Applied Surface Science 463 (2019) 545–555

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

The influence of alloying interactions on thin film growth stresses

Xuyang Zhou*, Gregory B. Thompson

The University of Alabama, Department of Metallurgical & Materials Engineering, Tuscaloosa, AL, USA

ARTICLE INFO

Keywords:
Stress evolution
Thin films
W-Fe
W-Cr
Atom probe tomography

ABSTRACT

A series of W-Fe and W-Cr thin films were sputter deposited and the intrinsic growth stresses determined by in situ wafer curvature measurements. Under the growth conditions studied, the elemental W film grew in a compressive stress state whereas the elemental Fe and Cr films grew in a tensile stress condition. By mixing Fe or Cr with W, the alloy stress state was bounded between the two elemental stresses which included a zero stress condition. The specific stress response is reported as a function of alloy type that is affected by grain size, grain boundary composition, localized phase separation, and energetic peening effects. Using the ambient temperature deposited zero stress composition, these films were re-deposited at 673K to drive the microstructure towards equilibrium. Under these conditions, both alloys exhibited similar compressive stress states during post-coalescence growth, with the post-deposition stress recovery being greater in the W-Fe film than that of the W-Cr film. This difference was contributed to the dissimilarity in grain sizes between the two films as well as how the solute partitioned in the matrix, *i.e.* at the grain boundary or as phase separated laths within the grains.

1. Introduction

Thin films are a vital architecture in several technologically important applications including tribological coatings [1], information storage [2], semiconductor transistor design [3,4], optical devices [5,6], and energy harvesting [7,8]. During deposition, thin films can generate significantly large intrinsic stresses that can lead to thin film device failures. For example, tensile stress can lead to cracking [9,10] and compressive stress is often associated with delamination, buckling, and blistering of the film from the substrate [10–12]. Stresses in integrated circuit connecters have been shown to promote the nucleation of whiskers and hillocks which results in short circuit failures [13,14]. Thus, the ability to control residual stress in thin films is vitally important to several technically relevant industries.

When a thin film is deposited, the intrinsic stress state evolves based on the different stages of growth. In the early or embryonic stage of growth, clusters of adatoms migrate together generating a compressive stress from the Laplacian stress effect. As the embryonic islands grow and approach each other, they will elastically strain at the expanse of the strain energy creating a tensile stress state to eliminate the free surface energy of the islands [15–17]. After the islands coalesce, elemental films with high adatom mobility, such as Cu [18], Ag [19] and Co [20], experience a post-coalescence compressive stress while films with low adatom mobility, like Fe [21] and Cr [21], tend to retain the coalescence-induced tensile condition with continued growth. To date, the post-coalescence stress state for the compressive stress generation is still a matter of much research and discussion [15,19,22–34]. In large part, this stress has been proposed to be generated by the migration of adatoms into grain boundaries that are driven by the differences in chemical potential at the surface and at the grain boundaries during deposition. [19].

Based on these post-coalescence stress state concepts, *i.e.* adatom partitioning to grain boundaries, Fu and Thompson [35,36] reported how preferential segregation in an alloy could be used to control the compressive film stress. In their work, an Fe-Pt alloy thin film was used and could retain a compressive stress, even in Fe-rich conditions (which, as mentioned above, Fe is nominally tensile). This film's compressive stress was characterized to have a preference of Pt residing in the grain boundaries. Even more intriguing was that by mixing these two elements together, a film with a zero residual stress could be achieved at a specific composition where the grain and grain boundary was compositionally homogeneous, *i.e.* no grain boundary segregation. Follow on work by Kaub and Thompson then showed that alloy stress manipulation was limited by the solute equilibrium concentration within the grain boundary using a Cu(Ni) alloy film [37]. Further alloying of Ni into Cu simply drove the Ni solute back into the Cu solution [37]. The authors here have reported how solute concentration can be used to manipulate the grain size to regulate the stress states using Fe (Cr) alloy films as the case studies [38]. In all of these reports, the grain size and/or grain boundary composition was identified as key variables

* Corresponding author.
E-mail address: xzhou41@crimson.ua.edu (X. Zhou).

https://doi.org/10.1016/j.apsusc.2018.08.212
Received 23 April 2018; Received in revised form 25 July 2018; Accepted 23 August 2018
Available online 24 August 2018
0169-4332/

in controlling the stress. Thus, alloy composition, much like deposition rate, pressure, and substrate temperature appears to act as a processing variable to regulate the resulting thin film residual stress either by microstructure control and/or its intrinsic thermodynamic attributes for segregation to grain boundaries [21,39–46].

In the follow-on work in the Cu(Ni) and Fe(Cr) films, the zero stress condition was not achieved that had previously been reported in Fe-Pt. This is because both Cu and Ni grow (nominally) in a compressive stress state as elemental films and Fe and Cr grow (nominally) in a tensile stress state as elemental films. Neither alloy was mixed with an element that grows in an opposite post-coalescence stress condition. Furthermore, in the Fe-Pt alloy film, where Fe is nominally tensile and Pt is nominally compressive, the zero stress state occurred when the composition within the grain at the grain boundary were equivalent. To date, there have been no follow-on studies to determine if other appropriately mixed alloy films can achieve a zero residual stress state, and, if so, is the homogenization of matrix and grain boundary composition needed. Clearly, depending on the interaction between the solvent and solute atoms, the microstructure and grain boundary chemistry of such an alloy will vary dependent on the collective thermodynamics of the system itself, such as positive and negative enthalpies of mixing. These variations could then generate different stress responses by phase development within the film's microstructure as well as the compositional evolution within the grain boundaries.

