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ANALYTICAL AND NUMERICAL MODELING OF SURFACE MORPHOLOGIES IN THIN FILMS

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ABSTRACT

Experimental studies have shown that strains due to thermal expansion mismatch between a film and its substrate can produce very large stresses in the film that can lead to the formation of holes and hillocks. Based on a phenomenological description of the evolution of a solid surface under both capillary and stress driving forces and for surface and grain boundary self-diffusion, this article provides, for the first time, analytical and numerical solutions for surface profiles of model geometries in polycrystalline thin films. The results can explain a variety of surface morphologies commonly observed experimentally and are discussed to give some practical insights on how to control the growth of holes and hillocks in thin films.

INTRODUCTION

The long term stability of thin films under a variety of conditions has been extensively studied both theoretically¹⁻⁹ and experimentally.¹⁰⁻²⁶ Models have been developed to describe surface morphologies for different ideal geometries.²⁷⁻³¹ These models have provided solutions for the profiles of surfaces evolving under capillary and stress driving forces. Excellent tutorials of the theoretical procedure used in such models can be found in a chapter by Mullins³² and an article by Srolovitz.³³ In these treatments, grain boundary (GB) self-diffusion as a transport mechanism is not included since it was not relevant to the particular cases that were modeled (i.e. single crystal surface under stress or thermal grooving in stress-free sheets). In most practical cases, however, morphological changes in polycrystalline thin solid films are not only driven by both capillary forces and stresses but involve transport of atoms along GBs. Only recently have models of thin films begun to include these two driving forces and transport mechanisms simultaneously,^{34,35} using earlier approaches that are more common in mechanical metallurgy to model crack growth.^{36,37} A similar trend is found in modeling the sintering of particles.^{38,39}

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The theoretical description of the motion of atoms goes through the usual steps^{27,32} of assigning a chemical potential in the solid (here, on the surface of that solid), expressing the gradients of chemical potential, the flux of atoms they create, and by translating the divergence of these fluxes into a rate of atoms accumulation via the continuity equation. Finally, this rate of accumulation of atoms can be related to the speed of motion of an element of surface along its normal and converted into a surface profile for each time.

In most studies that take a constitutive approach (as opposed to an atomistic one), Herring's expression for the chemical potential^{40,41} on the surface or in the GB is the starting point. The properties of the solid are usually assumed to be independent of crystallographic orientation. Finally, derivations can be made for various transport mechanisms such as volume diffusion, surface diffusion, GB diffusion, evaporation-condensation, and viscous flow.

As explained earlier, the model described in this article assumes that atoms motion can be driven simultaneously by stress and capillary forces. Modeling a free standing film or foil can be performed taking only surface tension into account, since thermal strain do not induce stresses when a body is free to expand in all directions. However, for a film on a substrate, stresses must be included since they can develop to very high levels as a result of thermal expansion mismatch.

This article will show results which apply specifically to polycrystalline films on non-reactive substrates and will therefore include a description of GBs that intersect a surface. The first section will formulate the motion of atoms in a GB under stress.³⁵ It will then be used to extend Mullins' original theory of thermal grooving for stationary²⁷ and moving⁴² GBs. Analytical solutions will be given for one-dimensional ideal cases^{35,43} and numerical solutions will be sought for two-dimensional surfaces with more complex (but more realistic) geometries such as triple junctions and hexagonal grains. The results, their meaning and how they can be usefully applied to decrease defects during thin film processing will be discussed.

