously, the nanocomposite films show as-deposited grain sizes approximately 35% smaller than pure Au (see Figure 9-2), which would result in a certain amount of increased hardness strictly a result of the smaller grain structure [2], [4]. The remaining increase in hardness is likely due to oxide particle strengthening which can be modeled according to the Ashby-Orowan model [109] and follows a -1/3 relationship with volume fraction [131].

![Figure 9-4. Nanoindentation hardness of as deposited (solid circles) and after annealing at 350°C (open circles) films. Pure Au, 0.5%ZnO and 2.0%ZnO were cycled 5 times while the other concentrations only underwent one thermal cycle.](image-url)
Previous energy dispersive spectroscopy (EDS) scans conducted on 5.0%ZnO films show approximately 20% of the Zn deposits at the grain boundaries, with the remaining dispersed throughout the grains. Assuming the percentage of ZnO deposited at the grain boundaries is consistent for low concentration nanocomposites, the volume fraction of ZnO available for particle strengthening, $x$, is actually 0.8$f$. Combining Hall-Petch and hard precipitate strengthening with the base strength of pure Au leads to a combined hardness model such that:

$$H_{\text{Au-ZnO}} = 2.7 \left[ \sigma_o + K_{\text{HP}} \left( d_{\text{Au-ZnO}}^{\frac{1}{2}} \right) + 2 \frac{Gb}{2\pi L} \ln \frac{2r}{2b} \right]$$  \hspace{1cm} (9-2)

Where $\sigma_o$ is a combination of the stress required to move a dislocation in the Au lattice and the indentation size effect which is typically seen in nanoindentation experiments, $K_{\text{HP}}$ is the grain boundary strengthening coefficient, $d$ is grain diameter, $G$ is the shear modulus, $b$ is the burgers vector, $L$ is the surface to surface particle spacing, and $r$ is the average particle radius.

Both the particle diameter and $\sigma_o$ are assumed to be independent of concentration and since the actual values are unknown, are used as fitting parameters when minimizing the combined least squares model. The grain-boundary strengthening component was calculated using the grain size distributions from the EBSD scans rather than strictly using the average grain size to incorporate wide and bimodal distributions found in annealed films. Using OIM software, area fractions of grain diameters were determined using 20 bins, included twins but excluded edge grains. The resulting hardness contribution from Hall-Petch strengthening was then calculated according to the relationship:

$$H_{\text{H-P}} = 2.7 K_{\text{HP}} \sum a_f \left( d_{\text{Au-ZnO}}^{\frac{1}{2}} \right)$$  \hspace{1cm} (9-3)
Where $a_f$ is the area fraction of grains with grain diameter, $d$. A study conducted by Emery [132], [133] on thin, small grained Au films showed a deviation from Hall-Petch behavior at grain sizes lower than 790 nm, with a strengthening coefficient lower than that observed in coarse grain films. Therefore, grains that are larger than 790 nm have a $K_{HP}= 7.9 \text{ GPa} \times \text{nm}^{1/2}$ while the coefficient for grains smaller than 790 nm was used as another fitting parameter. Figure 9-5 shows the contribution from each parameter according to the least squares fit for the combined as-deposited and annealed model with a particle diameter of 4.1 nm, $K_{HP}=5.13$ when grain size is below 790 nm and $\sigma_o= 223 \text{ MPa}$.

![Figure 9-5](image)

**Figure 9-5.** Comparison of experimental and predicted hardness based on the model presented in Equation 9-2, with specific contributions separated into intrinsic ($\sigma_o$), grain-boundary (Hall-Petch), and precipitation (Ashby-Orowan) strength components.

### 9.5.2. Annealing Effect on Resistivity

The electrical changes of each of the films as a result of annealing were investigated using the four-point probe technique to determine sheet resistance ($R_s$) of the films. From this value, the
resistivity was calculated based on the film thickness (verified from SEM cross-sectional measurements) and the geometric correction for sample size [122]. As-deposited resistivity of these Au-ZnO films follow an expected trend where increasing ZnO concentration creates increasing resistance in the film due to a larger amount of scattering from interactions with particles. However, the resistivity of the annealed films show an interesting phenomenon where ODS films are actually decreasing in resistivity, indicating a change in the microstructure which is dependent on concentration and leads to a decrease in the amount of scattering.

![Figure 9-6. Calculated resistivity based on four-point probe measurements of as-deposited (solid circles) and annealed (open circles) films. Samples with higher concentrations of ZnO particles show a reduction in resistivity after annealing at 350 °C.](image)

