Random Fluctuations and Pattern Growth:
Experiments and Models

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THEORETICAL ASPECTS OF POLYCRYSTALLINE PATTERN GROWTH IN Al/Ge FILMS

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ABSTRACT. These notes discuss recent theoretical approaches to polycrystalline fingering during annealing of amorphous Al/Ge thin films, and compare them to experiment.

Annealing of amorphous Al/Ge films can give rise to a highly branched polycrystalline pattern[1]. This demonstrates the existence of a remarkable new morphology, both for phase separation, and for pattern growth. As a pattern growth mode it is intermediate between diffusion limited aggregation (no crystallization, no nucleation) and dendritic single crystal growth (crystallization, but no nucleation). As a phase transformation morphology it is controlled by long range diffusion, not by interfacial mobility, but exhibits a linear time dependence for the radius of the precipitate ("colony")[1,2]. A typical precipitate ("colony") consists of a branched polycrystalline Ge core embedded in monocrystalline Al. The colonies are roughly circular and grow into the surrounding amorphous phase of $Al_x Ge_{1-x}$ with $x \sim 0.4$. See the contributions of G. Deutscher and Y. Lereah in this volume for more details on the morphology and the experiment.

My objective here will be to address the following three questions:

(a) Why is the phase boundary between crystalline Al and the amorphous phase stable although the colonies grow into the metastable amorphous phase?

(b) Why does the radius of a colony increase linearly with time, and which factors determine its velocity?

(c) What determines the strongly temperature dependent length scale of a colony?

1. Stability

During ordinary solidification from a melt the excess foreign atoms have to diffuse away from the solid/liquid interface. Because this diffusion process has to occur into the metastable phase and over large distances it will be more effective if the interfacial area is increased. This leads to the Mullins-Sekerka (MS) instability and a dendritic morphology for the growing crystal[3]. For the case of Al/Ge phase separation, the crystalline colonies also grow into the metastable amorphous phase, and one might expect to find the same MS-instability for the interface between the colony and the amorphous region. Instead, in the experiment, the shape of the colonies remains nearly circular during the growth process[1,2].

Growth of Germanium inside the colonies requires Ge-transfer from the amorphous region across the Al-rim to the polycrystalline Ge-aggregate. This can occur by diffusion of atomic Ge through regions of crystalline Al. Assuming that this is

indeed the dominant diffusion process which limits the growth of the colony one realizes an important difference to the case of the MS-instability: The concentration gradient of the (Ge) diffusion field, and the growth velocity (of the Al/amorphous interface) have opposite orientation.

Let me consider a perturbation of the circular colony shape. Behind the most advanced regions of the perturbed interface the concentration gradient of atomic Ge will be smallest. Remember that Ge diffuses backwards from the interface (opposite to the growth direction.) On the other hand the gradient is high close to those regions of the interface that lag behind, in contrast to the ordinary case where the gradient is largest close to advanced tips. For the Al/Ge colony the most advanced tips are therefore slowed down relative to the rest of the interface, and the perturbation will be damped out. This explains one of the reasons for the stability of the circular colony shape observed in the experiment.

2. Linear Growth and Velocity Selection

The discussion above and experimental evidence[1,2] suggest the following central features for the colony growth:

1. The dominant diffusion is that of atomic Ge backward from the Al/amorphous interface into the crystalline Al.
2. Atomic diffusion in the amorphous phase is very slow compared with the crystalline phase.
3. Nucleation and growth of Ge crystallites occurs only at the interface between Al and Ge.
4. Nucleation of Al crystals in the amorphous phase is much more frequent than that of Ge but still rare; it controls the initiation of new colonies.

The first of these assumptions is central to the following treatment. It results from the observation made in section 1 that the Al/Ge interface is separated from the amorphous phase by a continuous Al rim and can only grow if Ge atoms diffuse across this rim. It will be seen that the interplay between the Al/amorphous boundary and the Al/Ge boundary which act respectively as source and sink for Ge atoms gives rise to the linear growth law.