Based on these ideas, in this new work, we extend these previous alloying studies by exploring the relationship between composition and stress in mixed compressive-tensile systems using Fe or Cr (both of which nominally exhibit tensile growth responses [21]) with W (a nominally compressive growth film [39]). The tensile stress for either Fe or Cr is linked to its low adatom mobility [21]. Conversely, compressive stresses are often discussed in terms of higher mobility species [18–20] but W, having a very high melting point (~3300 °C), could be assumed to have rather limited surface diffusivity. To rationalize W's compressive stress, one must also consider the sputtering energy distribution. In sputtering, the energies of ejected atoms are not uniform but can span a range from 10^{-2} eV up to about 10^{4} eV [47]. This energy distribution has been described by the Thompson formula [47,48], $F(E) \propto E/(E+U)^3$ where E is the energy of the sputtered atoms from a polycrystalline target and U is the binding force normal to the surface. Typically, sputtered atom energies have a maximum near $U/2$ (which is several eV's) and a dissipating energy tail extending to tens to hundreds of eV's [49]. When comparing W's higher binding energy to Fe, it lends itself to having a higher probability for generating atoms with higher energies [39,50]. This increase in energy is believed to assist in the adatom diffusion into the grain boundary regions that have been proposed to create the compressive response in thin films [19]. Additionally, the impact energies of W adatoms can create peening effects that can also lead to compressive stresses [39]. To that point, Shen et al. [39] systematically studied the relationship between adatom energy and stress responses in W and reported that as the Ar pressure decreased from 7 Pa to 0.47 Pa, the W film stress went from +2 GPa (tensile stress) to −3 GPa (compressive stress). They then concluded that the reduction of ion collision at the low pressures enabled more energetic W adatoms to contribute to the atomic peening process [51].

Based in part from these types of findings, Chason et al. [52] summarized a model to sort out different effects on thin film stress. This model contains three components – the growth stress σ_{growth}, the ballistic impacts of energetic ions at grain boundaries $\sigma_{gb}^{energetic}$, and the defects created in the film $\sigma_{bulk}^{energetic}$ with the summation as

$$\sigma^{sputt} = \sigma_{growth} + \sigma_{gb}^{energetic} + \sigma_{bulk}^{energetic} \quad (1)$$

In this framework, high energetic adatoms could have a high probability to diffuse into grain boundaries resulting in a compressive growth stress via the first term in Eq. (1) with the impact of energetic W adatoms also generating atomic peening stresses via the last two terms in Eq. (1).

From the prior experimental and modeling work, we recognize that the deposition conditions clearly have a role in the resultant stress. With that understanding, the forthcoming experimental films were grown such that the elemental films' deposition exhibited the aforementioned responses so that the effect of mixing (at a fixed set of deposition parameters) can then be studied. Furthermore, by using the same compressive forming film (*i.e.*, W), one can ascertain how different tensile growing species alter the alloy stress state which can then help provide a more systemic understanding of how alloying yields a zero residual stress state.

For the case study materials, all three elements are body-centered cubic (BCC) at room temperature. Nonetheless, the thermodynamic equilibrium behavior upon mixing is different in each binary system, with the W-Cr system being immiscible (positive enthalpy of mixing) and W-Fe yielding several intermetallic phases (negative enthalpy of mixing) which include the Laves phase (Fe_2W) and the mu (μ) phase (Fe_7W_6) [53,54]. Consequently, both systems provide a different phase equilibrium response over the W compositions. Though such equilibrium phase behavior is predicted, the highly dynamic processing of sputtering often places multiple elements into a single solid solution creating, at least initially, the same (metastable) phase for both alloys.

2. Experimental

Elemental and alloyed thin films of Fe, Cr, W, $W_{1-x}Fe_x$, and $W_{1-x}Cr_x$ ($0 < x < 1$) were sputter deposited from 99.95% pure Fe, Cr, and W elemental targets in an AJA ATC-1500 stainless steel magneton-sputtering system. The films grew to an approximate thickness of 200 nm on 300 μm thick silicon [1 0 0] substrates which had a 100 nm thick thermally grown amorphous surface oxide. The base vacuum pressure prior deposition was $< 6 \times 10^{-6}$ Pa. For sputtering, ultra-high purity argon flowed as the working gas at 10 standard cubic centimeters per minute flow rate to a pressure of 0.27 Pa. The real-time deposition rates of elemental films were determined using a SQM-160 quartz crystal sensor. By adjusting the sputtering power, the collective sputtering rate for all films was set at 0.1 nm/s. Alloy films with the different compositions were achieved through co-sputtering the respective two elemental targets at various sputtering power combinations to yield this deposition rate while achieving the targeted composition. The composition of each alloy film was then verified by energy-dispersive X-ray spectroscopy (EDX) using an EDAX® detector in a FEI Quanta 3D dual electron-focus ion beam (FIB) microscope. For the *in situ* heating experiments during deposition, the reported temperature was calibrated using a k-Space® Bandit system that provides a non-contact measurement of the Si band edge's response with temperature. The *in situ* stress state during deposition was monitored using the k-Space Associates (kSA®) Multi-beam Optic Sensor (MOS) [55]. The details about this wafer curvature-based stress measurement technique can be found elsewhere [35,56]. But concisely stated, this technology shines a two-dimensional laser array onto a substrate surface and measures the displacement of the reflective rays as the substrate bends in response to the film's growth on the substrate. Using the Stoney equation [57], given below, the stress within the film is then measured and calculated.

$$\sigma_f = \frac{E_s}{6(1-\nu_s)}\frac{t_s^2}{t_f}\left(\frac{1}{R}-\frac{1}{R_0}\right) \quad (2)$$

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

Post-deposition, the films were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and atom probe tomography (APT). The XRD was performed in a $\theta-2\theta$ scan in an X'pert Philips diffractometer operated with Cu Kα radiation ($\lambda = 1.5406$ Å) at