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# Residual stress within nanoscale metallic multilayer systems during thermal cycling

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ABSTRACT

Projected applications for nanoscale metallic multilayers will include wide temperature ranges. Since film residual stress has been known to alter system reliability, stress development within new film structures with high interfacial densities should be characterized to identify potential long-term performance barriers. To understand factors contributing to thermal stress evolution within nanoscale metallic multilayers, stress in Cu/Nb systems adhered to Si substrates was calculated from curvature measurements collected during cycling between 25 °C and 400 °C. Additionally, stress within each type of component layers was calculated from shifts in the primary peak position from *in-situ* heated X-ray diffraction. The effects of both film architecture (layer thickness) and layer order in metallic multilayers were tracked and compared with monolithic Cu and Nb films (1 μm total thickness). Analysis indicated that the thermoelastic slope of nanoscale metallic multilayer films (with 20 nm and 100 nm individual layer thicknesses) depends on thermal expansion mismatch, elastic modulus of the components, and also interfacial density. The layer thickness (i.e. interfacial density) affected thermoelastic slope magnitude ($-1.23 \pm 0.09$ MPa/°C for 20 nm Cu/Nb *vs.* $-0.89 \pm 0.03$ MPa/°C for 100 nm Cu/Nb) while layer order had minimal impact on stress responses after the initial thermal cycle ($-0.82 \pm 0.07$ MPa/°C for 100 nm Cu/Nb). When comparing stress responses of monolithic Cu and Nb films to those of the Cu/Nb systems, the nanoscale metallic multilayers show a similar increase in stress above 200 °C to the Nb monolithic films, indicating that Nb components play a larger role in stress development than Cu. Phase specific stress calculations (Cu *vs.* Nb) from X-ray diffraction peak shifts in 20 nm Cu/Nb collected during heating reveal that the component layers within a multilayer film respond similarly to their monolithic counterparts.


## 1. Introduction

To enhance mechanical properties of thin films, research groups have started creating synthetic two-dimensional structures within films by selective deposition of metallic films. One of these such structures that have become prevalent recently are nanoscale metallic multilayers (NMMs). NMMs are composed of alternating metallic layers with nanometer-level ($<100$ nm) individual layer thicknesses that have shown superior strength [1–3], radiation damage resistance [4–6], and wear-resistance [7,8] when compared to their monolithic counterparts. These types of layered systems are referred to in many different manners by various researchers including NMMs, nanolaminates, multilayers, herringbone structures, nanoheterostructures, *et cetera*; however, many of the terms are synonymous. For the purposes of this work, these systems will be referred to as NMMs. In some cases, researchers have observed that these film systems have undergone both microstructural and mechanical instability during heating [9–12]. These microstructural and mechanical instabilities in NMM systems have been linked to residual stresses imposed by the substrate during thermal cycling [9–12].

Residual stress can be a significant factor in the response of a material to external stimuli, most notably the magnitudes of diffusion [13,14], deformation [15–17], and optical transmission [18]. This type of stress has been observed in both thin films and bulk metals. In bulk metals, the magnitude of residual stress is often below that of the yield stress level [19]. However, in thin-film systems, residual stresses have been observed to readily exceed 1 GPa in either tension or compression [19]. Intrinsic sources of residual stress in thin films include those due to the system's microstructure, or those originating from defects during film deposition [19]. Extrinsic sources of stress in thin-film systems can

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include those due to thermal expansion mismatches between the substrate and film constituent materials [19]. When researchers compare the stresses calculated in monolithic films during thermal cycles, they often observe a deviation between the stress hysteresis of the first and subsequent thermal cycles [20–22]. After the initial relief of intrinsic stresses from deposition, the primary source of stress within films during thermal cycling is typically assumed to arise from thermal expansion mismatch between the film and substrate. This study seeks to examine the development of residual stress in NMM Cu/Nb films adhered to Si during thermal cycling due to the role of stress on the microstructural instability [9–12]. This work is necessary to further understand the development of residual stresses in NMM film systems to foster their usage in practical settings such as high-strength coatings in extreme temperature environments for energy and defense applications [23].

Cu/Nb was chosen as a model system in this study due to its frequency in the literature [2,9,24–27] and because the constituent materials (Cu and Nb) do not form intermetallic compounds with one another [23,28]. To understand the thermal stress response of a composite film system, it is necessary to understand the constituents by themselves [29,30]. The thermal response of copper films has been studied extensively due to its importance in the microelectronics industry [20,21,31,32]. Thermal stress response in Nb films, however, has not been examined in the literature.

