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Influence of solute partitioning on the microstructure and growth stresses in nanocrystalline Fe(Cr) thin films

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ABSTRACT

This paper addresses how solute segregation and phase separation evolves the intrinsic growth stresses for Fe-4Cr and Fe-16Cr (at.%) nanocrystalline films. Ambient temperature deposition resulted in both alloys exhibiting a near equivalent tensile stress though the average grain sizes were approximately 50 nm and 100 nm respectively. Upon heating during deposition to 523 K and 673 K, the tensile stress was reduced in each film and it eventually became compressive for the higher deposition temperature. Interestingly, the Fe-16Cr film, at the higher heating temperature, diverted from the steady state compressive stress towards a tensile stress after approximately 150 nm of growth. The collective stress evolution of these films is discussed in terms of their phase separation, which can include spinodal deposition, as a function of Cr content and processing temperature. It was found that Cr acted as a grain refiner which appeared to dominate the film microstructure and associated stress response.

1. Introduction

Thin films are a technologically important material structure for a variety of industries including protective wear resistance surfaces in the tool and die industries, reflective coatings for optics, and electrical conduction control of logic devices for semiconductors [1–8]. These physical properties are influenced by the intrinsic residual stresses that are generated during deposition of the film [9–15]. In extreme cases, these stresses result in film delamination, buckling, and micro-cracking from the substrate causing device failures.

Thin film stress development is related to the adatom mobility and the competition between coalescence-induced tensile stress and compressive stress generation as these adatoms diffuse into grain boundaries [16–21]. These effects have been studied intently by controlling various deposition parameters including pressure [22] and growth rate [23]. In situ heating has also been shown to promote stress evolution by providing thermal energy that will exponentially increase the adatom mobility and change the thin films stress state. For example, Thurner [24] reported that low adatom mobility species, e.g. Fe or Cr, which nominally show tensile growth can transition to compressive growth with increasing deposition temperature. In many of these studies, a single element system was used. However, multi-species systems or alloys could offer an additional variable of control through the cooperative adatom diffusivity behavior between different atoms. Here, the thermodynamic tendencies for solid solution formation, phase separation, or the precipitation of a new crystalline phase would dramatically affect the film stress evolution. This would be particularly pronounced by providing additional heating during deposition that would assist the system towards equilibrium. This would be especially relevant in thin film growth where physical vapor deposition can yield non-equilibrium phases by the rapid “quenching” of the species from the vapor to solid state [25, 26].

In an alloy, one can expect the segregation of a particular species to grain boundaries. Such segregation could be a viable route for stress state manipulation through microstructural control of grain boundary chemistries as well as grain size, where solute could pin grains from growing [25–27]. We have recently reported growing a series of low Cr content Fe(Cr) thin films at room temperature and found an inverse relationship between the grain size and tensile stress with Cr content up to 8 at.% [27]. When Cr was below the solubility limit, the Fe(Cr) grains grew whereas as upon exceeding the solubility limit, the Cr concentration within the grain boundaries was noted to increase and refine the grain size. Collectively this resulted in a varied stress response with composition.

In this work, we continue our investigations into the alloying effects of Fe(Cr) but with temperature during deposition. Fe(Cr) is a spinodal decomposition system [28–30] and has been well studied in bulk because of its interest in irradiation based steels [29, 31]. In our initial thin film studies, the early onset of phase separation was noted with an increased presence of Cr in the high angle grain boundaries [32]. With

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the use of in situ heating done in this study, this phase separation should be even more pronounced and have a much more dramatic effect on the grain size, morphology, and stress states. For example, one can easily speculate that intrinsic Cr clustering within the grains created by the initial deposition but now heated by the substrate would stimulate the creation of new interfaces besides the island-to-island contacts during deposition. Such interfaces would change how the grains evolve and grow resulting in yet to be studied stress responses during deposition. Furthermore, depending on the film's composition within or outside the miscibility gap, the phase separation of Fe and Cr via spinodal decomposition, which does not have a thermodynamic barrier for phase separation [33], or nucleation and growth could give another interesting variable for early onset stress evolution in the deposition films.

Though both species will phase separate from each other, Fe does tolerate a limited solubility of Cr within its phase at room temperature, with such solubility increasing with temperature. Though the exact extent of solubility varies among different reports [28–30, 34], an agreeing explanation was found that the change in the enthalpy of mixing from negative to positive is around 5 at.% Cr. Thus, an ideally lower solute Fe(Cr) thin film, such as Fe-4Cr, would be in equilibrium as a solid solution at either room temperature or elevated temperature whereas a higher solute film, Fe-16Cr, would be well within the miscibility gap and phase separate. Using these two compositions, we aim to better understand the intrinsic links of phase separation on nanocrystalline film morphology and accompanying residual stress development during the film deposition process.

