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X-Ray Diffraction Studies of Forward and Reverse Plastic Flow in Nanoscale Layers During Thermal Cycling

Michael D. Gram^a, John S. Carpenter^{a,b}, E. Andrew Payzant^c, Amit Misra^d
and Peter M. Anderson^{a*}

^aMaterials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA; ^bMST-6: Metallurgy, Los Alamos National Laboratory, Los Alamos, NM 87545, USA; ^cCenter for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA; ^dMPA-CINT: Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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The biaxial stress–strain response of Cu and Ni layers within Cu/Ni nanolaminates was determined from in-plane X-ray diffraction during heating/cooling. Thinner (11 nm) Cu and Ni layers with coherent, cube-on-cube interfaces reached ~1.8 GPa (Cu) and ~2.9 GPa (Ni) without yielding. Thicker (21 nm) layers with semi-coherent interfaces exhibited unusual plastic phenomena, including extraordinary increases in stress during early yielding, reverse plastic flow at modest (~12%) unloading and evidence that plastic flow in Cu layers can reduce the flow strength of adjoining Ni layers. Estimates of dislocation line energy, pinning strength, net interfacial dislocation density and hardness are provided.

Keywords: Nanolaminates, X-Ray Diffraction, Interface Properties

For metallic laminates, the bulk, composite response rather than that of the individual constituents is often measured. Examples include nanoindentation,[1–3] micropillar compression,[4–6] and tensile testing.[7–9] Yet, a better understanding of the constituents—particularly in confined geometries—is needed to foster intelligent multilayer design. X-ray diffraction provides an established method to measure the evolution of lattice strains during deformation. It has been used *ex situ* for pre and post micropillar compression testing [10] and *in situ* for tensile testing of freestanding Cu/Nb multilayer thin films.[11] Grazing incidence X-ray diffraction provides direct measurement of in-plane lattice parameters, from which in-plane elastic strain (and stress) can be determined.[12]

This study utilizes differences in the thermal expansion coefficient of the Si substrate and metallic layers to investigate deformation behavior. Monitoring changes in the curvature of film-on-substrate assemblies during heating and cooling can furnish the in-plane stress–strain response of single layer films.[13–15] However, the average film response is obtained rather than that of the individual constituents. Instead, we use *in situ* X-ray diffraction during heating/cooling. This method

has been used to study single-layer metallic films on substrates.[16–19] For Al [18] and Cu films [20] on Si substrates, it provides values of film stress comparable to those from curvature measurements. Despite this extensive work, *in situ* X-ray diffraction has not been reported for multilayers.

The Cu/Ni multilayer films used in this and previous studies [21,22] were grown at the Center for Integrated Nanotechnologies (CINT) at Los Alamos National Laboratory. Nanolaminate films were sputtered on HF-cleaned (100) Si substrates. After initial deposition of a 100 nm thick single-crystal Cu buffer layer, layers were alternated to a total film thickness of 5 μm , then capped with a final Cu layer. Low deposition rates (5–6.5 $\text{\AA}/\text{s}$) at ambient temperature and pressures of 6.5 and 5 Torr were used for Cu and Ni, respectively. Selected area diffraction [22] and X-ray diffraction reveal (100) or ‘cube-on-cube’ epitaxial layers. The layers have columnar grains with low-angle grain boundaries, giving a single-crystal-like texture with an in-plane orientation relation $[001]_{\text{Cu,Ni}} \parallel [011]_{\text{Si}}$.

In-plane X-ray diffraction from a grazing incidence was performed during heating and cooling of Cu-11 nm/Ni-11 nm nanolaminates with coherent

*Corresponding author. Email: anderson.1@osu.edu

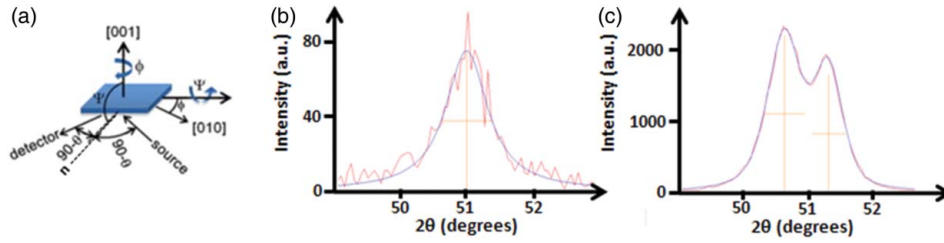


Figure 1. (a) Film geometry for X-ray diffraction at a grazing incidence; (b) measured 2θ diffraction pattern (jagged curve) and best fit (smooth curve) of the in-plane, coherent [010] peak for the Cu-11 nm/Ni-11 nm multilayer at 125°C; (c) measured 2θ diffraction pattern (smooth curve) and best fit (overlying curve) of in-plane [010] peaks for the Cu-21 nm/Ni-21 nm multilayer at room temperature.

interfaces and Cu-21 nm/Ni-21 nm nanolaminates with semi-coherent interfaces. A PANalytical X'Pert Pro MRD 4-axis X-ray diffractometer, coupled with a hybrid monochromator and a 0.27° parallel plate collimator, was used at the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory. An Anton Paar DHS 900 heated stage regulated the sample temperature under vacuum, thereby minimizing oxidation and the associated effects on stress–temperature behavior.[23] No evidence of oxidation was observed in post-heating diffraction patterns.

