CONSTRAINED DIFFUSIONAL CREEP IN ULTRA THIN COPPER FILMS DEPOSITED ON SUBSTRATES

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ABSTRACT

In a recent study of diffusional creep in polycrystalline thin films deposited on substrates, we have discovered a new class of defects called the grain boundary diffusion wedges (Gao *et al*., Acta Mat. **47**, pp. 2865-2878, 1999). These diffusion wedges are formed by stress driven mass transport between the free surface of the film and the grain boundaries during the process of substrate-constrained grain boundary diffusion. The mathematical modeling involves solution of integro-differential equations representing a strong coupling between elasticity and diffusion. The solution can be decomposed into diffusional eigenmodes reminiscent of crack-like opening displacement along the grain boundary which leads to a singular stress field at the root of the grain boundary. We find that the theoretical analysis successfully explains the difference between the mechanical behaviors of passivated and unpassivated copper films during thermal cycling on a silicon substrate. An important implication of our theoretical analysis is that dislocations with Burgers vector parallel to the interface can be nucleated at the root of the grain boundary. This is a new dislocation mechanism in thin films which contrasts to the well known Mathews-Freund-Nix mechanism of threading dislocation propagation. Recent TEM experiments at the Max Planck Institute for Metals Research have shown that, while threading dislocations dominate in passivated metal films, parallel glide dislocations begin to dominate in unpassivated copper films with thickness below 400 nm. This is consistent with our theoretical predictions. We have developed large scale molecular dynamics simulations of grain boundary diffusion wedges to clarify the nucleation mechanisms of parallel glide in thin films. Such atomic scale simulations of thin film diffusion not only show results which are consistent with both continuum theoretical and experimental studies, but also revealed the atomic processes of dislocation nucleation, climb, glide and storage in grain boundaries. The study should have far reaching implications for modeling deformation and diffusion in micro- and nanostructured materials.

1. INTRODUCTION

The study of the mechanical properties of materials at nano- and sub-micrometer scales is motivated by continuing miniaturization of engineering and electronic components, development of nanostructured materials, thin film technology and surface science. When the material volume is lowered, characteristic dimensions are reduced and material properties often deviate from the behavior of bulk materials. Small-scale materials are defined as materials where at least one dimension is reduced. For instance, thin films bond to substrates are a relevant example of materials in small dimensions since the film thickness h_f is small compared to the planar extension of the film and the thickness of the substrate. Thin films deposited on substrates have become an increasingly active area of research in the last decades. This can partly be attributed to the fact that these materials are becoming critically important in today's technologies, whereas changes in material behavior due to the effects of surfaces, interfaces and geometrical constraints are not completely understood. The focus of this paper is on mechanical properties of ultra thin sub-micron copper films on substrates. We show that in such materials, important effects of the film surface and grain boundaries are observed and that the constraint by the film-substrate interface governs the mechanical behavior Different inelastic deformation mechanisms are known to relax the internal and external stresses in a thin film. Experiment shows that for films of

thicknesses between approximately 2 and 0.5 μm, the flow stress increases in inverse proportion to the film thickness [1-3], thus

$$\sigma_Y \propto \frac{1}{h_f} . \qquad (1)$$

Originally, it was proposed that the strengthening of thin films results from the energetic effort associated with dislocation motion [4-6]. More recent theoretical and experimental work [7-11] indicates that the strength of thin metal films often results from a lack of active dislocation sources.

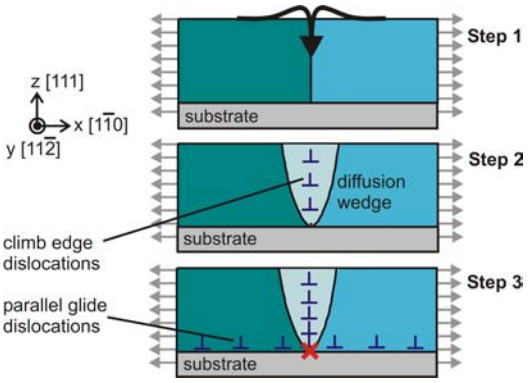

Figure 1: Continuum mechanics model of constrained diffusional creep [13]. Diffusional creep is modeled by climb of edge dislocations in the grain boundary. A singular, crack-like stress field develops in the long-time limit leading to very large resolved shear stress on glide planes parallel to the film surface, causing nucleation of parallel glide dislocations.