To approach the problem more formally replace the local concentration of atomic Ge by its angular average $c(r)$ and that of crystalline Ge by its angular average $\rho(r)$. Then one finds

$$\frac{\partial c}{\partial t} = D_L \nabla^2 c - \frac{\partial \rho}{\partial t} \tag{1a}$$

on the "left" inside the Al and

$$\frac{\partial c}{\partial t} = D_R \nabla^2 c \tag{1b}$$

in the amorphous phase on the "right" of the interface. D_L resp. D_R is the diffusion constant on the left resp. right. At the interface one has $c = c_L$ on the Al side ($r = R_-$) and $c = c_R$ on the amorphous side ($r = R_+$). The growth process is described in its simplest form through

$$\frac{\partial \rho}{\partial t} = Bc\rho. \tag{2}$$

The phenomenological rate constant B describes the growth of the branched Ge structure and thus incorporates nucleation and growth of Ge crystallites. At the Al/amorphous interface, $r = R(t)$, the diffusion field must obey mass conservation:

$$\frac{d}{dt}\left[R(t)(\Delta c + \rho(R))\right] = D_L \frac{\partial c}{\partial r}\bigg|_{r=R_-} - D_R \frac{\partial c}{\partial r}\bigg|_{r=R_+}. \tag{3}$$

Here $\rho(R)$ is a small seed concentration of crystalline Ge at the boundary. $\Delta c = c_R - c_L$ denotes the discontinuity in the concentration across the interface (miscibility gap).

The ramified Al/Ge boundary close to the Al/amorphous boundary acts as a sink for the diffusing Ge and from Eq. (3) this implies a finite concentration gradient and thus a finite velocity for the moving front. Transforming into the moving frame one writes

$$c(r,t) = c_0 f(z) \qquad \text{resp.} \qquad \rho(r,t) = c_0 g(z), \tag{4}$$

where $R = vt$, $z = (r - R)/\xi$, c_0 is the concentration of Ge in the amorphous phase and $\xi = D_L/v$ is the basic length scale in the problem. For sufficiently long times ($v^2 t/D_L \gg 1$) the curvature of the interface can be neglected and one obtains a closed nonlinear equation for f [4]

$$f' + f'' = \beta f(1 - f - f'), \tag{5}$$

with the boundary conditions

$$f(-\infty) = f'(-\infty) = 0 \tag{6a}$$

$$f(0) = \frac{c_L}{c_0} \tag{6b}$$

$$f'(0) = 1 - \frac{c_L}{c_0} - \epsilon, \tag{6c}$$

where $\beta = c_0 B D_L/v^2$ is a dimensionless control parameter and $\epsilon = g(0)$ is the small seed concentration at the interface introduced in Eq. (3). The solutions to Eq. (5) are displayed in Fig. 1 in $f - f'$-space. Trajectories fulfilling the boundary conditions at $z = -\infty$ emerge from the origin with a slope $f'/f = 1/\zeta = [-1 + (1 + 4\beta)^{1/2}]/2$. The straight line $1 - f - f' = 0$ is a separatrix. The boundary condition Eq. (6c) determines a straight line parallel to the separatrix. First choose a value for β, then follow the associated flow line starting from $(0,0)$ until it intercepts this straight line and read off the corresponding value $f(0) = c_L/c_0$. This determines β and thus v as a function of c_L (see inset of Fig. 1).