The sample orientation is shown in Figure 1(a), with an angle of incidence $\Psi = 88\text{--}89^\circ$ from the film surface normal. Penetration depths of $\sim 350\text{--}1,000$ nm are expected.[24] A full in-plane rotation, ϕ -scan, was performed to determine ϕ with the greatest diffraction intensity, corresponding to alignment of the (200) pole parallel to the diffraction axis $\mathbf{n}$. This ϕ was used in subsequent scans. The samples were heated by 50°C increments to 325°C , then cooled by 50°C decrements to room temperature. At each temperature, four separate 2θ scans were taken at a rate of $0.4^\circ/\text{min}$ (~ 10 min/scan). Each scan provided sufficient intensity to identify in-plane (200) diffraction peaks. The four scans were used to quantify changes in (200) diffraction peaks with time at a given temperature. Diffraction peaks were simultaneously fit using a pseudo-Voigt profile function in PANalytical HighScore Plus v3.0 software. The fitted peak positions furnished average (200) interplanar lattice spacings $d_{\text{Cu}}(T)$ and $d_{\text{Ni}}(T)$. Figure 1(b) and 1(c) shows example intensity vs. 2θ in-plane scans and fitted profiles for Cu-11 nm/Ni-11 nm and Cu-21 nm/Ni-21 nm samples, respectively. A single peak at a lattice spacing between those of Cu and Ni is observed in Figure 1(b) consistent with coherent Cu/Ni interfaces. The Cu and Ni peaks then separate as layer thickness increases as seen from Figure 1(c) since the lattice mismatch can no longer be accommodated elastically. Although both samples were tested under the same conditions, the same duration and with the same optics, the Cu-11 nm/Ni-11 nm sample shows significantly less intensity. The lower intensity leads to a less favorable signal-to-noise ratio as seen in Figure 1. The source of this variance

is unknown, but may be related to the greater number of interfaces in the Cu-11 nm/Ni-11 nm sample or slight misalignment.

The in-plane, direct component of *elastic* strain in a layer type (Cu or Ni) is given by

$$\varepsilon_{\text{el}}(T) = \ln \frac{d(T)}{d_0(T)}, \quad (1)$$

where $d(T)$ is the measured interplanar spacing at the heated temperature T and $d_0(T)$ is the corresponding stress-free value. The in-plane, direct component of *thermal* strain in a layer type is

$$\varepsilon_{\text{th}}(T) = \ln \frac{d_0(T)}{d_0(T_0)} = \alpha(T - T_0), \quad (2)$$

where $d_0(T)$ and $d_0(T_0)$ are the stress-free interplanar spacings at the heated and reference (room) temperatures, and α is the coefficient of thermal expansion of the layer. Combining Equations (1) and (2) provides a more convenient form for the elastic strain

$$\varepsilon_{\text{el}} = \ln \frac{d(T)}{d_0(T_0)} - \alpha(T - T_0). \quad (3)$$

The quantities $d(T)$ and T are provided from experimental measurements and $d_0(T_0)$ and α are furnished from literature values reported in Table 1. The direct component of stress in the in-plane (200) directions is provided by the anisotropic, elastic constitutive equation

$$\sigma(T) = \left(C_{11} + C_{12} - \frac{2C_{12}^2}{C_{11}} \right) \varepsilon_{\text{el}}, \quad (4)$$

where C_{11} and C_{12} are the anisotropic elastic moduli of the layer, reported in Table 1.

The in-plane, direct components of plastic strain are obtained by first noting that the layers and the Si substrate are oriented so that the in-plane directions $\text{Cu}_{[200]} \parallel \text{Ni}_{[200]} \parallel \text{Si}_{[220]}$. In the idealized reference case, the interfaces are coherent, so that the reference (200) interplanar spacing $d_0(T_0)$ of Cu is stretched to the current (220) interplanar spacing $D_0(T)$ of the thick (essentially

Table 1. Physical properties used for stress analysis.

	a_0 (Å)	α ($10^{-6}/^{\circ}\text{C}$)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
Cu	3.615	16.6	168	121	75
Ni	3.527	13.1	247	147	125
Si	5.431	2.6	166	64	80

Notes: Lattice parameters are from Cullity and Stock,[26] thermal expansion coefficients for Cu and Ni are from Krishnan [27] and for Si from Watanabe et al.[28] Anisotropic elastic constants are from Courtney.[29]

stress-free) Si substrate. In that case, Cu layers experience a total in-plane strain

$$\varepsilon_{\text{tot}} = \ln \frac{D_0(T)}{d_0(T_0)}. \quad (5)$$

An identical counterpart expression holds for coherent Ni layers. In reality, the deformation is too large to be accommodated by elastic and thermal strains. Instead, plastic deformation in the form of threading dislocation motion occurs (see inset Figure 6(a)). For the case of face-centered cubic (FCC) layers with a [001] interface normal, threading dislocation motion can form arrays of misfit dislocations with line directions along orthogonal

in-plane $\langle 110 \rangle$ directions.[25] The in-plane plastic strain is therefore the total strain minus the elastic and thermal strains:

$$\varepsilon_p(T) = \varepsilon_{\text{tot}}(T) - \varepsilon_{\text{el}}(T) - \varepsilon_{\text{th}}(T) = \ln \frac{D_0(T)}{d(T)}. \quad (6)$$

The second equality is obtained by substituting Equations (1) and (2) for $\varepsilon_{\text{el}}(T)$ and $\varepsilon_{\text{th}}(T)$, respectively. Since $D_0(T)$ is not measured directly, a useful quantity is the change in plastic strain during heating,

$$\begin{aligned} \Delta \varepsilon_p(T) &\equiv \varepsilon_p(T) - \varepsilon_p(T_0) = \Delta \varepsilon_{\text{tot}} - \Delta \varepsilon_{\text{th}} - \Delta \varepsilon_{\text{el}} \\ &= (\alpha_{\text{Si}} - \alpha)(T - T_0) - \Delta \varepsilon_{\text{el}}. \end{aligned} \quad (7)$$

This is independent of $D_0(T)$ and is readily calculated in terms of α_{Si} , α , and the measured values of d at T_0 and T , respectively. Physically, it states that the mismatch in thermal strain between the substrate and layer must be accommodated by elastic and plastic strain

The interfacial dislocation density produced by this process is $\rho_{\text{interface}} = 2/S$, where S is the in-plane, perpendicular spacing between dislocations (see upper inset, Figure 7). $\rho_{\text{interface}}$ is therefore the line length of interfacial dislocations per area of interface. For FCC metals with a [001] interface normal, the resulting in-plane