STEADY-STATE GB FLUX

This section briefly summarizes the description of the stress-induced motion of atoms along a flat GB. As explained in detail in ref. 35, a stress applied to the GB produces an exchange of atoms between the free surface of the film and the regions where the stress is extremum. When a film is bonded to its substrate, these regions of high biaxial stress are located at the film-substrate interface. When the stress is compressive (which usually occurs during heating for a metallic film on a metal oxide substrate), atoms migrate from the film-substrate interface to the free surface. Tensile stresses produce the inverse effect. If $z(x,t)$ describes the

surface profile, and σ is the average stress in the film in the direction perpendicular to the GB (resulting from thermal expansion coefficient mismatch), this flux condition can be expressed for a planar thin film geometry⁴³ with the following equation:

$$z'''(0,t) = -v_{gb}D_{gb}\sigma/\eta v_s D_s \gamma \equiv j, \quad (1)$$

where a prime denotes partial differentiation with respect to x (i.e. $z' = \partial z/\partial x$), η is the film thickness, v_s and v_{gb} are the surface and GB areal density of atoms, respectively, Ω is the atomic volume, T is the temperature, D_s and D_{gb} are the surface and GB self-diffusion coefficients, respectively, γ is the film-vapor surface tension, and j will be called the stress flux constant. One can immediately note that a compressive stress yields a positive flux constant j which physically means that atoms will flow out of the GB to accumulate onto the surface.

Five important approximations are made with respect to the effect of stress: 1) volume diffusion can be ignored in comparison with GB diffusion, 2) plastic deformation by slip or twinning does not interfere with GB diffusion creep, 3) the transient required to establish the steady-state stress gradient along the GB may be neglected, 4) the back-stress due to surface curvature is negligible compared to the thermal stress and 5) the isotropy of elastic properties prevents shear stresses from developing in the GB plane (such stresses could cause GB sliding). For a metal below half its melting temperature, the first four approximations are valid when the GB thickness (or length) is less than a few micrometers.³³ Hence, for commonly studied thin films, these approximations are satisfied. The fifth approximation is valid for instance for cubic metallic films with a (111) texture, or for highly isotropic materials.

ANALYTICAL SOLUTIONS

This section will summarize the analytical solutions that were obtained for one-dimensional surface profiles at a stationary and a moving GB. The one-dimensional surface profile $z(x,t)$ is now described in a frame of reference traveling with the GB in the direction parallel to the x -axis, with

instantaneous speed $V(t)$. If $\varepsilon = x - \int_{t_0}^t V(t)dt$ is the distance along the x -axis from the intersection of the GB with the free surface (where t_0 is the initial time), the general differential equation describing the surface can be written as:⁴²

$$Bz'''' - Vz' + \partial z/\partial t = 0, \quad (2)$$

where the prime now denotes partial differentiation with respect to ϵ (i.e. $z' = \partial z / \partial \epsilon$) and B is the Mullins constant ($B = v_s D_s \gamma \Omega^2 / k_B T$). A solution for Eq. (2) will now be presented for two cases: stationary and traveling GB.

Stationary GB

For a stationary GB, $\epsilon = x$ and the initial and boundary conditions can be written as:³³

$$z(x, 0) = 0 \quad (3)$$

$$z'(0, t) = m, \quad (4)$$

where m is the slope at the root of the GB groove ($m \equiv \gamma_{gb} / 2\gamma_s$). Eq. (3) expresses the initial flatness of the surface and Eq. (4) translates the fact that a constant dihedral angle must exist at the intersection of the GB as a result of the balance between surface and GB tensions. Finally, the previous section showed that the stress applied to the GB leads to a flux of atoms expressed in Eq. (1).

A solution to Eq. (2) subject to conditions (1), (3) and (4) could be found³⁵ using conventional Laplace transform techniques:

$$z(x, t) = m(Bt)^{1/4} \sum_{n=0}^{\infty} a_n \{x/(Bt)^{1/4}\}^n + j(Bt)^{3/4} \sum_{n=0}^{\infty} b_n \{x/(Bt)^{1/4}\}^n, \quad (5)$$

and the coefficients of the series can be calculated as follows:^{27,35}

$$a_{n+4} = a_n (n-1)/4(n+1)(n+2)(n+3)(n+4) \quad (6)$$

$$b_{n+4} = b_n (n-3)/4(n+1)(n+2)(n+3)(n+4), \quad (7)$$

with $a_0 = (2^{1/2} \Gamma[5/4])^{-1}$, $a_1 = 1$, $a_2 = -(2^{3/2} \Gamma[3/4])^{-1}$, $a_3 = 0$,
and $b_0 = (2^{1/2} \Gamma[7/4])^{-1}$, $b_1 = 0$, $b_2 = (2^{3/2} \Gamma[5/4])^{-1}$, $b_3 = 1/6$.