3. Length Scales

Before discussing the last question it is instructive to compare the theoretical consequences with experiment. The growth velocity is found to be constant as predicted. For slow velocities, i.e, $\beta \gg 1$, one derives the relation $v \approx (c_L/c_0)d_L/\xi\zeta$ [4]. It has been checked experimentally by comparing the temperature dependence of $D/\xi\zeta$ with that of v and was found to be in good agreement [2]. If the transformation
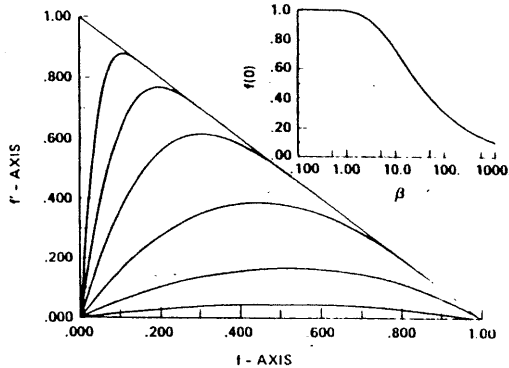
Fig. 1: Trajectories fulfilling the boundary conditions at $z = -\infty$ for selected values of β ($\beta = 0.2, 1, 5, 25, 100, 500$). Inset: Dependence of $f(0) = c_L/c_0$ on β for trajectories fulfilling all boundary conditions with $\epsilon = 0.001$.

were interface-controlled one might expect to find the same activated behaviour for v as for D_L and consequently a temperature independent length scale. This, however, is not borne out by experiment [2], and indeed the theory above predicts $v \propto (BD_L)^{1/2}$ showing that the temperature dependence of $\xi\zeta$ depends on that of B. Here lies a problem, because B is not a material parameter. Experimentally the activation energy of the nucleation rate has been measured [2], and it was found that the relation $v \propto (BD_L)^{1/2}$ is obeyed if B has the same activated behaviour as the nucleation rate. One also observes a broad distribution of crystallite sizes where the size of the largest Ge-crystallites is comparable to the width of a finger. These observations plus a theoretical consistency argument [4] suggest that the nucleation rate for Ge-grains at the Al/Ge interface plays a central role for the understanding of B, and for the length scale (resp. velocity) selection in the experiment.

As a first step let me pose the simpler question how nucleation alone determines a characteristic length for a competitive growth process. To be more specific consider the following highly idealized model for the growth of an isolated Ge-finger in the colony.

A polycrystalline Germanium finger is idealized as a rectangular shape of length L and width W, with $W < L$. To represent the grain structure consider the rectangular shape being filled with a hexagonal tiling. A grain corresponds to a connected region of elementary hexagons. Each grain is identified by a unique number. The rectangular shape grows unidirectionally keeping W constant. This idealizes the fact that most of the growth of a Ge-finger occurs close to its tip, while lateral growth is negligible. To simplify the growth dynamics assume that the rectangle grows stepwise through the addition of one layer of elementary hexagons at a time. The elementary hexagons may be thought of as critical nuclei which can either be incorporated into the existing grains touching the surface or nucleate a new crystallite. For simplicity assume that each of the elementary hexagons in the new layer can nucleate a new crystallite with probability p_{nu}. If an elementary hexagon does not nucleate a new grain, it is added to an existing grain in the previous layer according to the following rules: If the two hexagons in the previous layer which it touches (let me call them predecessors) belong to the same grain,

then the new hexagon will also be added to that grain, i.e., it acquires the same number. If the two predecessors have different numbers, then the number of the new hexagon is chosen with probability 1/2 from the numbers of its predecessors.

In this model the growth of a single grain starts with a single hexagon and ends when that grain ceases to touch the surface. This can be caused by the nucleation of other grains on its surface or by screening through neighboring grains. The grain growth is competitive in that each grain can only grow at the expense of its neighbours because the overall available surface area W is kept constant.

Before presenting some of the results for this model let me point out that they seem to be relatively insensitive to the artificial rectangular geometry of the model above. This is seen from the fact that qualitatively similar results are obtained in a model where analogous nucleation rules have been introduced into diffusion limited aggregation with surface tension [5]. In that case a branched polycrystalline structure with finite finger width is produced. Other variants of the model have taken preferential nucleation at already existing grain boundaries into account [5,6].