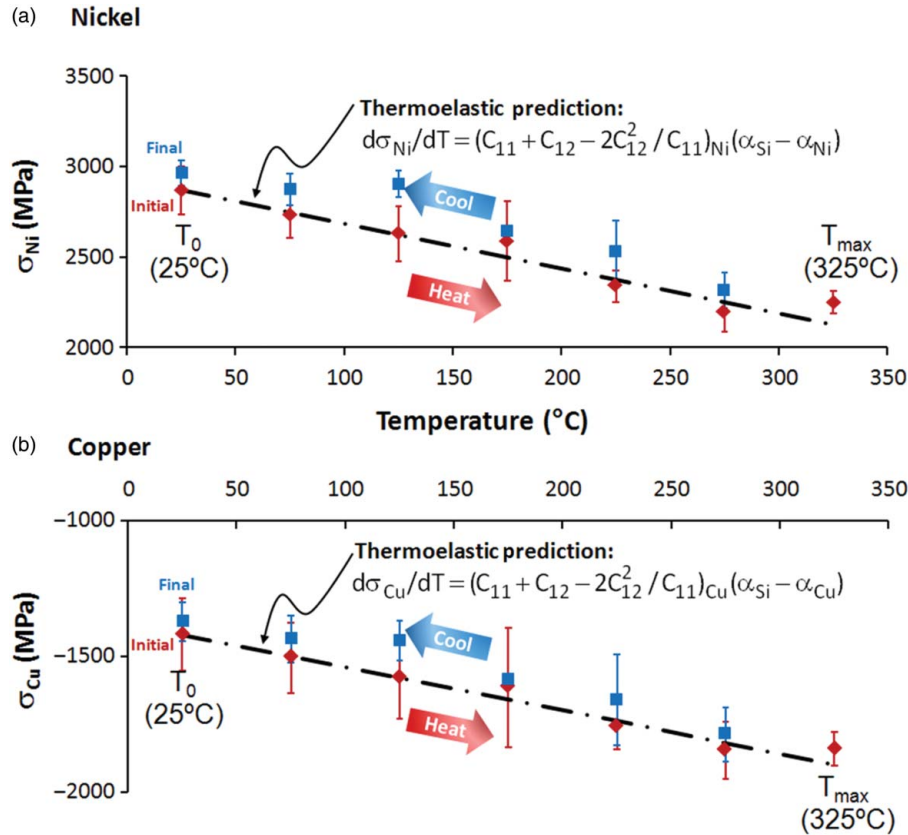


Figure 2. Average in-plane biaxial stress (a) σ_{Ni} and (b) σ_{Cu} vs. temperature for the Cu-11 nm/Ni-11 nm multilayer sample. The dashed lines and governing equations are predictions from Equation (4) assuming no inelastic deformation (i.e. thermoelastic only).

plastic strain in the layer is $\varepsilon_p = b_e/S$, where $b_e = (\sqrt{3}/2)b$ is the in-plane edge component of 60° interfacial dislocations.[25] Since both Cu and Ni layers can deform plastically, the *net* interfacial dislocation density depends on the *difference* in plastic deformation in Ni vs. Cu layers:

$$\rho_{\text{interface}}(T) \equiv \frac{2}{b_e}(\varepsilon_{p,\text{Ni}} - \varepsilon_{p,\text{Cu}}) = \frac{2}{b_e} \ln \left(\frac{d_{\text{Cu}}(T)}{d_{\text{Ni}}(T)} \right). \quad (8)$$

Thus, the interfacial dislocation density at temperature T depends on the measured interplanar spacings in Cu and Ni at that T . The case $\rho_{\text{interface}} = 0$ occurs in the coherent limit where the Cu and Ni interplanar spacings are equal.

The relevant room temperature lattice parameters, thermal expansion coefficients and anisotropic second-order elastic constants for Cu, Ni and Si are reported in Table 1. These values were used since estimates of $\sigma(T)$ changed $<12\%$ over the experimental T range, compared with those based on T -dependent expansion coefficients and elastic constants. Bulk values of thermal expansion coefficients were used since no direct measurements were available from these experiments. This assumption is supported by X-ray diffraction studies over the range 100–400°C, showing that 720 nm Al films on

Si substrates have $<9\%$ difference in thermal expansion coefficient compared with bulk.[30] However, a micro-cantilever approach reports a 60% decrease in thermal expansion coefficient for 0.3 μm vs. 1.7 μm thick Al films.[31] Such conflicts have not been resolved.[17]

Figure 2(a) and 2(b) shows $\sigma_{\text{Ni}}(T)$ and $\sigma_{\text{Cu}}(T)$, respectively, for the Cu-11 nm/Ni-11 nm sample. Ni layers are in tension (2.9 GPa) and the Cu layers are in compression (1.4 GPa) at room temperature since d_0 is smaller for Ni vs. Cu. Although these in-plane stresses are large, they are $\sim 50\%$ of the stresses for purely coherent interfaces. Also, the stresses in Cu and Ni are not equal and opposite due to the presence of the Cu seed layer and Si substrate. During heating, the metals expand more than the Si substrate since α_{Cu} and $\alpha_{\text{Ni}} > \alpha_{\text{Si}}$. Therefore, σ_{Ni} becomes less positive and σ_{Cu} becomes more negative during heating. The dashed line in each plot shows the predicted slope $d\sigma/dT$ for each layer assuming they deform thermoelastically (i.e. no plasticity). The slope is obtained by differentiating Equation (4) to obtain $d\sigma/dT$, where $d\varepsilon_{\text{el}}/dT = (\alpha_{\text{Si}} - \alpha)\Delta T$ from Equation (7). This approximation captures the experimental measurements to within an average of 4% error.

