

A Phase Field Model for Grain Growth and Thermal Grooving in Thin Films with Orientation Dependent Surface Energy

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Abstract. A phase field model for simulating grain growth and thermal grooving in thin films is presented. Orientation dependence of the surface free energy and misorientation dependence of the grain boundary free energy are included in the model. Moreover, the model can treat different mechanisms for groove formation, namely through volume diffusion, surface diffusion, evaporation-condensation, or a combination of these mechanisms. The evolution of a groove between two grains has been simulated for different surface and grain boundary energies and different groove formation mechanisms.

Introduction

The grain size, grain size distribution and grain orientation strongly influence the strength, electronic properties and durability of polycrystalline films. Due to the high ratio of surface to bulk material, surface energy has an important effect on grain growth in thin films [1]. In order to balance surface tension with grain boundary tension, grooves are formed where grain boundaries intersect the film surface [2,3]. It has been observed experimentally that the grooves exert a drag force on moving grain boundaries and can stop grain growth [4]. Furthermore, the surface energy of the grains may depend on their orientation. Favorably oriented grains with low surface energy may have a high driving force for grain growth and break free from the grooves, resulting in secondary recrystallization. This mechanism is often applied to obtain highly textured films with a huge grain size for micro-electronic devices [4–6].

Mullins [7, 8] and Zhang [9] distinguish three different mechanisms for groove formation, namely through volume diffusion, surface diffusion or evaporation-condensation. The groove morphology depends on which is the dominant mechanism.

In this article we present a phase field model for simulating the effect of thermal grooving and orientation dependent surface energy on grain growth in thin films. The three mechanisms of groove formation are considered in the model.

Model description

In order to describe the effect of surface tension on the evolution of the grains, the environment of the film, e.g. the atmosphere or substrate, is included in the simulations. A schematic representation of the simulation system for the case of a film with two grains is shown in figure 1. The model assumes that groove formation is controlled by diffusion processes, namely bulk or surface diffusion in the film, or diffusion of film material in the environment after evaporation or dissolution.

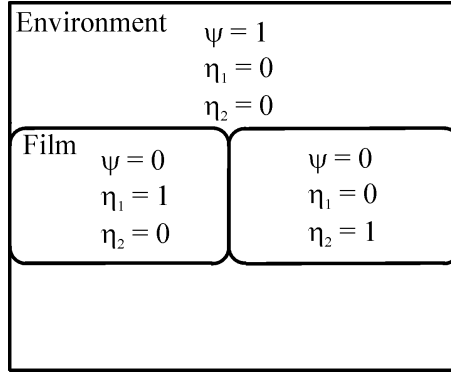


Fig. 1: System geometry and phase field variables used in the simulations.

The model is based on the grain growth model of Chen and Yang for normal grain growth [10,11], in which different grains are represented by different phase field variables $\eta_i(\vec{r}, t)$ that are continuous functions in space and time. In each grain one of the η_i 's equals 1 and all the other equal 0. An extra phase field variable $\psi(\vec{r}, t)$ is introduced into the model to distinguish between environment and film. It equals 1 in the environment and 0 in the film. $\psi(\vec{r}, t)$ is a conserved variable. It can be interpreted as a scaled composition variable. For example in the case of an Al-film in an argon atmosphere

$$\psi = \frac{c - c_{\text{film}}}{c_{\text{env}} - c_{\text{film}}} \quad (1)$$

where c is the local concentration of Ar, c_{film} the solubility of Ar in Al and c_{env} the equilibrium concentration of argon in Ar-gas above an Al-film.

