

# COMPETITIVE MOTIONS OF GRAIN-BOUNDARY AND FREE SURFACE IN SELECTING THIN FILM MORPHOLOGY

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## ABSTRACT

During annealing of a polycrystalline thin film, grain-boundaries and film surfaces move. If the grain-boundaries move faster, the grains having the lowest free energy grow at the expense of others, resulting in a continuous film with large grains. If the film surfaces move faster, they groove along their junctions with the grain-boundaries, breaking the film to islands. This paper describes analytic solutions for steady surface motions, and discusses the morphology selection.

## INTRODUCTION

Figure 1a shows schematically an as-deposited film on a single crystal substrate, where the grain size of the film is taken to be comparable to the film thickness. Some grains (indicated by vertical arrows) have a smaller free energy than other grains (indicated by oblique arrows). An anneal at an elevated temperature causes the grains to increase average size and reduce total grain-boundary area (Fig. 1b). If held at the elevated temperature for a longer time, the film may either undergo substantial grain growth (Fig. 1c), or break to islands (Fig. 1d). Both behaviors have been observed in many systems [e.g., 1-3].

Clearly the two types of motions—grain-boundary migration and free surface grooving—compete to determine the fate of a film. Grain-boundary migration may lead to a large-grained, textured, continuous film. Free surface grooving may break the film to islands. A film selects its morphology according to the relative speed of the two motions. Consequently, an energetic consideration by itself is inadequate to select the morphology. The system selects morphology *dynamically*, according to both energetics and kinetics.

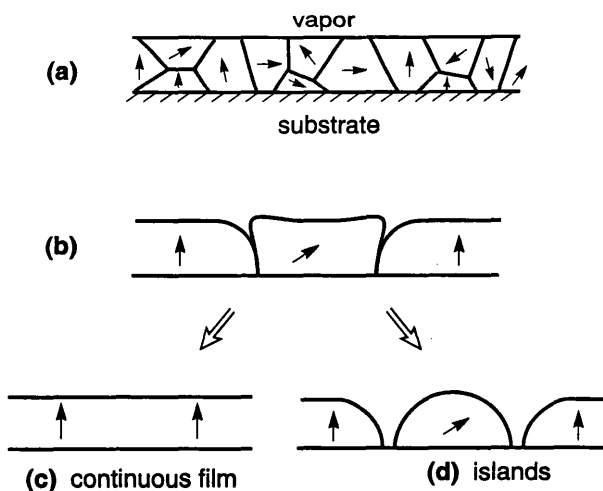


Fig. 1 Morphology selection: a continuous film or islands?

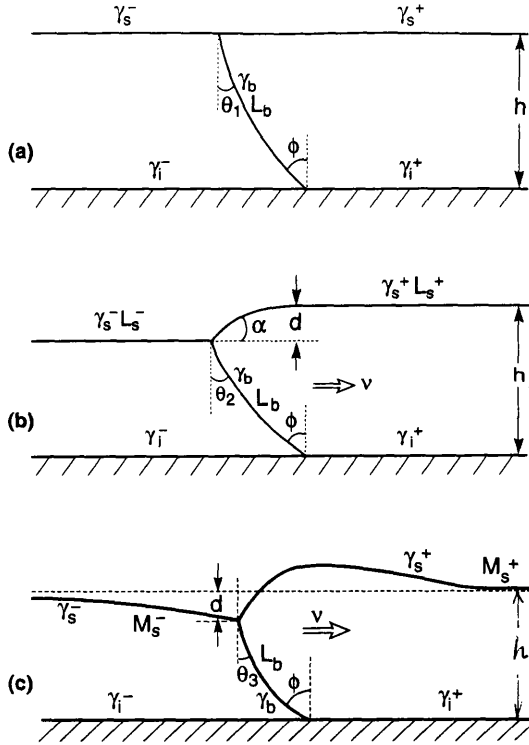


Fig. 2 Film surface either (a) remains flat, (b) moves by evaporation, or (c) moves by diffusion.

## THE MODEL

Figure 2 illustrates the model to be analyzed in this paper. We focus on the late stage when the grain size is much larger than the film thickness. The curvature in the plane of the film is negligible compared to the curvature in the cross-section of the film. The problem becomes two dimensional, and only the cross-sectional view is shown in Fig. 2. Three types of kinetics are assumed on the film surface. The surface either (a) remains flat, (b) moves by evaporation, or (c) moves by self-diffusion. Assume that elastic energy is negligible compared to the surface tensions in driving surface motions. The two grains, labeled as + and -, have different surface tensions  $\gamma_s^+$  and  $\gamma_s^-$ , and interface tensions  $\gamma_i^+$  and  $\gamma_i^-$ . The free energy of grain + is taken to be higher than that of grain -, namely,  $\gamma_s^+ + \gamma_i^+ > \gamma_s^- + \gamma_i^-$ . To simplify the analysis, we assume that the grain boundary and the film surfaces move in steady-state (i.e., with invariant shapes).