Figure 3(a) and 3(b) shows $\sigma_{\text{Ni}}(T)$ and $\sigma_{\text{Cu}}(T)$, respectively, for the Cu-21 nm/Ni-21 nm sample. The initial stresses in both layers are smaller than those in

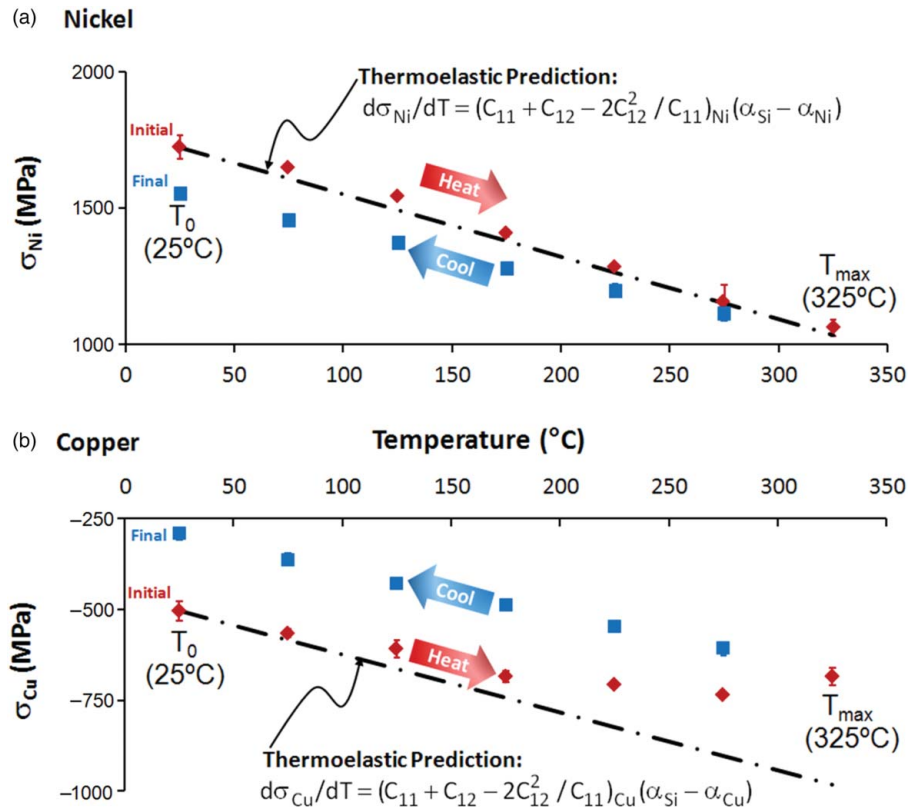


Figure 3. Average in-plane biaxial stress (a) σ_{Ni} and (b) σ_{Cu} vs. temperature for the Cu-21 nm/Ni-21 nm multilayer sample. The dashed lines and governing equations are predictions from Equation (4) assuming no inelastic deformation (i.e. thermoelastic only).

the Cu-11 nm/Ni-11 nm film, indicating a less coherent system. As before, the stresses in the Cu and Ni layers are not equal and opposite. Noticeable deviations from thermoelastic behavior are apparent, implying $\varepsilon_p(T) \neq 0$. In Ni, the deviation occurs only upon cooling. In Cu, the deviation occurs for heating above 200°C, as well as over most of the cooling range. After a thermal cycle, $|\sigma_{\text{Ni}}|$ is $\sim 10\%$ lower and $|\sigma_{\text{Cu}}|$ is 40% lower. This may reflect dislocation-based plasticity, interdiffusion between layers,[32,33] or diffusion-mediated processes such as constrained diffusional creep observed in single-phase thin films.[15,34]

Figure 4(a) and 4(b) shows $\sigma_{\text{Ni}}(T)$ and $\sigma_{\text{Cu}}(T)$, respectively, for the Cu-21 nm/Ni-21 nm sample, obtained from the four diffraction scans at each temperature. Each scan took ~ 10 min with ~ 2 min intervals between scans to reposition the goniometers. At each temperature, no evidence of uniform, time-dependent stress relaxation is observed from the first to fourth scans. The data for Ni at 275°C (heating) and Cu at 325°C do show monotonic decreases in stress of 12% and 7%, respectively, over these 40 min isothermal intervals, but the amount of decrease between consecutive scans is irregular. Overall, the aggregate of data supports time-independent plastic deformation rather than creep as the inelastic deformation.

Figure 5 shows transmission electron microscope (TEM) micrographs of the Cu-21 nm/Ni-21 nm sample after the thermal cycle. The layer structure remains intact (a) and layer thickness is unchanged (b), suggesting that large-scale diffusion and morphological instability does not occur.[35] The initially planar Si–Cu seed layer interface becomes nonplanar and nearby regions become polycrystalline (c), suggesting formation of copper silicides as in [36]. Diffusion is aided by lack of an appropriate barrier layer. Nevertheless, this region is small compared with the overall film thickness and is not expected to account for the observed changes in σ_{Cu} or σ_{Ni} . Other evidence of minimal interdiffusion is that the stress-free lattice parameter of Cu and Ni, calculated using the $\sin^2 \Psi$ -method and a procedure similar to Daniels et al.,[32] changes by $<0.2\%$ after the thermal cycle. The lack of a systematic, time-dependent stress evolution at constant temperature is consistent with a time-independent inelastic mode of deformation such as confined layer slip, i.e. glide of single Orowan-type loops bounded by two interfaces.[37,38]

Figure 6 shows (a) σ_{Ni} vs. $\Delta\varepsilon_{\text{p,Ni}}$ and (b) σ_{Cu} vs. $\Delta\varepsilon_{\text{p,Cu}}$ for the Cu-21 nm/Ni-21 nm sample. During heating, σ_{Ni} decreases with $\Delta\varepsilon_{\text{p,Ni}} \approx 0$, consistent with elastic unloading. During cooling, σ_{Ni} increases $\sim$ linearly by ~ 500 MPa as plastic strain increases by $\Delta\varepsilon_{\text{p,Ni}} \approx 0.1\%$. Gaps in the unloading vs. loading traces have been observed in conventional [39,40] and nanocrystalline metals [41] following complete unloading and/or stress reversal under isothermal conditions. Here, the Ni layers

are unloaded to only 60% of the initial stress. The elastic unloading indicates that dislocation loops in Ni (see inset, Figure 6(a)) are unable to reverse direction during unloading, yet they readily move forward upon reloading. A possible explanation is that deformation in adjoining Cu layers has altered interfacial structure during unloading, thereby lowering the threshold for yield in Ni layers.