Fig. 1 illustrates the solution; the stress-free thermal groove profile is plotted with the solutions for which capillary effects (first series in Eq. (5)) have a magnitude twice that of stress effects at the time; the lower and upper curves show the case of compressive and tensile stress, respectively.

GB Traveling at Constant Velocity

For a GB moving at constant velocity for which thermal grooving does not occur ($m = 0$), the surface profile solutions $z_-(\epsilon, t)$ on the left side ($\epsilon \leq 0$) and $z_+(\epsilon, t)$ on the right side ($\epsilon \geq 0$) of the GB must satisfy the following conditions:

$$z_-(0) = z_+(0) \quad (8)$$

$$z_-'(0) = z_+'(0) \quad (9)$$

$$z_-'''(0) = -j \quad (10)$$

$$z_+'''(0) = j, \quad (11)$$

where the flux constant j is given in Eq. (1). Eqs. (8) and (9) ensure that the profile and the slope are continuous at the intersection of the GB with the surface ($\varepsilon = 0$) while Eqs. (10) and (11) express the constant flux in or out of the GB due to stress. The solution for Eq. (4) subject to boundary conditions (8)-(11) can easily be found.³³

$$\varepsilon \leq 0: \quad z_-(\varepsilon) = j/\alpha^3 \{2 - \exp(\alpha\varepsilon)\} \quad (12)$$

$$\varepsilon \geq 0: \quad z_+(\varepsilon) = 2j/(3^{1/2}\alpha^3) \exp(-\alpha\varepsilon/2) \sin(3^{1/2}\alpha\varepsilon/2 + 2\pi/3), \quad (13)$$

where $\alpha^3 = V/B$. Eqs. (12) and (13) describe the steady-state profile of the ridge (or canal, according to the sign of j), which does not change shape and whose dimensions only vary by a scaling factor function of j , B and V .

Figure 1. Profile of an isolated thermal groove at a GB under compressive stress³⁵, no stress and tensile stress. The lateral changes of dimensions of each grain due to accumulation or depletion of atoms on the surface with the conservation of volume condition are not represented on this figure. The vertical sides of the two crystals indeed move closer together when the stress is compressive.

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The case of a stress-free traveling GB under pure thermal grooving conditions, was solved earlier by Mullins⁴² and can be described by the following equations:

$$\varepsilon \leq 0: \quad z_-(\varepsilon) = -m/3\alpha \exp(\alpha\varepsilon) \quad (14)$$

$$\varepsilon \geq 0: \quad z_+(\varepsilon) = -2m/3\alpha \exp(-\alpha\varepsilon/2) \cos(3^{1/2}\alpha\varepsilon/2 + \pi/3). \quad (15)$$

The normalized characteristic shapes of the two sets of solutions are plotted in Fig. 2 for $m = 1$ and $j = 1$.

Figure 2. Normalized surface profile of the steady-state solution of a traveling GB plateau⁴³ (under compressive stress) and traveling groove.⁴² The profiles are plotted for $B = 1$, $V = 1$, $j = 1$ and $m = 1$ and the GB is moving from left to right. The horizon of the film is defined by the horizontal dashed line ($z = 0$). Notice that the vertical dimensions of the figure are scaled by a factor of about 5.

The traveling ridge (or canal) leaves an accumulation plateau (or depletion crater) behind its moving front. The height h of the plateau (or depth of the crater), defined as the vertical distance between its top (or bottom) and the horizon of the film, as well as the slope of the surface m_σ at the GB (see Fig. 3), are constant. Similarly to the static GB problem, a linear combination of the two solutions can satisfy the boundary conditions when action by both capillarity and stresses occurs simultaneously.