We first summarize Mullins's solution for the steady-state grain boundary motion [4]. Figure 3 shows a segment of grain-boundary migrating in the  $x$ -direction in a steady state at a velocity  $v$ . The coordinates  $x$  and  $y$  move with the surfaces. Let  $ds$  be a curve element,  $\psi$  the angle from the  $x$ -axis to the normal vector of the element, and  $K$  the curvature. The migration velocity normal to the grain-boundary,  $v_n$ , is taken to be proportional to the curvature, namely,  $v_n = L_b \gamma_b K$ , where  $\gamma_b$  is the grain-boundary energy, and  $L_b$  the grain-boundary mobility. The grain-boundary moves

toward the center of the curvature, and must concave in the direction of the velocity. The shape of the steadily migrating grain-boundary is described (with  $\psi$  as a parameter) by

$$x - x_0 = -\frac{L_b \gamma_b}{v} \ln(\cos \psi), \quad (1)$$

$$y - y_0 = -\frac{L_b \gamma_b}{v} \psi, \quad (2)$$

where  $x_0$  and  $y_0$  are constants to be determined by boundary conditions. The velocity  $v$  is so far undetermined, and will be determined later.

For all three situations in Fig. 2, the film-substrate interface is assumed to be immobile. At its junction with the grain-boundary, the surface tensions balance in the horizontal direction, relating the grain-boundary angle at the junction,  $\phi$ , to various surface tensions:

$$\sin \phi = (\gamma_i^+ - \gamma_i^-) / \gamma_b. \quad (3)$$

The larger the interface energy difference, the larger the angle  $\phi$ .

The grain-boundary angle at the junction are indicated as  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$  for the three situations in Fig. 2. They will be calculated in the following sections. To move steadily to the right, the grain-boundary must concave to the right. Consequently, the angles at the two triple junctions must satisfy  $\phi > \theta_i$ . *This is the condition under which the steady-state motion exists subject to each surface kinetics.*

#### GRAIN-BOUNDARY MIGRATION WHEN THE FILM SURFACE IS IMMOBILE

Figure 2a illustrates the case where the film surface is immobile, and the grain-boundary migration is the only kinetic process. At the junction of the film surface and the grain-boundary, the surface tensions balance in the horizontal direction, giving

$$\sin \theta_1 = (\gamma_s^- - \gamma_s^+) / \gamma_b. \quad (4)$$

The grain-boundary migrates to the right when  $\phi > \theta_1$ . According to (3) and (4), this condition is equivalent to  $\gamma_s^+ + \gamma_i^+ > \gamma_s^- + \gamma_i^-$ . Consequently, when the film surface is immobile, the grain-boundary migrates steadily if the two grains have different free energies. With the angles  $\theta_1$  and  $\phi$  as the boundary conditions, Equation (2) determines the steady-state grain-boundary velocity,  $v = L_b \gamma_b (\phi - \theta_1) / h$ .

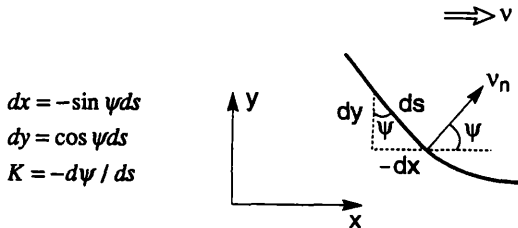


Fig. 3 A segment of a grain-boundary moving in a steady-state.

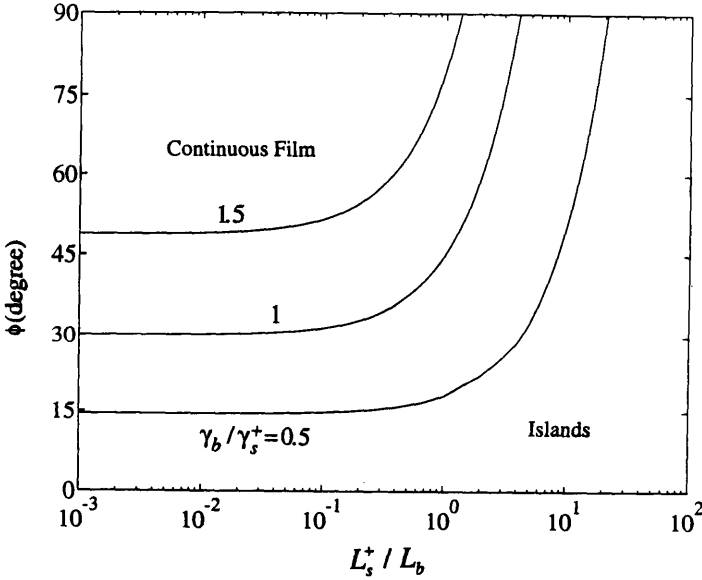


Fig. 4 Morphology selection map when mass evaporates on the film surface.