A peculiar feature is the large increase in stress $\Delta\sigma_{\text{Ni}} \sim 500$ MPa during the initial plastic strain increment $\Delta\varepsilon_{\text{p,Ni}} \approx 0.1\%$. For comparison, 1 μm Ni thin films show $\Delta\sigma \sim 200$ MPa,[19] nanocrystalline Ni (29 nm average grain size) shows ~ 240 MPa,[42] and conventional grain size Ni shows ~ 5 MPa.[43] For consistency, these values are all measured during the initial 0.1% increment in plastic strain. The large value in the present experiments reflects that continued motion of existing dislocations or activation of new sources requires extraordinary increases in stress. Numerical and analytic calculations document strong interactions between threading and misfit dislocations [44,45] in multilayer thin films. Also, dislocation models of the work to increase interfacial misfit dislocation density [46] in multilayer thin films support such large experimental values.

Figure 6(b) shows $\Delta\sigma_{\text{Cu}} \sim 200$ MPa during heating. σ_{Cu} plateaus at ~ 740 MPa (compression). During initial unloading (cooling), Cu layers unload elastically by 80 MPa (Point H6 to C1 in Figure 6(b)). Then *reverse* plastic deformation commences with continued unloading. Here, $\Delta\sigma = -400$ MPa over the increment $\Delta\varepsilon_{\text{p,Cu}} \approx 0.1\%$. This magnitude of stress change is comparable to those in loading/unloading of passivated Cu films (thickness = 340 nm) during plane-strain bulge tests.[47] Although the changes in $\Delta\sigma_{\text{Cu}}$ and $\Delta\sigma_{\text{Ni}}$ are large in this initial plastic regime, corresponding changes in the macrostress on the Cu-21 nm/Ni-21 nm film, measured by micropillar compression, is only $\Delta\sigma \sim 100$ MPa.[48]

An unusual feature in Figure 6(b) is the $\sim$ linear recovery of plastic strain over a large (300 MPa) unloading range. Xiang and Vlassak [47,49] also observe plastic strain recovery in Cu layers (340–890 nm) using plane-strain bulge tests; Keller et al. [23] report similar effects using substrate curvature tests. Both groups report large plastic strain recovery only if the Cu layer is passivated. Like the present work, the Xiang and Vlassak study reports plastic strain recovery prior to a reversal in the sign of applied stress. They attribute it to back stresses from dislocation pile-ups at the passivation/film interface. However, the nanoscale layers in the present study are more than an order of magnitude thinner, so that they are too small for significant pile-ups.[1] Rather, the phenomena can stem from the driving force to remove dislocation line length at interfaces. This process is depicted in Figure 6(b) insets and it has been observed in microscopy [38,50–52] and simulations.[44, 53–56]

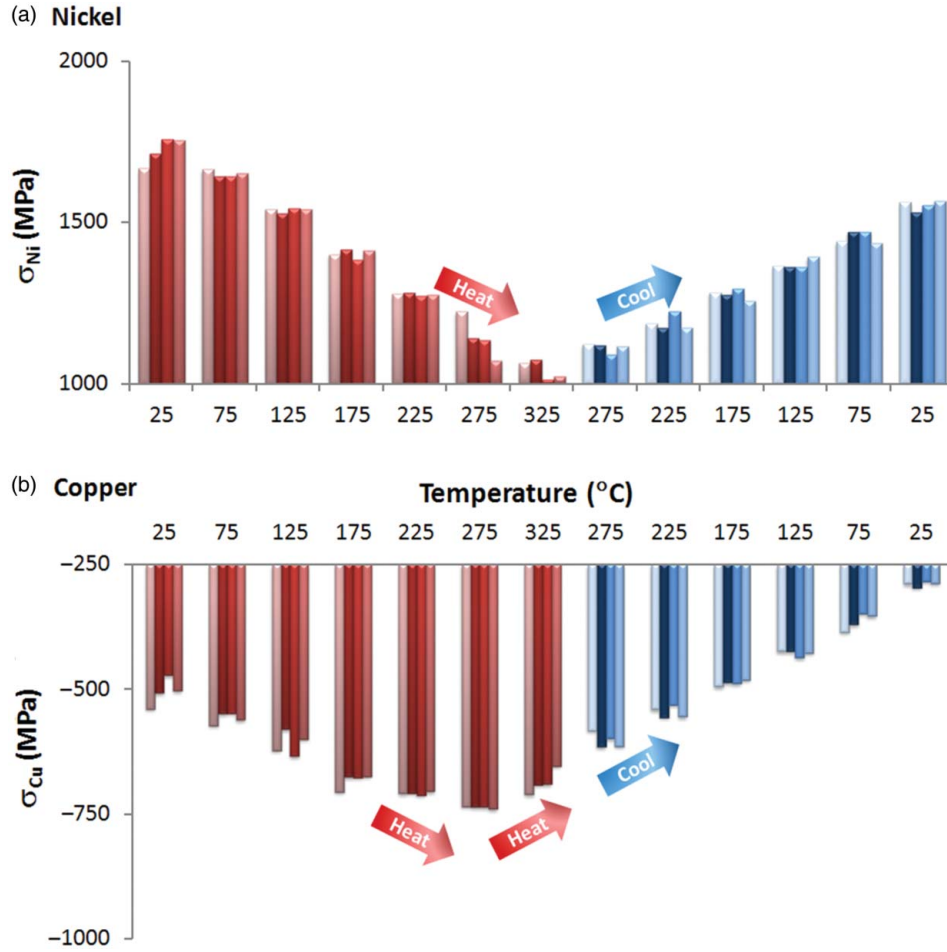


Figure 4. Average in-plane biaxial stress (a) σ_{Ni} and (b) σ_{Cu} vs. temperature in the Cu-21 nm/Ni-21 nm multilayer sample, showing the results for four separate 10 min 2θ scans at each temperature. Overall, no systematic, time-dependent stress relaxation is evident.