Using Eqs. (12) and (13), where stress is the dominant driving force (no GB grooving), the velocity of the traveling GB and the flux constant j can be related to the height of the plateau (or depth of the crater) and the slope m_σ at the GB:

$$V = -B (2m_\sigma/h)^3 \quad (16)$$

$$j = 4m_\sigma^3/h^2. \quad (17)$$

The assumption of constant GB velocity should be valid for sufficiently high velocities since the temperature is constant and the average stress can be assumed to be fairly constant for a short period of time. If the GB

has moved away during the cooling process, m_σ can still be measured as it is the slope of the surface at the edge of the plateau (or crater) at the height $h/2$. Eqs. (16) and (17) should therefore allow measurements of GB velocity and GB self-diffusion coefficients.

Figure 3. Sketch of a cross-section of the film defining h and m_σ . The formation of a ridge at the GB tends to push it forward to decrease the GB area.

NUMERICAL SOLUTIONS

Numerical solutions of Eq. (2) subject to various boundary conditions were also sought to model more realistic polycrystalline thin films geometries. An implicit finite difference method was used to compute the solutions. The details of the method, the various tests performed to check the computer code, the technique used to convert computed values into physical quantities, and the accuracy of the results are given in refs. 9, 35 and 44. The surfaces were taken to be initially flat and were described using dimensionless variables. The surface profiles were calculated for different cases. Here, the results for two model cases are summarized: 1) a triple junction where three stationary GBs meet at a 120° angle and 2) the growth of an hexagonal grain under compressive stress.

For constant compressive equal biaxial stresses, the solution of the 120° stationary triple junction shows the growth of a bump at the intersection of the three GBs (see Figs. 4(a) and (b)). Similarly, under tensile stresses, a deep pit rapidly develops at the triple junction (see Figs. 4 (c) and (d)). The coordinates on the z axis of the surface representations are exaggerated with respect to the x and y axes by about 5 times. In these figures, Mullins constant, the stress flux constant j , and the time were chosen so that both contributions (due to capillarity and stress) have similar orders of magnitude and can therefore be visualized. Under tensile stresses (which typically develop during cooling) the capillary pitting action at triple junctions is accelerated. The relative magnitude of the two driving forces, the angles at the triple junction,⁴⁴ and the grain size are factors that will either favor pinholes or holes that propagate along GBs (i.e. branched-out holes).

The calculations for compressive stresses show that the GBs and the triple points can be placed in a metastable position since the accumulation of atoms tends to increase the GB area. An approach allowing GB motion therefore becomes necessary when hillock growth is to be modeled since

the pile-up of atoms at the GB tends to push it away from that pile. Also, when an as-deposited film with small initial grain size is heated, the driving force for GB motion can be quite high. To illustrate these conditions, the growth of a hexagonal grain under compressive stress was modeled. The grain is modeled to grow with its GBs moving at constant velocity. The results are plotted in Fig. 5. The shape of the surface exhibits a typical moatlike hillock morphology.

These results were found to be quantitatively in good agreement with experimentally measured (using atomic force microscopy) surface profiles of hillocks on annealed pure aluminum films deposited onto oxidized silicon substrates. This comparison between experimental and modeled surface profiles will be presented in a forthcoming article.⁴⁵

DISCUSSION

This theoretical model can clearly explain the mechanism of holes and hillocks formation during a thermal cycle and describe their growth in a quantitative manner. The results can therefore provide useful information on how to keep the population of holes and hillocks under control and how to influence grain growth through GB mobility.

A program aimed at enhancing grain growth would attempt to take advantage of capillary forces and stresses and optimizing their respective effects by using them at the appropriate time. Such an attempt would involve knowledge of the height of the ridge, for a given temperature increment, that would free GBs from their thermal grooves, and the mobility of the GBs at the new temperature, so as to tune the time between successive temperature increments in such a way that the GBs in their new position cannot be pinned by the freshly formed thermal grooves.