#### SIMULTANEOUS GRAIN-BOUNDARY MIGRATION AND SURFACE EVAPORATION

Figure 2b illustrates the case where mass evaporates on the surfaces of the two grains evaporate at the mobilities  $L_s^+$  and  $L_s^-$ , respectively. Assume that the vapor is in equilibrium with the flat film surfaces. Near the triple junction, however, the surface is disturbed by the grain-boundary, causing mass to evaporate. The amount of evaporation is taken to be much smaller than the amount of the vapor, so that evaporation does not change the chemical potential of the vapor phase during the anneal. Under these assumptions, the equation governing surface evaporation has the same form as grain-boundary migration, with  $L_b \gamma_b$  replaced by the surface properties  $L_s \gamma_s$ . The steady-state solution derived for grain-boundary motion is applicable for surface motion. The entire configuration moves at a uniform speed  $v$  to the right; all the surfaces concave in the direction of the velocity. Grain - must have a flat surface, because a curved surface would concave in the wrong direction. Evaporation causes the growing grain to be thinner than the parent grain by depth  $d$ , Fig. 2b.

Now at the top triple junction the surface tensions balance in both the vertical and the horizontal directions; the surfaces meet at angles determined by  $\gamma_b$ ,  $\gamma_s^+$  and  $\gamma_s^-$  according to the law of force balance. The rigid rotation of the junction is fixed by the requirement that surface - be flat. Consequently, the two angles in Fig. 2b,  $\theta_2$  and  $\alpha$ , are given by

$$\sin \theta_2 = \frac{(\gamma_b)^2 + (\gamma_s^-)^2 - (\gamma_s^+)^2}{2\gamma_b \gamma_s^-}, \quad \gamma_s^+ \sin \alpha = \gamma_b \cos \theta_2. \quad (5)$$

The condition under which the steady-state exists,  $\phi > \theta_2$ , places a restriction among the various surface tensions according to (3) and (5).

Applying (2) to the grain-boundary and surface +, we have  $v(h-d) = L_b \gamma_b (\phi - \theta_2)$  and  $vd = L_s^+ \gamma_s^+ \alpha$ . The two equations, solved simultaneously, determine the velocity and groove depth:

$$v = \frac{L_b \gamma_b (\phi - \theta_2) + L_s^+ \gamma_s^+ \alpha}{h}, \quad \frac{d}{h} = \frac{1}{1 + \frac{L_b \gamma_b (\phi - \theta_2)}{L_s^+ \gamma_s^+ \alpha}} \quad (6)$$

We adopt a criterion that the film is broken if the steady groove depth exceeds a certain fraction of the film thickness. This criterion divides the parameter space into two regions, one corresponding to continuous films, and the other to islands. To be definite, we set the criterion to be  $d/h = 4/5$ . Consider two grains having identical surface tensions,  $\gamma_s^+ = \gamma_s^- \equiv \gamma_s$ . In Fig. 4, for a given  $\gamma_b / \gamma_s$ , the film remains continuous after the anneal if the parameter set falls above the corresponding curve.

### SIMULTANEOUS GRAIN-BOUNDARY MIGRATION AND SURFACE DIFFUSION

Figure 2c illustrates the case where mass diffuses on the surfaces of the two grains. Mullins [5] solved the problem of a steadily translating groove. In the analysis, he included surface diffusion, but not the grain-boundary kinetics. Relevant results from his work are summarized here. The two grains are assumed to have identical surface properties,  $\gamma_s^+ = \gamma_s^-$  and  $M_s^- = M_s^+$ .

When mass diffuses on a surface, the normal velocity of the surface is determined by,

$$v_n = -M_s \gamma_s \partial^2 K / \partial s^2. \quad (7)$$

Here  $M_s = \Omega D_s \delta_s / kT$ , where  $D_s$  is the self-diffusivity on the film surface,  $\delta_s$  the effective thickness of mass participating in diffusion,  $\Omega$  the atomic volume,  $k$  Boltzmann's constant, and  $T$  the absolute temperature. Mullins assumed that  $M_s$  and  $\gamma_s$  are the same on the two grain surfaces.