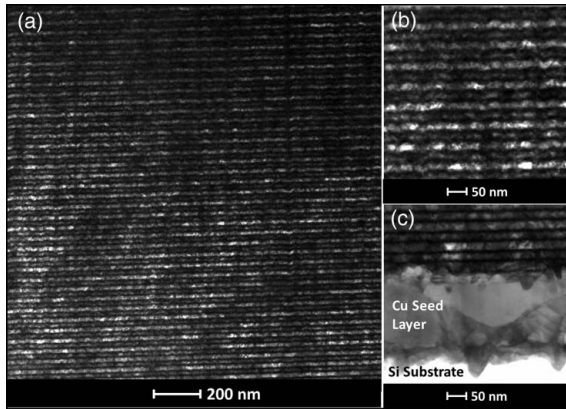


Figure 5. Bright-field TEM micrographs of the Cu-21 nm/Ni-21 nm after a single thermal cycle showing: (a, b) layer structure is maintained, with significant dislocation content at interfaces; (c) evidence that the Cu seed layer has reacted with the Si substrate but represents a small fraction of the overall film thickness.

Figure 7 shows interfacial dislocation density $\rho_{interface}$ (Equation (8)) vs. T for the Cu-21 nm/Ni-21 nm film. During heating, $\rho_{interface}$ increases $\sim 22\%$ as Cu

layers plastically compress and deposit dislocation content while Ni layers remain elastic ('Heat' inset, Figure 7). During cooling, $\rho_{interface} \sim \text{constant}$ as Cu and Ni layers co-stretch by comparable plastic strain. Here, existing or new dislocation loops in Ni advance by forward slip while loops in Cu layers retract by reverse slip ('Cool' inset, Figure 7).

Carpenter et al. [21] conclude that accumulation of interfacial dislocation content can serve to pin forward/reverse motion. It can also reduce the pinning dimension S for dislocations to bow-out from interfaces, thus impeding dislocation nucleation into adjoining layers. The average pinning strength in Cu can be estimated by comparing the biaxial stress for forward (heating) and reverse (cooling) modes (Figure 6(b)):

$$\begin{aligned}\sigma_{Cu,forward(heat)} &= \frac{2w}{b_e h} + \sigma_{Cu,pin}; \\ \sigma_{Cu,reverse(cool)} &= \frac{2w}{b_e h} - \sigma_{Cu,pin}.\end{aligned}\quad (9)$$

These equations are derived from dislocation models of confined layer slip, where dislocations with average