To extract a length scale from this nucleation and growth model consider the grain length $X_\parallel$ along the growth direction. $X_\parallel$ is a random variable defined as the maximum linear extension of a grain in the direction perpendicular to to the growth surface. An approximate probability density $P(X_\parallel)$ for this quantity can be obtained in closed form in the limit of small p_{nu} [6]. Its asymptotic expansion is found to have the scaling form

$$P(X_\parallel) \sim X_\parallel^{-3/2} \exp\left(\frac{-X_\parallel}{\ell_\parallel}\right), \qquad (7)$$

where

$$\ell_\parallel = \left(\frac{1}{2} - [\nu(1-\nu)]^{1/2}\right)^{-1}. \qquad (8)$$

Here ν is a monotone function of the nucleation probability p_{nu} with $\nu(0) = 1/2$. The power law with exponent 3/2 is cutoff with an exponential function, and for $p_{nu} \to 0$ the decay length is divergent.

The form for $P(X_\parallel)$ can be easily checked by simulation. In Fig. 2 the density $P(X_\parallel)$ is plotted on a log-log scale for a system of width $W = 3000$ with the values $p_{nu} = 1\%$ (circles) and $p_{nu} = 0.1\%$ (crosses) for the nucleation probability. In the simulations $L = 10^4$ layers of size $W = 3000$ were added. The initial layer consisted of a few hundred different grains, and periodic boundary conditions were imposed identifying the first and the last element in each layer. In Fig. 2 a straight line of slope -3/2 has been drawn for comparison. Despite the approximations implicit in Eq. (7) and the relatively small scale of the simulation (3×10^7 hexagons) theory and simulation are in good agreement.

These results show that nucleation enters only into the cutoff function of the grain length distribution, and does not influence the exponent which is determined purely by the competitive growth process. Although the model does not involve the characteristic interplay of the two interfaces discussed in section 2, it shows that the nucleation parameter ν alone determines a characteristic length for the resulting grain structure. This in itself may be important for other growth models [6]. The model does however not give a better understanding of the parameter B in the previous section. For that a more detailed model of the nucleation process at the
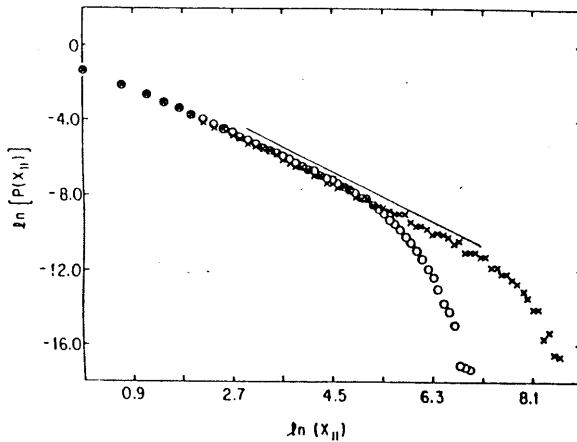
Fig. 2: Probability density $P(X_{\parallel})$ of grain length for $p_{nu} = 0.001$ (crosses) and $p_{nu} = 0.01$ (circles). The straight line has slope -3/2.

Al/Ge interface is needed. It must be pointed out that the model above ignores all subsequent grain growth resulting from the reduction of the interfacial energy in the initial grain structure (Ostwald ripening), and the resulting grain size distributions can therefore not be expected to agree with those in the experiment.

In summary these notes have discussed some theoretical aspects of polycrystalline fingering in Al/Ge. The stability question was answered on the basis of the classical Mullins Sekerka analysis. The colony growth has been described in an averaged fashion. Within this phenomenological approach the linear growth law and the velocity selection were seen to follow from the boundary conditions. The theoretical predictions have been compared against experiment. This comparison indicated that nucleation of Ge at the Al/Ge interface plays a central role. Subsequently a simple model for a single polycrystalline finger involving nucleation and competitive growth has been introduced. It was studied analytically and by simulation. The distribution of grain lengths for this model was found to follow a scaling form with an exponential cutoff function whose decay rate depends only on the nucleation rate. The theoretical expression and the simulation results for the distribution appear to be in good agreement.

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6. R. Hilfer, to be published.