2. Experimental

The two alloy films - Fe-4Cr or Fe-16Cr (at.%) - were magnetron sputter deposited in an AJA ATC-1500 system using 99.95% pure pre-alloyed targets. During deposition, the target-substrate distance was 40 cm with a gun to substrate tilt angle of 0.5 rad. The films were grown to an approximate thickness of 300 nm onto 300 μm thick silicon [100] substrates which had a protective 100 nm amorphous silicon oxide surface to prevent deleterious reactions with the substrate with heating. The temperature was calibrated using a k-Space® Bandit system on a previous Si substrate where the Si wafer's band edge changed with known temperature values. The sputtering rate was found to be approximately 0.100 nm/s for Fe-4Cr and 0.106 nm/s for Fe-16Cr and was relatively invariant to changes over the in situ deposition temperatures studied. The deposition rates were determined by dividing the film thickness, measured from X-ray reflectivity (XRR) [35] and confirmed by the transmission electron microscopy (TEM) cross-sectional micrographs, by the deposition time. XRR was performed on an X'pert Philips diffractometer operated with Cu K_α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA. Prior to deposition, the chamber had a base pressure $< 6 \times 10^{-6}$ Pa evacuated by mechanical and turbo-pumps. High-purity Argon then flowed into the sputtering chamber as a working gas at a rate of 10 standard cubic centimeters per minutes to a pressure of 0.27 Pa.

The in situ stress state was measured through a k-Space® Multi-beam Optic Sensor attached to the base of the chamber [36]. By reflecting a series of laser spots from the substrate to a charge-coupled detector, the relative position of the spots moved as the substrate bends in response to the growth stresses. Using the Stoney equation, given below, the stress within the film was calculated.

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

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.

The phase identification of the films was characterized by X-ray diffraction (XRD) via a Philips diffractometer with Cu K_α radiation as the source operated at 45 kV and 40 mA as well as by electron diffraction using an FEI Tecnai F20 (scanning) transmission electron microscope ((S)TEM). The in-plane and out-plane microstructures were also characterized in the TEM from either traditional cutting, dimpling, and ion-milling 3 mm discs (plan-view) or focus ion beam (FIB) extraction and milling techniques (for the cross-sections). With the assistance of the NanoMEGA ASTAR™ platform [37–39], the grain sizes, grain boundary character, as well as grain orientation distribution, were quantified using precession electron diffraction (PED) in the TEM. The PED scanning was operated with a 0.2° precession angle and a scanning step size of 3 nm, in the same regions of interest (ROI), which was 0.9 μm × 0.9 μm for in-plane, 1.4 μm × 0.3 μm for out-of-plane. After scanning, the data was converted for analysis using TSL OIM Analysis 7 software. Grain based and kernel based misorientation analyses were employed to identify grains and any varying local misorientations within the grains respectively. The Local Orientation Spread (LOS) method was used to calculate the misorientation between each point in the kernel with LOS maps created used those averaged values for the kernel. The LOS can then provide a visual map of crystalline imperfections within the grain, such as sub-grain boundary formations. The readers are referred to references [40, 41] for further details. In this paper, the first nearest neighbor at a maximum misorientation spread of 5° was employed. Pole figures were also constructed from the PED data for texture analysis and compared to the XRD data collected on a Bruker D8 GADDS diffractometer.

The overall composition and local element distribution in the films were characterized by Atom Probe Tomography (APT). The required needle-shaped geometry for these specimens was prepared in the film's cross-section using a FIB lift-out technique and annular milling procedure described in reference [42] in either a TESCAN LYRA FIB- Field Emission Scanning Electron Microscope (SEM) or an FEI Quanta 3D dual beam FIB-SEM. With the APT tip prepared, the specimen was loaded into a Hummingbird TEM holder and placed into the FEI Tecnai F20 S(TEM) operated at 200 keV. The grain-to-grain mapping of the film was conducted using the PED at a precession angle again of 0.2° but now at a scanning step size of 2 nm. Afterwards, the tip was field evaporated in a Cameca Instruments Local Electrode Atom Probe (LEAP®) 5000 XS operated at a specimen set point of 57 K, 500 kHz laser pulse repetition rate for a 1.0% ions per pulse detection rate with a laser energy of 50 pJ. The prior PED analysis of the tips grain structure was then overlaid onto the APT reconstructed chemical map with further details on this procedure found in reference [32].

3. Results

Fig. 1 shows the in situ stress evolution of the 300 nm thick Fe-4Cr and Fe-16Cr films deposited at room temperature (RT), 523 K, and 673 K. The RT films for both alloys exhibited near equivalent steady-state tensile stress, ~0.65 GPa, in the post coalescence regime evident by the linear response. This is more clearly plotted as the instantaneous stress, Fig. 1(b). At the higher deposition temperatures, the tensile stress was reduced and even became compressive for the highest deposition temperature of 673 K. But, unlike the RT deposition, the instantaneous stress response varied with thickness.

At 523 K, both alloy films retained the tensile stress states with near invariant instantaneous stress responses after the early stages of post-coalescence growth ($> \approx 100$ nm), Fig. 1(a). However, the increased temperature lowered the overall absolute stress value. Upon in situ depositing at 673 K, a more dramatic change in the stress evolution was found. Both films exhibited an evolving growth stress during deposition, with the stress values over the thickness range studied being compressive. Of the two films, the Fe-16Cr did reveal a more dramatic change in stress with thickness with a trend to revert back to a tensile state for thicknesses beyond ≈150 nm. This type of non-steady state