In copper films, the regime where plastic relaxation is limited by dislocation nucleation and carried by glide of threading dislocations reaches down to film thicknesses of about $h_f \approx 400$ nm [10]. For yet thinner films experiments reveal a film-thickness-independent flow stress [8, 10, 12]. This observation contradicts the existing theories of plasticity in thin films. In-situ transmission electron microscopy observations of the deformation of such ultra thin films reveal dislocation motion parallel to the film-substrate interface [8, 10, 12]. This glide mechanism is unexpected, because in the global biaxial stress field there is no resolved shear stress on parallel glide planes. This indicates that there must be a mechanism involving long-range internal stresses that decay only slowly on the length scale of the film thickness. For sufficiently thin films these internal stresses have a pronounced effect on the mechanical behavior. It has been proposed that constrained diffusional creep may be the origin of this novel deformation mechanism [13]. In the model of constrained diffusional creep, it is assumed that through climb of edge dislocations along the grain boundary, material is transported from the surface toward the substrate, leading to a crack-like stress field with large resolved shear stress on glide planes parallel to the film surface. This explains the occurrence of parallel glide dislocations. The model is schematically summarized in Figure 1. Despite progresses in atomistic and continuum modeling [13-19], deformation by parallel glide dislocation motion in ultra thin films is not well understood as of today. In this paper, we propose atomistic and continuum studies to investigate the behavior of such thin films below 400 nm.

In this paper we focus on fully atomistic modeling of constrained diffusional creep in thin copper films. Unlike in previous studies of quasi-two-dimensional simulations [16], here we describe simulation results of a polycrystalline model. We discuss the dependence of the grain boundary structure on the diffusivities and show that nucleation of parallel glide dislocations occurs from those grain boundaries with highest diffusivities leading to fastest grain boundary traction relaxation, in agreement with the predictions by theory [13, 15]. The simulation results close the theory-experiment-simulation linkage.

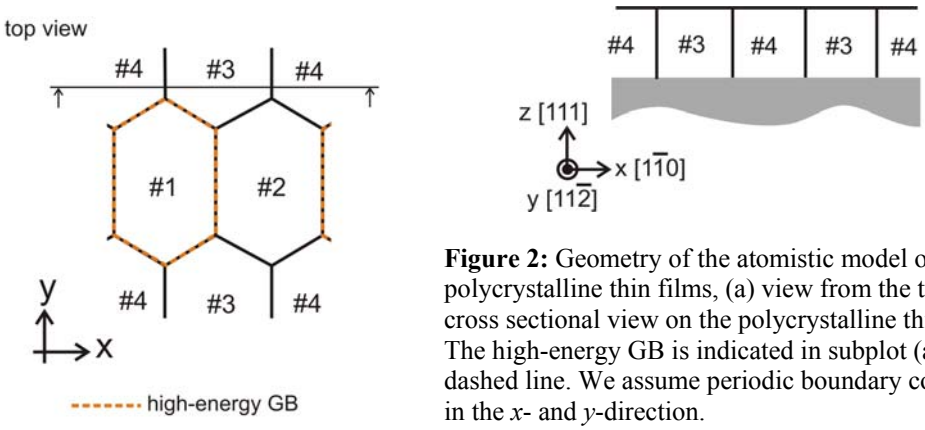

Figure 2: Geometry of the atomistic model of polycrystalline thin films, (a) view from the top, and (b) cross sectional view on the polycrystalline thin film. The high-energy GB is indicated in subplot (a) by the dashed line. We assume periodic boundary conditions in the *x*- and *y*-direction.