The total free energy is formulated as a volume integral over the film and the environment

$$F = \int_V \left[f_0(\eta_1, \eta_2, \dots, \eta_p, \psi) + \frac{\kappa}{2} \sum_{i=1}^p (\vec{\nabla} \eta_i)^2 + \frac{\kappa}{2} (\vec{\nabla} \psi)^2 \right] dV \quad (2)$$

with

$$f_0 = m \left(\sum_{i=1}^p \left(\frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \left(\frac{\psi^4}{4} - \frac{\psi^2}{2} \right) + \sum_{j<i}^p \gamma_{i,j} \eta_i^2 \eta_j^2 + \sum_{i=1}^p \gamma_{i,\psi} \eta_i^2 \psi^2 \right), \quad (3)$$

the specific free energy as function of the phase field variables. The minima of the specific free energy correspond with the values of the phase field variables in the different domains in the simulation system. Within the film, f_0 has minima at $\psi = 0$, one of the $\eta_i = \pm 1$ and the other $\eta_i = 0$. In the environment, f_0 is minimal for $\psi = \pm 1$ and all $\eta_i = 0$. In the presented simulations, only the minima with $\eta_i = 1$ or $\psi = 1$ are considered. m is a parameter related to the depth of the free energy well. p is the number of grain orientations considered in the simulation.

Orientation dependence of the surface free energy is introduced through the parameters $\gamma_{i,j}$ and $\gamma_{i,\psi}$ and by giving κ the following dependence on the phase field variables [12,13]

$$\kappa = \frac{\sum_{j<i}^p \kappa_{i,j} \eta_i^2 \eta_j^2 + \sum_{i=1}^p \kappa_{i,\psi} \eta_i^2 \psi^2}{\sum_{j<i}^p \eta_i^2 \eta_j^2 + \sum_{i=1}^p \eta_i^2 \psi^2}. \quad (4)$$

This formulation also allows to let the grain boundary energy depend on the misorientation between neighboring grains. At each interface, only one of the terms in the summation differs from 0. Accordingly, $\kappa = \kappa_{i,j}$ at the interface between grains i and j . The $\kappa_{i,j}$ and $\gamma_{i,j}$ are related to the free energy of the grain boundary between the grains with orientations i and j and the $\kappa_{i,\psi}$ and $\gamma_{i,\psi}$ to the surface free energy of grain i . The model assumes that the interfacial free energies do not depend on the orientation of the interface with respect to the crystal structure of the grains.

Based on the theory of Cahn and Hilliard for systems with diffuse interfaces [14], it can be calculated that for a system with a free energy of the form (2) and (3) the widths of the interfaces are proportional to

$$l_{i,j} \propto \sqrt{\frac{\kappa_{i,j}}{(\Delta f_0)_{\max}}} = \sqrt{\frac{32\kappa_{i,j}}{m(1+2\gamma_{i,j})}}, \quad (5)$$

with $(\Delta f_0)_{\max} = f_0 - f_{0,\min}$ and the interfacial free energies equal

$$\sigma_{i,j} = \frac{1}{\sqrt{3}} \sqrt{\kappa_{i,j} m (1 + 2\gamma_{i,j})}.$$

All types of interfaces are given the same thickness in the simulations for numerical convenience. Hence, for each interface, the parameters $\kappa_{i,j}$ and $\gamma_{i,j}$ must satisfy the relation

$$\frac{\kappa_{i,j}}{m(1+2\gamma_{i,j})} = \text{cte}. \quad (6)$$

The evolution of the non-conserved phase field variables $\eta_i(\vec{r}, t)$ is given by a generalized Ginzburg-Landau equation

$$\frac{\partial \eta_i}{\partial t} = -L \left[\frac{\partial f_0}{\partial \eta_i} + \frac{1}{2} \left(\frac{\partial \kappa}{\partial \eta_i} \right) \left(\sum_{j=1}^p (\vec{\nabla} \eta_j)^2 + (\vec{\nabla} \psi)^2 \right) - \kappa \nabla^2 \eta_i - \vec{\nabla} \kappa \cdot \vec{\nabla} \eta_i \right]. \quad (7)$$

The kinetic coefficient L is related to the mobility of the grain boundaries. The temporal evolution of the conserved phase field variable $\psi(\vec{r}, t)$ governs a generalized Cahn-Hilliard equation

$$\frac{\partial \psi}{\partial t} = \vec{\nabla} \cdot M \vec{\nabla} \left[\frac{\partial f_0}{\partial \psi} + \frac{1}{2} \left(\frac{\partial \kappa}{\partial \psi} \right) \left(\sum_{i=1}^p (\vec{\nabla} \eta_i)^2 + (\vec{\nabla} \psi)^2 \right) - \kappa \nabla^2 \psi - \vec{\nabla} \kappa \cdot \vec{\nabla} \psi \right]. \quad (8)$$