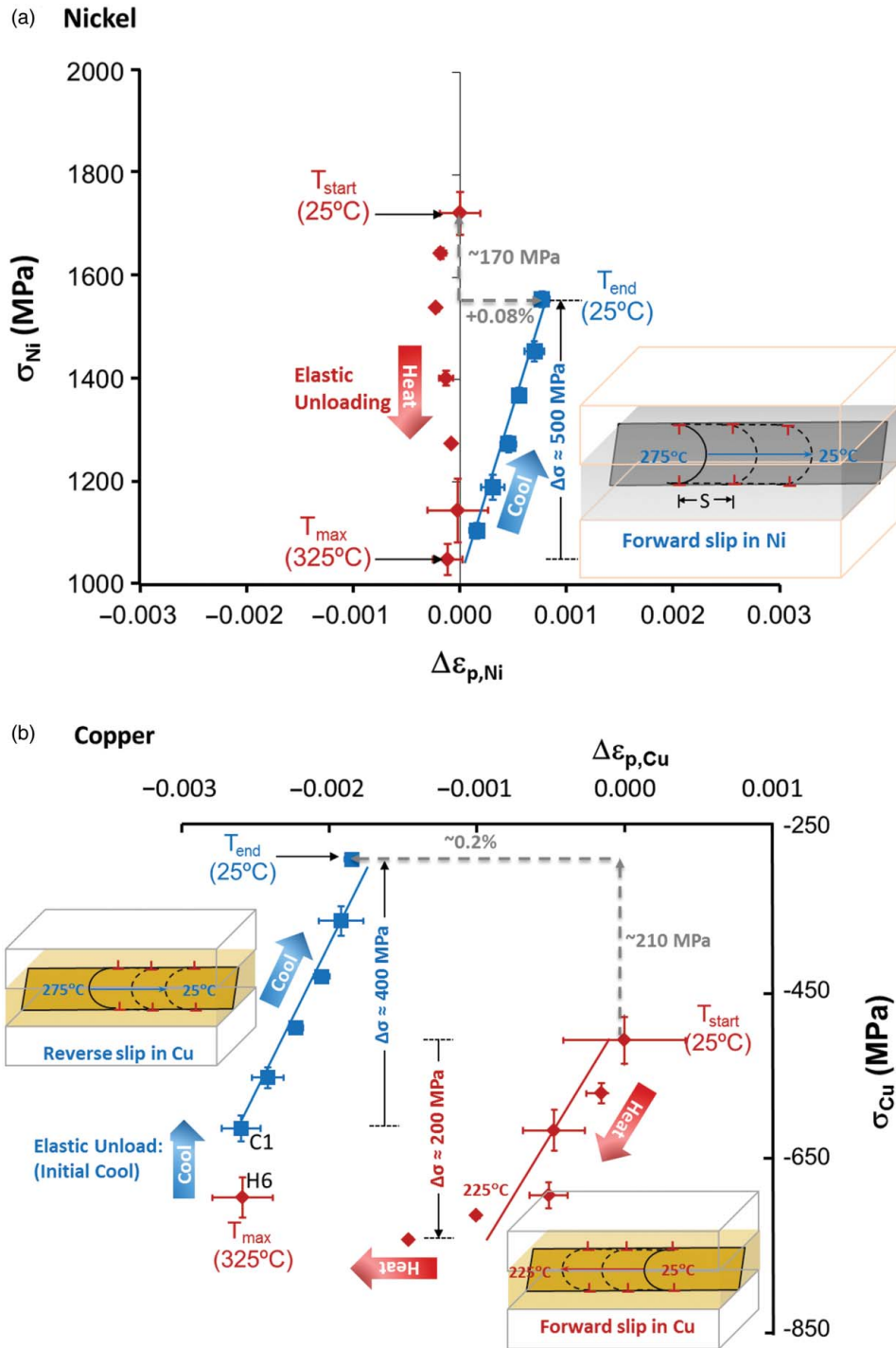


Figure 6. Average in-plane biaxial stress (a) σ_{Ni} and (b) σ_{Cu} vs. increment in plastic strain in the Cu-21 nm/Ni-21 nm multilayer sample. (a) Ni layers unload elastically during heating and reload plastically during cooling. Inset shows forward confined layer slip of dislocations in Ni. (b) Cu layers load plastically during heating, unload elastically during initial cooling, and then unload plastically during continued cooling. Inset (right) shows forward confined layer slip during heating and inset (left) shows reverse confined layer slip during continued cooling.

energy per unit length w are deposited at interfaces. The local stress provides the available work, $\sigma_{\text{Cu}} b_e h$, to create the increase, $2w$, in dislocation line energy when the loop advances.[13] Equating these work and energy

terms furnishes the contribution $2w/b_e h$ in Equation (7). $\sigma_{\text{Cu, pin}}$ is the additional stress required to overcome pinning obstacles—e.g. existing interface dislocations with average spacing S . For the cool/reverse mode, the

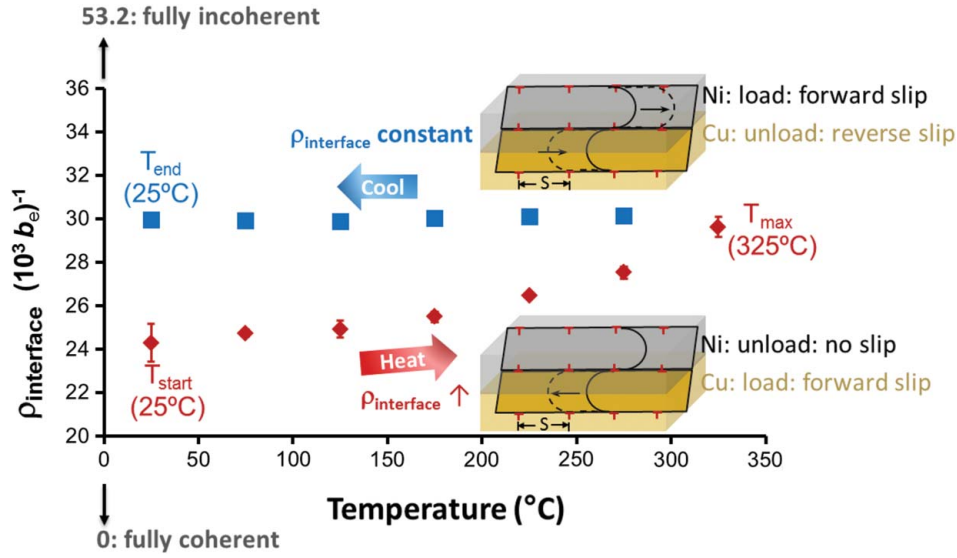


Figure 7. Evolution of net interfacial dislocation density $\rho_{\text{interface}}$ with temperature for the Cu-21 nm/Ni-21 nm film; during heating, $\rho_{\text{interface}}$ increases due to forward slip in Cu layers. During cooling, $\rho_{\text{interface}} \sim \text{constant}$ due to $\sim$ equal codeformation in Cu and Ni layers. Insets show forward and reverse confined layer slip in the presence of interfacial dislocations with spacing S and in-plane Burgers vector of magnitude b_e .

pinning stress opposes that motion and thus has the reverse sign.

Estimates of the pinning stress and average line energy are provided by applying Equation (9) to the difference in stress $\sigma_{\text{Cu,forward}} = 690 \pm 24$ MPa at point H6 vs. $\sigma_{\text{Cu,reverse}} = 609 \pm 15$ MPa at point C1 (Figure 6(b)). The unloading is elastic, suggesting there is a difference in stress to move the same dislocation structure in the forward vs. reverse direction. An estimate $\sigma_{\text{Cu,pin}} = 41 \pm 20$ MPa is calculated using $\sigma_{\text{Cu,pin}} = 0.5(\sigma_{\text{Cu,forward}} - \sigma_{\text{Cu,reverse}})$ from Equation (9). Similarly, an estimate $w_{\text{Cu}} = 0.85 \pm 0.03$ nJ/m is obtained using $w = 0.25b_e h(\sigma_{\text{Cu,forward}} + \sigma_{\text{Cu,reverse}})$ from Equation (9), with $b_{e(101)/2} = 0.125$ nm (averaged between Cu and Ni) and layer thickness $h = 21$ nm. Thus, w_{Cu} is smaller than typical estimates of bulk line energy $0.5C_{44,\text{Cu}}b^2 = 2.4$ nJ/m.[57] This is consistent with interfaces that lower dislocation line energy, thereby trapping the dislocation.[58]

The trends in pinning strength and line energy during heating and cooling are complicated by the interplay between temperature and interfacial dislocation density. During heating, interfacial dislocation density $\rho_{\text{interface}}$ is estimated to increase by 22% (Figure 7), corresponding to a decrease in average misfit dislocation spacing S from 41 to $34b_e$. During the process, the Cu flow stress increases by 180 MPa (35%), despite potential softening induced by the temperature increase. During cooling, reverse flow occurs incrementally over a ~ 300 MPa decrease in $|\sigma_{\text{Cu}}|$, Figure 6(b). Similar trends are observed in electrodeposited nanocrystalline Ni and are attributed to a wide grain-to-grain distribution in critical stress for slip.[59] In the context of Figure 6(b), the large increase in $|\sigma_{\text{Cu}}|$

upon heating may reflect that regions with favorable values of residual stress or relatively low threshold stress for slip are able to deform initially, thus redistributing stress to less favorable regions. Similarly, the unloading region with a decrease in $|\sigma_{\text{Cu}}|$ may reflect a wide distribution of internal stress and critical threshold for reverse motion.