Studies have shown that internal stresses can also lead to electron scattering and an increase in resistivity [134], [135]. Traditional methods of second phase interactions on the resistivity of a material is merely dependent on the volume fraction of the second phase and has no relationship
to the particle spacing, leading to an inaccurate representation of resistivity due to fine disperse particles. Therefore, a new model is suggested which treats fine particles similar to solid solution atoms, assuming a random dispersion. Since the stress field around ZnO particles leading to electron scattering is presumably affecting the resistivity in a similar way as solid-solution atoms, the same basic relationship is assumed for particle strengthening where the coefficient is dependent on the interface structure. A resistivity model incorporating thermal vibrations [119], grain boundary scattering [136], scattering due to internal stresses [134], and interactions with ZnO particles [119] was developed resulting in a general equation for an ODS Au film:

$$\rho_{Au-ZnO} = \rho_{Au} [1 + \alpha_o (T - 273)] \left(3 \left[\frac{1}{3} - \frac{1}{2} \alpha + \alpha^2 - \alpha^3 \ln \left(1 + \frac{1}{\alpha}\right)\right]\right)^{-1}$$

$$+ C_{ZnO} [x(1 - x)] + C_\sigma (\sigma_{ann})$$

(9-4)

$$\alpha = \frac{\lambda}{d \left(1 - R\right)}$$

Where $\lambda$ is the mean free path of the electrons (44 nm at 298K), $d$ is the grain diameter according to EBSD scans, $R$ is the probability of reflection at a grain boundary, $x$ is the volume fraction of deposited Zn in the grains, and $C_{ZnO}$ is the scattering coefficient due to ZnO particles in the matrix. The grain boundary scattering contribution was calculated based on a similar area fraction approach as was used to calculate the Hall-Petch strengthening component in Section 4.1. However, since twin boundaries are an ordered boundary and would not contribute to much electrical scattering [137], they are removed from grain size calculations. As was noted earlier, approximately 20% of Zn deposited at the grain boundaries during growth, therefore it is assumed
that the probability of reflection at the grain boundaries in the higher ZnO containing films would be larger. Since previous investigations on resistivity in nanocrystalline Au films shows $R$ values ranging from 0.35-0.47, a linear relationship for $R$ is assumed, ranging from 0.35-0.43, depending on the ZnO concentration. $C_{ZnO}$ (before and after annealing) and $C_{\sigma}$ are used as fitting parameters since the relationship due to these contributions is not known. Figure 9-8 shows a summary of the calculated film resistivity components determined from the best fit of this model.

![Graph showing resistivity comparison](image)

**Figure 9-7.** Comparison of experimental and predicted resistivity of as-deposited (a) and annealed (b) films based on the model suggested in Equation 3, with specific contributions from thermal vibrations, grain-boundary scattering, internal stresses created during annealing ($\sigma_{\text{ann}}$), and precipitate interactions.
9.6. Discussion

The current study shows there is a minimum concentration of ZnO required to successfully prohibit grain growth due to coupled stress-temperature conditions. Due to the gradual increase in grain size for 0.5% ZnO and the stable microstructure seen in 2.0% ZnO, this threshold lies somewhere between the two. Since stress-induced grain growth is typically due to grain rotation, grain boundary sliding and diffusion, the increasing amount of ZnO particles found at the grain boundaries is likely decreasing these terms. ZnO particles in the grains are also likely resisting grain boundary migration similar to how they block dislocation motion. Since hardness measurements of annealed films drop directly with grain size, this suggests there is no change in particle spacing due to Oswald ripening or diffusion to the grain boundaries. This isn’t surprising since diffusion would be extremely slow at these temperatures. This suggests that the change in resistivity due to annealing is a change in the interaction of the ZnO particles with the Au matrix and is dependent on ZnO concentration. If the interface between ZnO particles and the Au matrix start off as semi-coherent, similar to those seen in Guinier-Preston zones \[138\] in solid-solution strengthened metals, there would be a significant local strain field around the particles which could lead to significant electron scattering. As the films undergo a stress-temperature coupled annealing cycle, dislocations can move to relieve the strain caused by the semi-coherent interface, changing it to an incoherent interface which has a much lower strain field and would lead to less electron scattering, thus reducing the resistivity of the film. This also suggests that the change in resistivity is dependent on the ZnO concentration, which is apparent in the present investigation. Additionally, the switch from semi-coherent to fully incoherent interface around the particles would not result in a drastic change in particle strengthening since particle size and spacing is constant which is also seen in these results. Figure 9-8 shows a summary of the changes in both
hardness and resistivity as a result of the present annealing study. Specifically, increasing ZnO concentrations provide a more stable microstructure that retains strengthening benefits while maintaining high conductivity. The decreasing resistivity as a result of annealing is an added benefit, not generally seen in other systems.

![Graph showing change in mechanical and electrical properties vs. ZnO concentration](image)

**Figure 9-8.** Summary of the relative change in mechanical and electrical properties for the different concentrations of ZnO present in the films as a result of the annealing conditions investigated in this study. Higher concentration films show a minimal change in strength corresponding to a reduction in resistivity as a result of these annealing conditions.