To distinguish between bulk and interface diffusion M has the following spatial dependence

$$M = \frac{M_\eta (\sum_{i=1}^p \eta_i^2) + M_\psi \psi^2}{\sum_{i=1}^p \eta_i^2 + \psi^2} \quad \text{for} \quad \sum_{j<i}^p \eta_i^2 \eta_j^2 + \sum_{i=1}^p \eta_i^2 \psi^2 < 10e - 6 \quad (9)$$

$$M = \frac{M_{\text{gb}} \left(\sum_{j<i}^p \eta_i^2 \eta_j^2 \right) + M_{\text{s}} \left(\sum_{i=1}^p \eta_i^2 \psi^2 \right)}{\sum_{j<i}^p \eta_i^2 \eta_j^2 + \sum_{i=1}^p \eta_i^2 \psi^2} \quad \text{for} \quad \sum_{j<i}^p \eta_i^2 \eta_j^2 + \sum_{i=1}^p \eta_i^2 \psi^2 > 10e - 6 \quad (10)$$

$$(11)$$

M_η and M_ψ are related to the bulk diffusion coefficients of respectively the film and the environment. M_{gb} and M_{s} describe respectively grain boundary and surface diffusion.

Simulations

The evolution of a groove between two grains was simulated using the system geometry depicted in figure 1. The system was discretized using 256×256 grid points. The thickness of the film was 128 grid points. The lattice spacing Δx was taken equal to 0.5×10^{-8} m. For all simulations, $L = 1 \text{ s}^{-1}$, $m = 1 \text{ J/m}^3$, $\Delta t = 0.01 \text{ s}$. Simulations were performed for different values of the parameters κ , γ and M .

A central finite difference scheme based on 3 grid points in each dimension was used to approximate the laplacian and a central scheme based on the 2 neighboring grid points for the gradients. An explicit Euler technique was used for the time stepping. Periodic boundary conditions were applied.

Since equation (4) is not defined within the grains where $\sum \eta_i^2 \eta_j^2 = 0$, the parameter κ was only calculated at the interfaces, namely where $\sum_{j<i}^p \eta_i^2 \eta_j^2 + \sum_{i=1}^p \eta_i^2 \psi^2 > 10e - 6$.

To prevent ψ from taking values outside the interval $[(0 - c_{\text{film}})/(c_{\text{env}} - c_{\text{film}}), (1 - c_{\text{film}})/(c_{\text{env}} - c_{\text{film}})]$, the term $\partial f_0 / \partial \psi$ was implemented as

$$\frac{\partial f_0}{\partial \psi} \quad \text{for} \quad \frac{0 - c_{\text{film}}}{c_{\text{env}} - c_{\text{film}}} \leq \psi \leq \frac{1 - c_{\text{film}}}{c_{\text{env}} - c_{\text{film}}}$$

$$-1 \quad \text{for} \quad \psi < \frac{0 - c_{\text{film}}}{c_{\text{env}} - c_{\text{film}}} \quad \text{and} \quad 1 \quad \text{for} \quad \psi > \frac{1 - c_{\text{film}}}{c_{\text{env}} - c_{\text{film}}}$$

Furthermore, for one iteration step ($\Delta t = 0.01 \text{ s}$) for the Ginzburg-Landau equations, 200 iterations using a time step $\Delta t/200$ are performed for the Cahn-Hilliard equation.

