

An Application of Nucleation Theory to Thin-Film Annealing

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Abstract

The growth process of a binary system that has been heat treated and quenched has been modeled using the Becker-Doring nucleation theory. Growth rate and composition profiles have been evaluated. The model clearly favors the precipitations of components rather than the formation of large clusters that may span the entire system. Comparison of calculated composition with those obtained from an Invariant Field Approximation indicates the current method to give better estimates of the composition.

1.0 Introduction

In thin-film formation, film material often condenses on metallic or non-metallic substrates. The resulting films are often not dense, under large stress, contain enormous amount of defects and in a deposition from a multi-component system with a hope of obtaining alloyed thin-film, the composition could be far from being uniform. To gain better film structure and composition, thin-films need to be annealed. All these processes, deposition and annealing, are studied under the general subject of nucleation and growth. This subject has received very little experimental attention, largely due to the twin difficulties of experimental reproducibility and reliable measurement techniques. This work attempts to approach the subject of annealing via numerical modeling based on the Becker & Doring mechanism [1].

The Becker and Doring theory as reviewed in King and Wattis [2] describes the growth and fragmentation of the clusters in terms of stepwise addition or removal of single particles to or from the clusters of similar particles. This theory has been applied to wide range of physical/chemical and biological interests. Here it is applied to the study of the growth process of a binary solution that has been heat treated and then quenched. Similar studies have been made in respect of other solutions and conditions, for example Weber et-al [3]. The growth of binary alloy in thin-film form is studied here.

Nucleation Theory

A system may be thought to be composed of clusters of varying sizes, j characterized by densities c_j per unit volume that evolve with time. Conservation laws would require the volume fraction occupied by all clusters to be a constant $V_f(t) = \int c_j(t) dV = V_{total} / \sum_j c_j$. Numerically, the summation is made up to some j_{max} and

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some critical size j^* that is the mean of the distribution.

One of the central assumptions of this theory as it pertains to cluster growth in binary solutions is that hetrophase fluctuations lead to the decay of metastable states. That is, a small volume fraction of solute material is uniformly distributed as a single phase and following a 'quench', cluster fluctuations starts the nucleation process through which the clusters grow or shrink in size according to the condensation and evaporation mechanisms available.

According to Becker and Doring [1], the first formulators of the theory, rate equations could be set-up to describe changes in the cluster distribution functions. The general equations for wide range of systems could be written as [4--6]

$$\frac{d}{dt}c_j = \frac{1}{2} \sum_{k=1}^{j-1} a_{k,j-1}c_k c_{j-k} - \sum_{k=1}^{\infty} a_{jk}c_j c_k + \sum_{k=j+1}^{\infty} b_{j,k-j}c_k - \frac{1}{2} \sum_{k=1}^{j-1} b_{k,j-1}c_j$$

The rate coefficients a_{jk} for condensation and b_{jk} for evaporation of the j cluster are, in principle, time dependent. As a cluster grows, the monomer population is depleted and a_{jk} will necessarily decrease with time. Minimization of the free energy of cluster [7,8] lead to the equilibrium, or most probable cluster size distribution, c_j^{eq} such that

$$a_j c_j^{eq} = b_{j+1}c_{j+1}^{eq}$$

for $k=1$. According to which

$$c_j^{eq} = c_0 e^{\frac{-\Delta F_j}{K\beta T}}$$

with c_0 as a constant and ΔF_j the free energy of the cluster

Application of boundary condition especially as it relates to the fixed monomer population density would require [9]

$$\lim_{j \rightarrow 0} \frac{c_j(t)}{c_j^{eq}} = 1$$

and

$$\lim_{j \rightarrow \infty} \frac{c_j(t)}{c_j^{eq}} = 0$$

and at steady state

$$\frac{\partial}{\partial t} c_j^{ss}(t) = 0$$

Zeldovitch [10] obtained for the ratio of the steady state to equilibrium density

$$\frac{c_j^{ss}}{c_j^{eq}} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{j - j^*}{\sqrt{g/2}} \right) \right]$$

where j^* is the equilibrium cluster size and g , known as the Zeldovitch parameter, gives the region in which the ratio changes from unity to zero.

Results and Discussion

The ratio of the steady state to the equilibrium density is illustrated in Figure 1 for various values of the Zeldovitch parameter g . The critical size parameter j^* has been scaled to zero and could be seen that the ratio is close to unity around $j \approx j^*$ and rapidly goes to zero for cluster sizes greater than j^* . This justifies the employment of the critical size as a basis for truncating the distribution.

Clearly, the parameter g controls the width of the region in which the ratio drops to zero. Important as it is, it could be noticed that it took almost three orders of magnitude for the width to increase appreciably.