A key parameter to understanding the thermal stress development of films is the elastic (linear) slope of the stress as a function of temperature that can typically be found on cooling, which is known as the thermoelastic slope [22]. This parameter gives an indication of how much stress is being developed from changes in temperature with a greater magnitude indicating greater stress. Keller et al. has described thermoelastic slope of a film, $m$, in monolithic film systems on a substrate as:

$$m = \left(\frac{E_f}{1-\nu_f}\right)\Delta\alpha \tag{1}$$

where it depends on elastic components: $E_f$, elastic modulus of the film and Poisson's ratio of the film, $\nu_f$, and thermal expansion mismatch between the film and substrate, $\Delta\alpha$ [31]. Based on predictions using Eq. (1) Cu/Nb should have an estimated thermoelastic slope of $-1.8$ MPa/°C based on literature values of CTE for Cu, Nb, and Si (using the difference between Si and a combined mean value for both Cu and Nb) [33,34], approximate elastic modulus from nanoindentation (125 GPa), and an assumed Poisson's ratio ($\nu \approx 0.37$, [35]).

Only two studies have been found that sought to examine the thermal stress progression for nanoscale multilayer systems [30,36]. Windt studied the thermal stress response of multilayer films with sub-10 nm individual layers of Mo, W, Si, and C (also on Si substrates) to examine the role of nanoscale multilayer architecture on thermal stress development [30]. Windt's study did not examine how varying the magnitudes of layer thickness might impact stress, but solely focused on characterizing the difference between sub-10 nm individual layer thickness (1–5 nm) multilayer films [30]. Similarly, Gram et al. examined the stress responses of 11 nm and 21 nm Cu/Ni NMMs during heating [36]. In Windt's study, it was observed that the varying architectures in either a net tensile or net compressive stress after heating depended on individual layer thickness. This variation in stress response was attributed to the role of interfacial stresses in the systems [30], which are defined as those associated with the layer interfaces (one layer to another) [37]. These stresses have been attributed to local CTE variation [30] and the surface energies assiociated with the interface [37]. The role of interfacial stresses aside from the film/substrate interface in monolithic films and macro-multilayers is negligible due to low interfacial density, but could become appreciable for nanoscale layer thicknesses. Gram et al. identified that there is a separate stress response in the component layers (Cu *vs.* Ni), as was shown with *in-situ* heated XRD, and that the thicker 21 nm layered system showed greater deviation from the predicted thermoelastic slope [36].

In this study stress was approximated in two separate contexts; first to estimate the residual stress developed during deposition (how the substrate changes before and after the film is initially deposited) to serve as starting values for the study. Second, the curvature was monitored continuously throughout a thermal cycle in two different *in-situ* systems, substrate curvature and XRD, to show the progression of thermal stress during heating and cooling. This complimentary approach to examining stress response allowed for the determination of differences between the phase specific stress and the composite stress in the Cu/Nb NMM architecture (phase specific: Cu or Nb *vs.* composite: Cu and Nb).

## 2. Experimental methods

### 2.1. Fabrication of thin film systems

Cu/Nb NMM and monolithic Cu and Nb films were deposited to examine the influence of film architecture and geometry on residual stress development during thermal cycling. All films were deposited on (100) Si substrates (350–400 μm thickness) using a Kurt J. Lesker sputter deposition system using a process detailed previously [9]. The deposition rates obtained were 4.0 nm/min for Cu and 2.9 nm/min for Nb. Six types of samples were deposited for this study, 20 nm Cu/Nb, 20 nm Nb/Cu (50 total layers), 100 nm Cu/Nb, 100 nm Nb/Cu (10 total layers), as well as monolithic Cu and Nb films. In all films the total thickness was kept constant at 1 μm. The two different notations for the NMM systems (Cu/Nb and Nb/Cu) indicate the layer order (geometry) with Cu/Nb having the Cu layer deposited first and Nb layer deposited subsequently, and the reverse for the Nb/Cu samples. The two different geometries were used to examine the influence of the base layer on the stress development. Additionally, the monolithic Cu film contained an Nb adhesion layer (approximate thickness: 5 nm). A matrix of the samples produced for this study is included in Table 1.

### 2.2. Characterization methods

As-deposited film residual stress (due to deposition parameters) was calculated using the changes in substrate curvature before and after film deposition as measured by stylus profilometry (Veeco Dektak[3]). This curvature was measured using 20 mm line scans, with seven radial measurements taken per sample both before and after deposition. These measurements were then used along with the constraints imposed by the Si substrate [38] to calculate residual stress using Stoney's equation [39].

Additionally, initial hardness was calculated from

**Table 1**
Film systems produced for studying the effects of architecture and geometry on performance during and after thermal cycling.

| | Layer Geometry | | |
|---|---|---|---|
| | Cu/Nb NMM Systems | Nb/Cu NMM Systems | Monolithic Systems |
| Layer Architecture | 20 nm Cu/Nb<br>100 nm Cu/Nb | 20 nm Nb/Cu<br>100 nm Nb/Cu | 1 μm Cu<br>1 μm Nb |

Total thickness of each system was 1 μm