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Evolution of *in situ* growth stresses and interfacial structure in phase changing Cu/V multilayered thin films

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ABSTRACT

As the layer thickness is reduced in a Cu/V multilayered thin film, a change in phase from face centered cubic (fcc)-to-body centered cubic (bcc) can result for Cu. A series of Cu/V multilayered films with equal layer thicknesses that spanned bilayer spacing values from 40 nm to 0.6 nm have been sputtered deposited with their *in situ* growth stress monitored during the deposition. When the bilayer spacing was reduced, and the layers maintained their bulk phase stability, the tensile stress in the multilayer film reduced. This has been contributed to compressive strain generated at the interfaces even with Cu forming stacking faults in response to the strain. When the bilayer was at 2 nm, the Cu layer phase transformed to bcc and adopted its own lattice parameter separate from that of bcc V. Further reductions in bilayer spacing retained a crystalline bcc phase but with a matching lattice spacing between the layers. Significant intermixing was quantified by atom probe tomography even though the elements are immiscible in the bulk state. The change in phase also resulted in an increase in the film's overall tensile growth stress.

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1. Introduction

When material dimensions are on the order of the nanometer size regime, several interesting properties are observed including increases in hardness [1], reduction of metaling points [2], and changes in structure or phase [3]. Arguably, of these properties, the change in phase most often is serendipitously discovered [4–10]. In an effort to better understanding the governing principles of nanoscale phase stability, the concepts of strain induced [11–13] and thermodynamic stabilized [3,14–17] models have been proposed. For the former concept, the formation of a metastable phase occurs in order to reduce lattice-mismatch-induced strain energies in the crystal structure [12,13]. In the thermodynamic approach [3], the change in phase is the result of reduction of interfacial energy dominating the volumetric energy penalty for creating a new crystal structure. Both ideas are similar in that the interfaces have a significant impact on phase stability, with the strain-energy construction suggesting the change in phase to be metastable whereas the thermodynamic model regards the new phase to be in equilibrium based on an energy balance.

To study these ideas, multilayered thin films are an ideal architecture where one can have a fixed surface area over the substrate while simply changing the thickness to precisely control the volume. Thus, changes in atomic layer thicknesses provide the ability to systematically probe volumetric-to-surface energy balances as well as strain energy contributions that scale with volume. Moreover, a multilayer provides control of two different material volumes in contact with each other where the changes in the interface can be accommodated by either epitaxial orientation relationships and/or different volume fractions that regulate the mechanical responses in each of the layers. By tailoring individual layer thicknesses, the structural and chemical properties at these interfaces can then be easily modified and studied with respect to how phase stability changes in the layers [15,18]. In addition, thin films often develop significant residual stresses during deposition that exceed the elastic limits for their bulk counterparts [19,20]. This adds an interesting variable that can also influence the phase stability of each material.

Dregia et al. [3] provided a simple thermodynamic model between the Gibbians volumetric and interfacial energy changes between phases to help predict when a phase change is possible. In this model, the influence of strain energies can be incorporated into the volumetric energy contributors for predicting the equilibrium structure. In a two-component multilayer, the energy balance

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equation is written as

$$\Delta g = 2\Delta\gamma + \Delta G_i \mathrm{f}_i \lambda + \Delta G_j (1 - \mathrm{f}_i)\lambda \quad (1)$$

where f_i is the volume fraction of element i, ΔG_i or ΔG_j are the volumetric energies of the i or j species respectively, λ is the bilayer thickness (sum of each individual layer thickness), $\Delta\gamma$ is the interfacial free energy reduction associated with the change in phase at the interface, and Δg is the normalized total free energy, ΔG, divided by the fixed surface area of the film. One of the nice outcomes of this model is a predictive map that has regions of phase stability as a function of the volume fraction and the bilayer spacing with each region bounded by the energy ratio of the volumetric free energy change associated with a particular phase transformation divided by the interfacial free energy reduction for that transformation.

This model has been successfully applied to Ti/Al [14], Zr/Nb [15], Ti/Nb [16,18], Cu/Fe [21], and most recently to Cu/Nb [22]. Of these systems, Cu/Fe and Cu/Nb are thermodynamically immiscible or, in other words, there is an energetic penalty to mix. This is particularly important in that mixing through the interface and into the bulk of the other film can provide an additional chemical contribution to changing the volumetric free energy barrier for the phase transformation. Thus, by having a preference not to mix, systems are driven to potentially yield intrinsic stability behavior in the nanometer regime and potentially other interesting secondary transformations such as vitrification noted in Cu/Nb [22] and Ti/Fe [23].

When these phase transformations occur, the strains created in the film, as noted above, will also influence the stabilization energy criteria. In recent years, applying laser interferometry to measure the *in situ* growth stresses during these transformations has provided insights into how the phase stability evolves. In Ti/Nb, as the bcc Ti layer grew on the bcc Nb surface, a tensile stress developed which then relaxed and the Ti film grew compressive once it became hcp [18]. In Cu/Nb, upon phase transforming, the film underwent a compressive stress relaxation [22]. Each of these stress responses were associated with how the new phase was accommodated in their respective multilayer.