### 9.7. Conclusions

Wafer curvature experiments conducted on Au-ZnO thin films were utilized to explore the temperature-stress response of films with different concentrations of ZnO. Stress-temperature profiles show increasing yield with increasing ZnO concentration as is expected from oxide dispersion strengthening. A change in the cooling profile for the lower concentration films suggests a change in the microstructure, which is verified from EBSD characterization. All films
show an increase in tensile stress as a result of thermal cycling. EBSD characterization of the cycled films shows an order of magnitude increase in grain size for pure Au and 0.1%ZnO films as well as a significant twinning. Films containing higher concentrations of ZnO showed no significant grain growth as a result of these thermal cycles. Multiple cycling of pure Au, 0.5%ZnO and 2.0%ZnO show stable microstructures for pure Au and 2.0%, with no additional grain growth. However, the 0.5% ZnO continues to show additional grain growth which suggests the concentration threshold to stop grain growth is somewhere between 0.5% and 2.0%ZnO. Nanoindentation experiments conducted on as deposited and annealed films show increasing hardness with ZnO concentration while the drop in hardness observed following annealing is almost completely attributed to the resulting grain growth. Four-point probe resistivity measurements showed increasing resistivity as ZnO concentration increases, as is expected through traditional models. However the annealed films showed a significant drop in resistivity, which is attributed to a change in the particle-matrix interface structure.

A model that generally describes the hardness and sheet resistance has been developed based on the assumption that the impact of nm-scale ZnO precipitates on the mechanical and electrical behavior of Au films is most likely dominated by a transition from semi-coherent to incoherent interfaces. The presence of ZnO and/or excess Zn in solid solution at grain boundaries refines the grain size during growth as well as limits grain growth during annealing. The final result in the two-phase films is that dilute additions of ZnO to Au produce electrical contact surfaces that are more microstructurally stable and mechanically robust than pure gold while only moderately increasing the resistivity over pure gold.
9.8. Acknowledgements

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CHAPTER 10: Conclusions

Nano-scale strengthening mechanisms for thin films were investigated for systems that are governed by two different strengthening techniques: nano-laminate strengthening and oxide dispersion strengthening. Nanoindentation, micro-pillar compression, and micro-tensile investigations on nano-scale metallic multilayers (NMM) were conducted at both room temperature and elevated temperature testing conditions to investigate changes in deformation mechanisms at different operating temperatures. Nanoindentation, nano-wear, annealing, and electrical tests were conducted on the ODS Au-ZnO films to investigate the response of these films at different concentrations and probe the overall stability of the system as a function of ZnO concentration.

Both room temperature and elevated temperature response of the Cu/Ni/Nb tri-layer NMM films were investigated to determine layer thickness response on the deformation mechanisms. Through both nanoindentation as well as micro-pillar compression tests, tri-layer NMM films with smaller layer thicknesses show a greater strain-hardening ability and a greater hardness than those with larger layer thicknesses. A similar tri-component bi-layer system (Cu-Ni/Nb), which removed the coherent interface from the film, verified the hypothesis that tri-layer systems have a unique capability of increased strain-hardening ability due to the presence of a coherent interface. Micro-pillar compression testing of both Cu/Ni/Nb films and Cu-Ni/Nb films showed similar temperature sensitivity responses, where smaller layer thicknesses exhibit a smaller relative strength drop when tested at elevated temperatures. Since this phenomena holds true for both tri-layer and bi-layer films, the incoherent interface dictates the elevated temperature response and is not a result of alloying at the Cu/Ni interface. Additionally, both nanoindentation as well as micro-pillar compression tests show an increase in the room temperature strength of these multilayer films after
annealing suggests a change in microstructure has occurred, unlike that seen in other multilayer systems. X-ray diffraction experiments proved that the annealing conditions applied here did not result in complete alloying of the Cu-Ni.

Co-deposition of Au with ZnO particles provides an ODS films which shows significant hardening over a pure Au film. These particles have shown to change the structure of the films during deposition by refining the grain size and reducing the (111) preferred orientation. Since the hardness of ZnO-containing films increased beyond that expected solely from a reduction in grain size, this additional strength is due to precipitation strengthening. Wear studies on Au-ZnO films showed decreasing wear depth with higher ZnO concentrations. A threshold for stress-induced grain-refinement as opposed to grain growth is seen at ZnO concentrations greater than 0.1 vol%. Thermal cycling of these films show significant grain growth in the lower concentration films whereas the higher concentrations maintain the as-deposited microstructure through several thermal cycles. The threshold for microstructural thermal stability is at least 1.0 vol% ZnO. Additionally, nanoindentation experiments conducted on as-deposited and annealed films show increasing hardness with ZnO concentration while the drop in hardness observed following annealing is almost completely attributed to the resulting grain growth. However, four-point probe resistivity measurements on annealed films showed a significant drop in resistivity for the higher concentration ZnO films, which has been suggested to be a result of a change in the particle-matrix interface structure. A model that connects the hardness and resistivity of these films as a function of ZnO concentration has been developed based on the assumption that the impact of nm-scale ZnO precipitates on the mechanical and electrical behavior of Au films is most likely dominated by a transition from semi-coherent to incoherent interfaces. The presence of ZnO at grain boundaries limits grain growth during annealing while not significantly affecting the resistance of
the film. In general, dilute additions of ZnO to Au produce electrical contact surfaces that are more microstructurally stable and mechanically robust than pure gold while only moderately increasing the resistivity over pure gold.
REFERENCES