Grain growth enhancement has already been achieved experimentally using special heating cycles or techniques such as laser reflow,⁴⁶ rapid thermal annealing, and step ramping.⁴⁷ In the context of the results shown in the previous section, such methods seem to enhance grain growth by redistributing material emanating from the GBs more uniformly on the surface. In the case of pulse heating for instance, GB velocities are probably so high that the ridge height is negligible and thermal grooves do not have time to become sufficiently deep. Hillock formation and surface non-planarity should also influence the GB mobility as further grain growth takes place. If hillocks tend to repel the GBs which produced them, the mount they leave behind presents a barrier for GBs which would later attempt to sweep these areas. Further growth is therefore expected to be more difficult. An inert capping layer deposited at lower temperature before any thermal cycle could probably help in forcing grain growth to occur in two dimension and decrease the magnitude of thickness variations due to grooving or hillocking.

Figure 4. Evolution of the surface at a 120° triple junction.⁴⁴ Hillock formation under compressive stress: (a) $t = 10^4$ and (b) $t = 10^5$. Hole formation under tensile stress: (c) $t = 10^4$ and (d) $t = 10^5$.

Figure 5. Surface profile of an hexagonal grain growing under compressive stress.⁴³ The profile is computed for $B = 0.1$, $j = 0.001$ and $V = 0.0025$ after $t = 5,000$. The shape of the surface can be identified to that of experimental moatlike hillock.

Hillock density and size are two correlated parameters since the total volume change of the film (in the elastic regime) is determined by the thermal strain and the film thickness. A number of experimental studies^{1,18,23,25,48,49} have attempted to empirically describe the relationship between hillock size and density and experimental parameters such as film thickness, annealing temperature, alloying element concentration, and crystallographic orientation. The theory here showed that decreasing the size and density of the hillocks could be attempted by controlling: 1) the GB mobility and the diffusion kinetics, 2) the stress variation with temperature and time, and 3) the growth process, the number of GBs and the spatial redistribution of atoms. Control of GB mobility and diffusion kinetics can be achieved by additions of alloying elements (by GB pinning with solute atoms or precipitates), and the choice of the annealing temperature. Controlling stress is more difficult. However, the choice of the deposition temperature, the presence of a passivation layer, the addition of precipitate-forming elements, and the film thickness can at least help in modifying the initial stress and the rate of stress change; precipitates and solute atoms can strengthen the film and the passivation layer may change the stress gradient in the film. The spatial redistribution of atoms can be modified by creating barriers to diffusion (using layering, passivating the film or alloying). Also, producing sinks for atoms by ion bombardment can sometimes achieve similar goals. Finally, the growth process can highly be influenced by the film preparation method, the nature of the substrate, or the presence of an underlayer, the substrate temperature during deposition (which can promote different types of growth),^{50,51} the initial texture, and grain size distribution in the film.

CONCLUSION

This model extends the analysis of thermal grooving at GBs in thin sheet systems to the case of thin films on a substrate by including stress effects resulting from thermal expansion mismatch. Based on the assumption that surface and GB diffusion are the dominant transport mechanisms and that the materials properties are isotropic, the model can for the first time describe quantitatively the evolution of the surface profile of a polycrystalline thin film. Analytical and numerical solutions for ideal cases where GBs are either stationary or are allowed to move can explain a variety of thin films morphologies commonly encountered experimentally. Channel and pinhole formation seem to result from thermal grooving and cooling during an anneal where GBs are immobile and stresses are tensile. On the other hand, hillock formation seems to occur as grain growth takes place during the heating stage of the anneal and stresses are compressive.

The model can be used to describe some of the effects of stress on grain growth kinetics through GB mobility, and can be applied to provide

practical information on how to control the formation of holes and hillocks in thin films. Finally, the model offers the prospect of developing a novel method to measure directly materials properties such as GB velocity and self-diffusion coefficient of metals (such as aluminum) for which such data is not yet available.

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