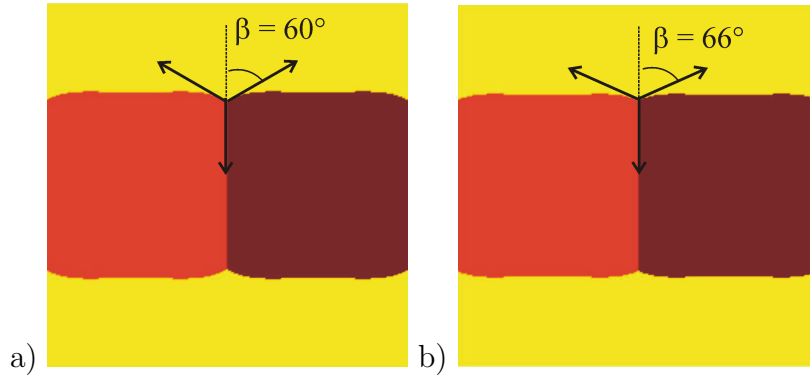


Fig. 2: Simulation images for 2 different ratios of the surface and grain boundary free energy. Both grains have the same surface free energy. a) $\sigma_s = \sigma_{\text{gb}} = \sqrt{2} \text{ J/m}^2$: $\kappa = 2 \text{ J/m}^3$, $\gamma = 1$. b) $\sigma_{\text{gb}} = \sqrt{2} \text{ J/m}^2$, $\sigma_s = 1.25\sqrt{2} \text{ J/m}^2 = (5/4)\sigma_{\text{gb}}$: $\kappa_{1,2} = 2 \text{ J/m}^3$, $\kappa_{\psi,1} = \kappa_{\psi,2} = 2.5 \text{ J/m}^3$, $\gamma_{1,2} = 1$, $\gamma_{\psi,1} = \gamma_{\psi,2} = 11/8$.

Equilibrium angle When the surface free energies of both grains are equal, the equilibrium angle of the groove¹ depends on the ratio of the surface free energy σ_s and the grain boundary free energy σ_{gb} according to Young's law

$$\sigma_{\text{gb}} = 2\sigma_s \cos(\beta). \quad (12)$$

The simulation images for two different ratios of σ_s and σ_{gb} in figure 2 show that the equilibrium angle is well reproduced in the simulations.

¹Since it is assumed that groove formation is controlled by diffusion processes, one may expect that the equilibrium angle is established during growth of the groove.

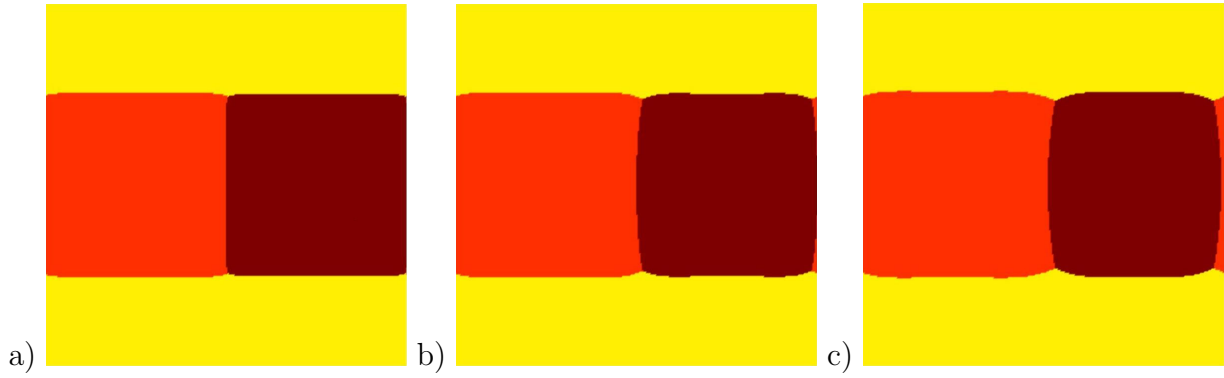


Fig. 3: Evolution of a system with two grains with different surface free energy: $\sigma_{s,1} = \sqrt{2}$ J/m², $\sigma_{s,2} = 1.25\sqrt{2}$ J/m² = (5/4) $\sigma_{s,1}$. Simulation images at time a) t = 5 s, b) t = 60 s, c) t = 200 s. Model parameters: $\kappa_{1,2} = 2$ J/m³, $\kappa_{1,\psi} = 2$ J/m³, $\kappa_{1,\psi} = 2.5$ J/m³, $\gamma_{1,2} = 1$, $\gamma_{1,\psi} = 1$, $\gamma_{2,\psi} = 11/8$, $M = 1 \times 10^{-16}$ m²/s.