The corresponding trends for Ni show that during heating/unloading, there is no reverse plasticity. This implies a large resistance to reverse plasticity ($\sigma_{\text{Ni,pin}}$), which is estimated from Equation (9) to be $\sigma_{\text{Ni,pin}} > 0.5(\sigma_{\text{Ni,25°C}} - \sigma_{\text{Ni,325°C}}) \sim 340$ MPa. During cooling/reloading, it is remarkable that Ni readily undergoes forward yield, without any prior reverse yield. A hypothesis is that the increase in interfacial dislocation density ($\rho_{\text{interface}}$) during heating has introduced new sources that readily operate upon reloading. Thus, heating appears to work harden Cu layers but soften Ni layers.

Instrumented nanoindentation tests (MTS Nanoindenter XP with Continuous Stiffness Measurement) reveal room temperature hardness reductions of $\sim 2\%$ (Cu-11 nm/Ni-11 nm) and $\sim 11\%$ (Cu-21 nm/Ni-21 nm) caused by the heating/cooling cycle. Table 2 shows the supporting pre- and post-thermal cycle values of hardness H and elastic modulus E , averaged between depths of 200–500 nm for 20 indents per sample. Corresponding values of biaxial stresses σ_{Cu} and σ_{Ni} , average in-plane stress Σ_{ip} on the multilayer film, and stress difference $|\sigma_{\text{Ni}} - \sigma_{\text{Cu}}|$ values are provided. Based on finite element analyses by Chen et al., the pre and post changes in Σ_{ip} are predicted to change H by 1% or less.[60] This effect may account for the the minor ($\sim 2\%$) H reduction in the Cu-11 nm/Ni-11 nm film, but not the larger ($\sim 11\%$) H reduction in the Cu-21 nm/Ni-21 nm film.

Table 2. Hardness, elastic modulus and layer stresses pre- and post-thermal cycle.

	σ_{Cu} (GPa)	σ_{Ni} (GPa)	$ \sigma_{\text{Ni}} - \sigma_{\text{Cu}} $ (GPa)	Σ_{ip} (GPa)	H (GPa)	E (GPa)
<i>Cu-11 nm/Ni-11 nm</i>						
Pre	-1.42 ± 0.07	2.87 ± 0.13	4.29 ± 0.15	0.73 ± 0.15	4.60 ± 0.05	156 ± 1
Post	-1.37 ± 0.03	2.97 ± 0.07	4.34 ± 0.08	0.80 ± 0.08	4.49 ± 0.04	156 ± 1
<i>Cu-21 nm/Ni-21 nm</i>						
Pre	-0.50 ± 0.03	1.72 ± 0.04	2.22 ± 0.05	0.61 ± 0.05	4.44 ± 0.08	154 ± 2
Post	-0.29 ± 0.01	1.55 ± 0.02	1.84 ± 0.02	0.63 ± 0.02	3.97 ± 0.09	150 ± 2

Other candidates for the large decrease include the 22% increase in $\rho_{\text{interface}}$ and the accompanying decrease in $|\sigma_{\text{Ni}} - \sigma_{\text{Cu}}|$. Prior work suggests that FCC/FCC samples derive strength from large $|\sigma_{\text{Ni}} - \sigma_{\text{Cu}}|$, which is maximized in the coherent interface limit.[61] More recent work shows that sputtered Cu/Ni films with optimal combinations of $\rho_{\text{interface}}$ and $|\sigma_{\text{Ni}} - \sigma_{\text{Cu}}|$ can give H values exceeding that for coherent films.[21] In the present work, the heat/cool cycle appears to manipulate $\rho_{\text{interface}}$ and $|\sigma_{\text{Ni}} - \sigma_{\text{Cu}}|$ in a deleterious way. More work is needed to elucidate the complicated dependence of H on stress state and interface structure, specifically the relative contributions of $\rho_{\text{interface}}$, $|\sigma_{\text{Ni}} - \sigma_{\text{Cu}}|$ and Σ_{ip} on H .

To summarize, this work extends the use of heated in-plane X-ray diffraction to investigate constituent deformation behavior in multilayer thin films. The Cu-11 nm/Ni-11 nm multilayer with coherent interfaces displayed negligible plastic deformation even though $\sigma_{\text{Ni}} \sim 2.9$ GPa and $\sigma_{\text{Cu}} \sim 1.8$ GPa were achieved during heating/cooling. The Cu-21 nm/Ni-21 nm case with semi-coherent interfaces did plastically deform, revealing peculiar features:

- Enhanced reverse yielding in Cu layers, where reverse plastic flow occurs without changing the sign of average stress in Cu layers.
- Large changes in flow stress, $\Delta\sigma_{\text{Ni}} = 500$ MPa and $\Delta\sigma_{\text{Cu}} = 200$ –400 MPa, during initial forward vs. reverse yield. This feature is interpreted in terms of a large spatial distribution in residual and/or critical stress for confined layer slip within layers.
- Estimate of line energy ~ 0.8 nJ/m for dislocations deposited at [001] Cu/Ni interfaces during fully plastic flow. This estimate is $\sim 1/3$ typical line energy estimates ($1/2C_{44,\text{Cu}}b^2$) for bulk Cu, suggesting that on average, dislocations may be readily attracted to [001] Cu/Ni interfaces.
- Evidence that heating/cooling Cu-21 nm/Ni-21 nm multilayers reduces hardness by $\sim 11\%$. This H reduction is accompanied by a reduced internal (coherency) stress and increased net interfacial dislocation density.

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