The steady velocity,  $v$ , and the material constants define a length,  $(M_s \gamma_s / v)^{1/3}$ . This length sets the *scale* of the steady-state profile of the free surfaces. In particular, the groove depth,  $d$ , is proportional to this length. The *shape* of the translating moving groove depends on the ratio  $\gamma_b / \gamma_s$ . Under the assumption that the surface slope is small, the steady groove depth,  $d$ , must be linear in  $\gamma_b / \gamma_s$ . Mullins found that

$$d = \frac{\gamma_b}{3\gamma_s} (M_s \gamma_s / v)^{1/3}. \quad (8)$$

Surface diffusion rotates the surfaces at the triple junction. Dimensional consideration dictates that the rotation angle,  $\theta_3$  in Fig. 2c, only depend on  $\gamma_b / \gamma_s$ . Under the small slope assumption,  $\theta_3$  must be linear in  $\gamma_b / \gamma_s$ . Mullins's solution gives  $\theta_3 = \gamma_b / (6\gamma_s)$ . The total volume of the two grains is conserved, and the groove piles a bump on the parent grain, as shown schematically in Fig. 2c. Surface diffusion does not require that a steadily moving surface concave to the direction of the velocity, so that the growing grain has a curved surface.

We now add the grain-boundary kinetics. For the grain-boundary in Fig. 2c to move steadily to the right, the various surface properties must be such that  $\phi > \theta_3$ . Equation (2) gives the grain-boundary velocity:

$$v = L_b \gamma_b (\phi - \theta_3) / (h - d). \quad (9)$$

Equations (8) and (9) are coupled algebraic equations for the steady state groove depth  $d$  and the steady state velocity  $v$ .

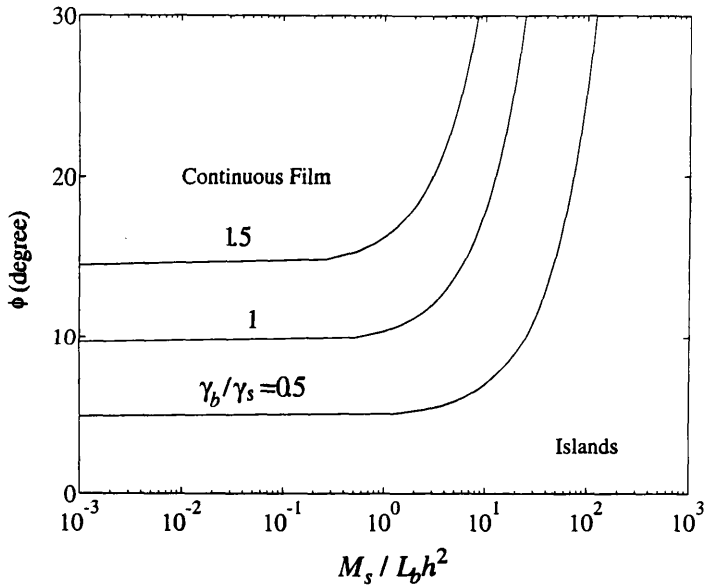


Fig. 5 Morphology selection map when mass diffuses on the film surface.

By setting  $d/h = 4/5$  in (8) and (9), we draw in Fig. 5 a morphology selection map for the case where the grains have identical surface properties,  $\gamma_s^+ = \gamma_s^-$  and  $M_s^- = M_s^+$ . A film remains continuous if  $\phi$  is large,  $\gamma_b / \gamma_s$  is small,  $M_s / L_b$  is small, and  $h$  is large. For a given  $\gamma_b / \gamma_s$ , the film breaks to islands if the parameter set falls below the corresponding curve.

#### CONCLUDING REMARKS

Three types of surface kinetics are considered. They affect the condition for steady state migration through angles  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  in Fig. 2, and the steady groove depth. These considerations allow us to draw morphology selection maps, Figs. 4 and 5. To ascertain the robustness of the steady-state motions, we have simulated transient surface motions [6]. For systems satisfying the steady-state condition, the simulations show that the steady-states are stable, and can be reached from initial geometries of larger variations. For systems violating the steady-state, the simulations show that the surface grooves and breaks the film; the time to groove through the film thickness is dictated by the surface mobility.

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#### REFERENCES

1. C. V. Thompson and J. Floro, and H.I. Smith, *J. Appl. Phys.*, **67**, 4099 (1990).
2. K. T. Miller and F. F. Lange, *J. Mater. Res.*, **6**, 2387 (1991).
3. T. Wagner, M. Lorenz, and M. Ruhle, *J. Mater. Res.*, **11**, 1255 (1996).
4. W. W. Mullins, *J. Appl. Phys.*, **27**, 900 (1956).
5. W. W. Mullins, *Acta Met.*, **6**, 414 (1958).
6. B. Sun, Z. Suo and W. Yang, *Acta Mater.* In press (1997).