2. MODELING OF CONSTRAINED DIFFUSIONAL CREEP IN POLYCRYSTALLINE THIN FILMS

Atomistic modeling of plasticity in thin films is just at its beginning, and few studies of such systems have been reported in the literature. Recently, atomistic simulations of two-dimensional thin film systems were discussed [20]. In this study, the yield strength was investigated and nucleation and motion of threading dislocations was in the focus. However, the model did not contain grain boundaries despite the fact that grain boundaries can serve as fertile sources for dislocations and could play an important role in plasticity of thin films. Some previous studies focused on constrained diffusional creep in quasi-two dimensional plane strain models, where nucleation of parallel glide dislocations was studied [16, 21]. In contrast to these simplistic models, we propose a three-dimensional model of thin films with a more realistic microstructure and focus on modeling of constrained diffusional creep and parallel glide dislocation nucleation. The model studied in this section is a polycrystalline thin film consisting of hexagonal shaped grains, as shown in Figure 2. The choice of this geometry is motivated by the grain microstructure found in experiments [8, 10, 12]. An advantage of this model over the geometry used in previous models [16] is that fully-periodic boundary conditions in the *x*- and *y*-direction can be assumed, avoiding effects by rigid boundaries during application of loading [16]. We will focus on dislocation nucleation and motion from grain boundaries and the grain boundary-substrate interface. One of the important objectives will be to study the effect of grain boundary traction relaxation by diffusional creep on the dislocation mechanism that operates in the film. As known from previous studies [17], the structure of the grain boundaries has significant influence on the nucleation of dislocations. Here we investigate the role of the grain boundary structure on diffusional creep and associated dislocation mechanisms. Here we will show that grain boundary relaxation by diffusional creep gives rise to dominance of parallel glide dislocations, in accordance with experiment. In contrast, in grains where grain boundary tractions are not relaxed, threading dislocations prevail.

2.1 ATOMISTIC MODELING

We extend the two-dimensional studies reported earlier [16, 21] to the three-dimensional case. We apply a biaxial loading rate on the order of 1 percent total strain per nanosecond. The temperature is, as in the two-dimensional studies [16], chosen around 90 % of the melting temperature. Our simulation tool is classical molecular dynamics, which has proven to be capable of describing small-scale materials phenomena associated with materials failure in the past,

including diffusional creep [16, 17, 19, 22-24]. We use a multi-body EAM potential to model the thin copper film [25]. We model a film of thickness $h_f \approx 11$ nm with a grain diameter of about 22 nm in the *x*-direction (experimentalists find a similar grain size to film thickness ratio between two and three). The simulation sample is constructed such that there are high-energy as well as low-energy grain boundaries. This is motivated by our objective to investigate the effect of grain boundary structure on the deformation mechanisms. As shown in Figure 2, grain #1 is completely surrounded by high-energy grain boundaries, and the other grains feature low-energy grain boundaries (grain #1 is in its reference configuration, grain #2 is rotated by 35.4 degrees, grain #3 by 44.7 degrees and grain #4 by 53.4 degrees). The system contains about 2 million atoms.