In Figures 2 and 3, the free energy of the binary alloy is plotted as a function of the atomic fraction of a component of the alloy for various temperatures. It can be seen that (Figure 2) the free energy is minimum at high temperatures and all curves are symmetrical about the $x=0.5$ composition. Low temperature (600 -- 900 K) curves indicate two minima each for the free energy. The first set at $x=0.05, 0.10, 0.15, 0.20$ and the second set at $x=0.95, 0.90, 0.85, 0.80$ for temperatures of 600, 700, 800 and 900K respectively.

The analysis of the free energy minimization at high temperatures may indicate the high probability that may be expected for the precipitation of a component of a binary alloy that is annealed and then quenched at high temperatures. In Figure 3, surface plot is presented for the free energy as function of both atomic fraction and temperature.

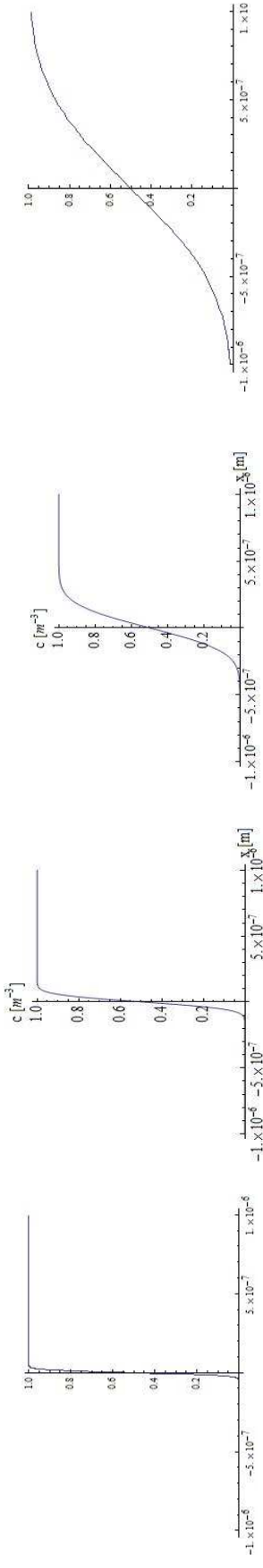
The growth kinetic of the two component A-50 at. % B\$ alloy model assumes the solution to be treated by annealing at 1573K and then quenched to 1273K and the nucleation of B-rich (or A-rich) precipitate is traced. In Figure 4, the concentration, in atomic percent is plotted as a function of the cluster size (r). It could be noticed that the cluster grows to about 50 μm in the simulation time of about two minutes. The composition, of the precipitate, saturates much before it grows to a size of 30 μm and approximates to about 50 at.% which is the host solution composition.

In Figure 5, the rate of the cluster growth is presented. The rate of growths seems faster at the point of quench and slows down drastically as the cluster increases in size. To demonstrate the rapid growth in the initial time a logarithmic plot of the rate is presented in Figure 5 (b). It could be noticed that the rate drops by more than two orders of magnitude in the first 5 -- 10 seconds.

An alternative procedure for the modeling of the growth process is that of the Invariant Field Approximation (IFA) [8]. In the IFA approach, the cluster composition is assumed to be given by the solution of the Laplace equation, $\nabla^2 c = 0$. In Figure 4, the concentration profile obtained from this approximation is compared with that given by the method presented here. It can be seen that the IFA under-estimates the composition at all cluster sizes. The IFA solution was obtained by the integration of the homogeneous second order differential equation with the choice of the two constants governed by the host composition (0.5 or 50%) and that of the seed cluster ($\approx 100\%$).

Conclusion

The Becker-Doring theory appears to provide reasonable description of the nucleation and growth process. The description obtained here also indicates the high probability of precipitation, in that, the ratio of the steady state to the equilibrium density (concentration) does not favor the growth of large clusters. It can be inferred that the possibility of a single cluster growing and continuing to grow until it spans the whole system is remote indeed.



(a) (b) (c) (d)

Figure 1: Normalized cluster size as a function of the Zeldovich parameter (a) $g = 10^0$ (b) $g = 10^1$ (c) $g = 10^2$ (d) $g = 10^3$