Orientation dependence of the surface free energy Figure 3 shows a consecution of simulation images for a system where the grains have a different surface free energy. The grain boundary obtains a curvature outside the plane of the film to balance the interfacial tensions at the root of the groove. Since grain boundaries move towards their center of curvature, the grain with low surface energy grows at the expense of the other grain. The equilibrium angles between the grain boundary and the grain surfaces continuously adapt to the new position of the grain boundary. As a consequence, the grain boundary keeps moving until the grain with high surface energy has disappeared.

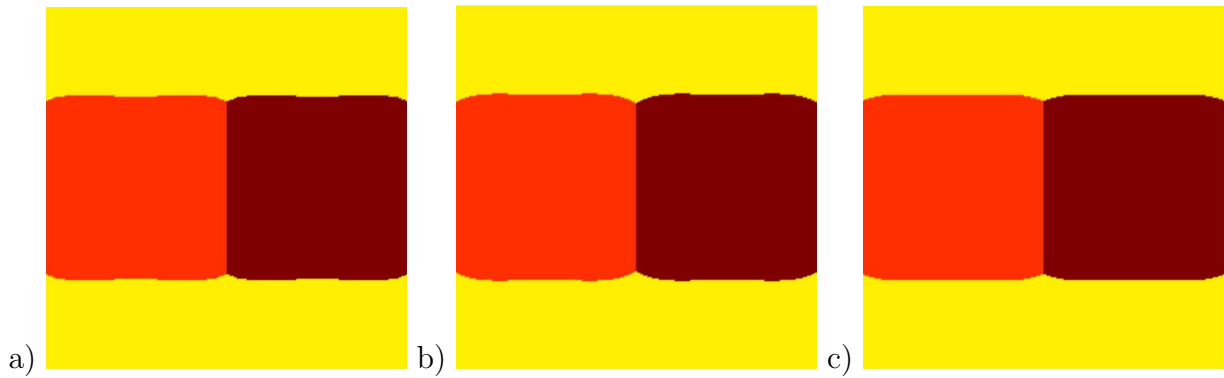


Fig. 4: Groove morphology for different groove formation mechanisms. a) Surface diffusion is dominant: $M_\eta = M_\psi = M_{gb} = 0$, $M_s = 1 \times 10^{-16}$ m²/s, b) Bulk diffusion is dominant: $M = cte = 1 \times 10^{-16}$ m²/s c) Groove is formed by evaporation and condensation of film material: $M_\eta = M_{gb} = 0$, $M_s = M_\psi = 1 \times 10^{-16}$ m²/s, solubility of film material in environment is 0.001 ($c_{env} = 0.999$). For the three simulations $\kappa = 2$ and $\gamma = 1$.

Different mechanisms for groove formation In figure 4 simulation images for the three different groove formation mechanisms distinguished by Mullins and Zhang [7,9] are compared. When bulk or surface diffusion is dominant, there is a maximum in the surface profile near the groove. The hill is wider for surface diffusion. In the case of groove formation through evaporation-condensation, there is no maximum in the surface profile. These steady-state groove profiles are in qualitative agreement with the analytical calculations of Mullins and Zhang,

except that their calculations predict an extra minimum next to the hill when surface diffusion is dominant. More simulations for a larger grain size and with a better resolution should be performed to analyze the groove profiles further. Furthermore, since the width of the interfaces in phase field simulations usually differs from the real interfacial width, it must be studied how to relate the diffusion mobilities to diffusion coefficients for interface diffusion.

Conclusions and outlook

A phase field model is presented for simulating grain growth and thermal grooving in polycrystalline films. To incorporate surface tension and to describe the shape of the grooves, both the film and its environment are considered in the simulations. The model can treat orientation dependent surface energy and misorientation dependent grain boundary energy. Furthermore, it allows to distinguish between bulk and surface diffusion. To validate the model, 2D simulations were performed of the evolution of a groove between two grains. Results are in qualitative agreement with analytical theories, however further quantitative validation using a better resolution is required. In the future, the model will be applied to simulate in 3D grain growth and thermal grooving for thin films containing many grains. Then the effect of thermal pitting at grain boundary vertices can be studied as well.

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