During the deposition process, most films will undergo an initial compressive stress response that is associated with Laplacian stresses from the atomic-scale migration of adatoms into embryonic islands [24,25]. Once the islands have formed, tensile stresses are generated as each island elastically strains towards the other to minimize surface/boundary energies [26]. Subsequent stresses will then become either tensile, if the adatoms have lower mobility on the surface, or compressive if the adatom have higher mobility on the surface. In general, low mobility elements include V, Fe and Cr [27] where higher mobility elements include Cu, Nb and Ti [28]. Obviously changes in processing, such as deposition temperature, deposition rate, and chamber pressure can modify these mobility behaviors.

Wan et al. [18] have recently discussed the relationship between phase stability and *in situ* growth stresses in the growth of Ti/Nb multilayered thin films. Based on their results, the growth stresses affected both the phase transformation as well as the interfacial intermixing. The bcc Ti phase was stabilized by a significant interdiffusion of Nb atoms (~20 at%) into the Ti layers. This intermixing was caused by differences in the surface free energy of Ti and Nb where the lower surface energy adatom migrated itself to the surface during growth and became encased in the other layer. In another case of phase transformation and its related growth stresses, the authors here reported semi-coherent to coherent interfacial structure changes that accompanied various fcc-to-bcc and bcc-to-fcc transformations in Cu and Nb respectively. These changes in the interfacial structure were associated with the phase of each layer being modified by the stress behavior between the different multilayered films [22]. Furthermore, when the layer thicknesses were sufficiently thin in Cu/Nb, the multilayer even vitrified indicating yet another phase stability region in these films.

The phase stability of bcc Cu has been an area of active study for many decades [29]. In 1924, Bain proposed a lattice strain based model to show how fcc structures, like fcc γ-Fe, could be converted to bcc α-Fe. Arguably, this 'Bain model' has been the foundation for understanding strain based mechanisms necessary to stabilize bcc Cu in the decades that proceeded its publication. Much of the interest in bcc Cu resides in its precipitation in steels [30]. It has been found that when Cu clusters, these cluster initially adopt a bcc phase eventually transforming to fcc as they coarsen [31]. As clusters (and precipitates) play a dominate role in strengthening, understanding the governing behavior of this phase change has been technologically important. More recently, the fabrication of Cu-based nanolaminates have been of strong interest to the irradiation community. Here, these nanolaminates create a sufficient number of interfaces that trap irradiation induced defects [32]. The phase stability of the Cu is thus important in the diffusivity of such defects in the nanolaminates. These nanolaminates have also been ideal case studies to understand slip behavior at interfaces between phases, such as Cu/Nb [33]. Thus, changes in Cu's stability at these interfaces will directly alter the means of dislocation propagation.

In this paper, we aim to expand beyond the Cu/Nb work by studying Cu/V. Though both systems are immiscible, Cu/V offers several interesting differences in the lattice strain matching at the interface, which as noted above, is hypothesized to influence both the phase stability and the growth stresses. For example, the Kurdjumov–Sachs orientation relationship provides for ~2.5% lattice strain for Cu/V but is ~11.6% in Cu/Nb [34]. Clearly, the lower mismatch strain will change the associated free energies and provide for a very interesting (and comparative) study. In addition, the adatom mobility of the bcc elements are different with V being intrinsically low (or nominally tensile generating) and Nb being intrinsically high (or normally compressive generating). All of these factors will impact the interfacial structure evolution and corresponding *in situ* growth stress that contribute to phase stability in thin multilayered materials.

2. Experimental procedure

A series of Cu/V multilayers with equivalent individual layer thicknesses that varied from 0.3 nm to 20 nm or bilayer thickness from 0.6 nm to 40 nm were sputter-deposited onto [001] Si substrates to a total layer thickness of ~200 nm. The films were grown by direct current sputter deposition at room temperature (~25 °C) in an AJA ATC-1500 sputtering chamber. The pressure of the sputtering chamber was $<1.33 \times 10^{-6}$ Pa prior to sputtering and kept at 0.133 Pa while ultra-high-purity argon was flowed through the chamber at a flow rate of 0.01 L/min as the working gas.

A *k*-Space Associates multi-beam optic sensor (MOS) was used to measure the *in situ* growth stresses during deposition [35]. The stresses in these films were calculated based on the substrate curvature changes using the Stoney equation [36] given as

$$\sigma_f = \frac{E_S}{6(1-\nu_S)} \frac{t_S^2}{t_f} \left(\frac{1}{R} - \frac{1}{R_0}\right) \quad (2)$$

where σ_f is the film stress, E_s is the Young's modulus of the substrate, ν_s is the Poisson's ratio for the substrate, t_s is the substrate thickness, t_f is the film thickness, and $1/R_0$ and $1/R$ are measured curvatures of the film before and during/after deposition,

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