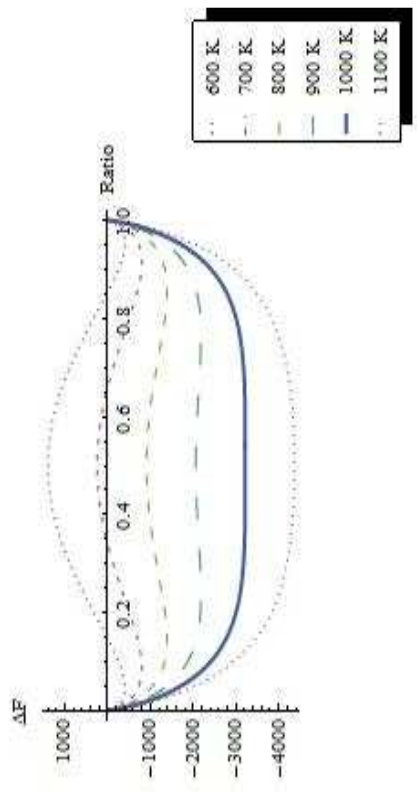


Figure 2: Free energy as function of composition in Binary Alloy

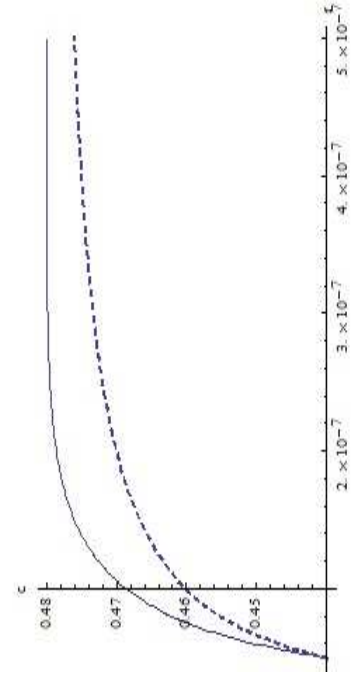


Figure 4 Cluster size as a function of growth time. Dashed line is from invariant field approximation while the full line is from this work

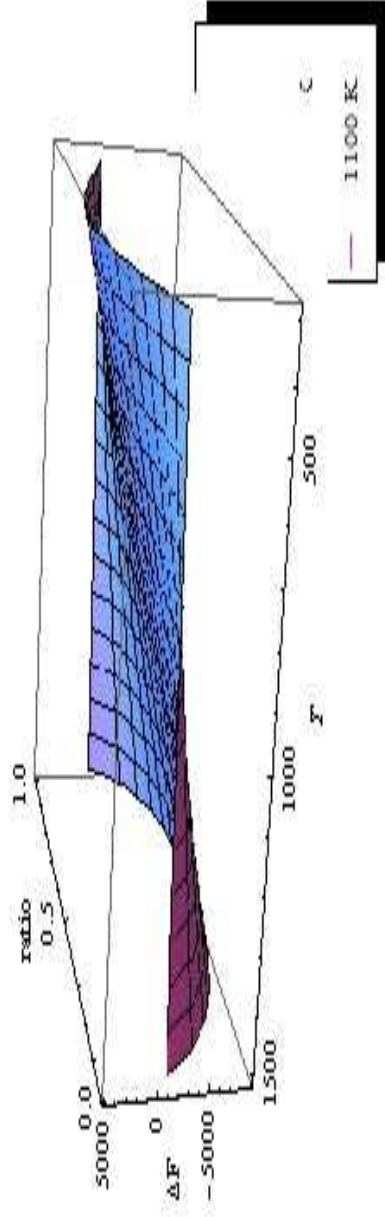


Figure 3 Free energy surface – as function of composition and temperature

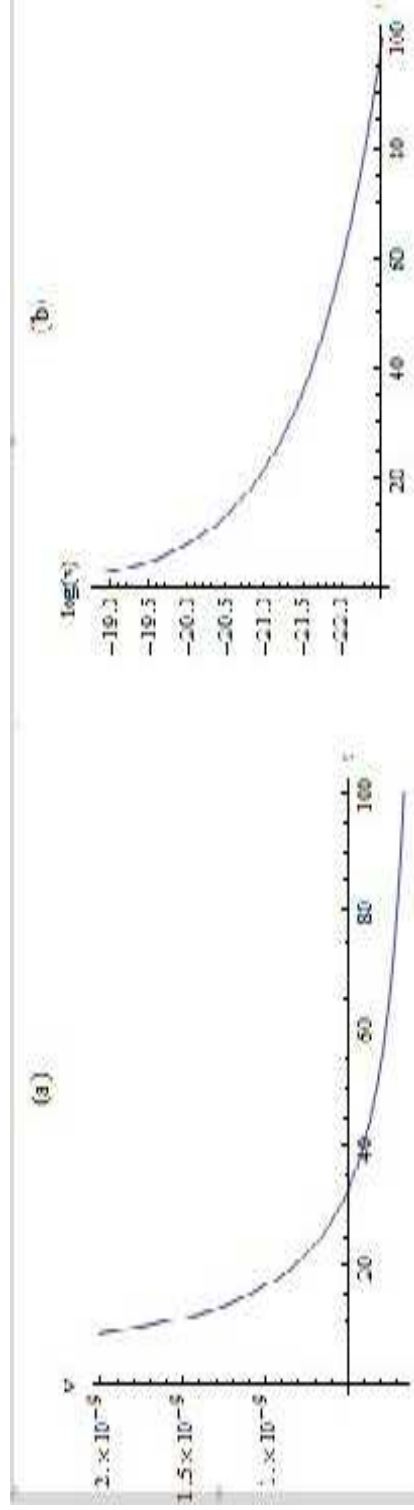


Figure 5 Rate of cluster growth (a) on a Linear scale (b) Logarithmic scale

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