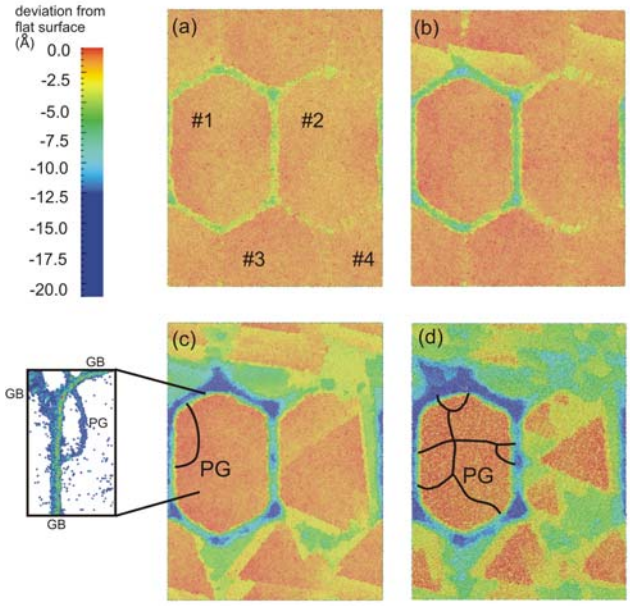

Figure 3: Plot of the surface profile of the polycrystalline thin film. The color refers to the surface height (red=high, blue=low). This color scheme allows determining diffusive deformation along specific grain boundaries surrounding grain #1. The results reveal existence of surface grooves at high-energy grain boundaries that are up to 2 nm deep (that is 18 % of film thickness). The results therefore indicate that parallel glide dislocations are only nucleated at grain boundaries whose tractions are relaxed by diffusional creep (see exclusively PG dislocations in grain #1). This result strongly supports theoretical predictions [13, 15].

2.2 CONSTRAINED GRAIN BOUNDARY DIFFUSION

At elevated temperatures, high-energy grain boundaries transform into liquid-like intergranular layers [26, 27], whereas low-energy grain boundaries establish as arrays of misfit dislocations [17]. Formation of grain boundary diffusion wedges is accompanied by surface grooving at the grain boundary interface. Therefore, the surface height profile provides an indication of diffusive activities in the grain. Figure 3 plots the surface profile of a polycrystalline sample during different stages of the simulation (similar to AFM results). We observe that, in agreement with the predictions in the literature [26, 27], high-energy grain boundaries provide very fast diffusion paths, in contrast to low-energy grain boundaries. This strongly underlines the notion that the grain boundary structure needs to be taken account when diffusivities are determined. Compared with all other diffusion paths, grain triple junctions provide the fastest paths for diffusion. This is verified since at grain triple junctions, the surface grooves are deepest (see Figure 3).

2.3 NUCLEATION OF PARALLEL GLIDE DISLOCATIONS

According to the hypothesis by continuum theory [13, 15], parallel glide dislocations should exclusively be nucleated along grain boundaries whose tractions are relaxed by diffusional creep, and threading dislocations should dominate elsewhere. Since high-energy grain boundaries are predominant paths for diffusion [16, 26, 27], in grains neighboring such high-energy grain boundaries, parallel glide dislocations should dominate plasticity. In our sample, we find no other dislocation activity than parallel glide dislocations in grain #1. We observe nucleation of first parallel glide dislocations (see Figure 3c) at a biaxial strain of about 1.6 %. In other grains where little grain boundary relaxation is possible by diffusional creep, threading dislocations are easily nucleated (due to generation of a surface step, they appear as lines on the surface in Figure 7). Predominant nucleation site are, in agreement with previous results of studies of plasticity in thin films at low temperature [17], misfit dislocations at the grain boundary. The parallel glide dislocations are shown in Figures3 and d as a black line. Their shape is determined using the energy method as exemplified in the blow-up of Figure 7c. Additional analysis was performed based on geometrical methods identical to those applied in [16]. Additional dislocations appear as the loading is increased and the dislocations form a complex network (Figure 3d).

3. DISCUSSION AND CONCLUSIONS

Our results extend this understanding, since the governing character of the grain boundary structure in thin films is found also when deformation is mediated by diffusional creep. This is in qualitative agreement with the discussion in [26, 27], where it was proposed that the grain boundary structure has a significant influence on the diffusivities. In view of the model of constrained diffusional creep [13, 15], the grain boundary structure determines how fast the tractions along the grain boundaries are relaxed and a singular stress field develops. The dominance of grain boundary processes during deformation of ultra thin films is in qualitative agreement with recent investigations of other small-scale materials, such as nanostructured materials [26, 27].

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