

## Atomic scale crystal growth processes

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**Abstract** Computer simulations have played a central role in the development of our understanding of the atomic scale processes involved in crystal growth. The assumptions underlying computer modeling will be discussed and our recent work on modeling of the kinetic formation of thermodynamically unstable phases in alloys or mixtures will be reviewed. Our Monte Carlo computer simulations have reproduced the experimental results on the rapid recrystallization of laser-melted doped silicon. An analytical model for this phenomenon has been developed, and its applicability to other materials will be discussed.

### 1. Introduction

The wide availability of extremely powerful computers has ushered in a new era in which simulation is the preferred method for the modeling of physical processes. The development of our understanding of the atomic scale processes involved in crystal growth, where computer simulations have played a central role, is an example of the power of these methods. It has now become apparent that computer simulations have not only been useful, but will continue to be essential for this development.

Significant departures from the segregation effects predicted using equilibrium phase relationships have been observed in many experimental studies of the rapid crystallization of semiconductors and metal alloys. The most detailed experimental studies of the failure of the quasiequilibrium model have been made on laser-melted doped silicon where the segregation coefficients ( $k$ -values) are found to increase dramatically with growth rate. Our extensive Monte Carlo simulations have reproduced these experimental results, including both the growth rate and orientation dependence of the segregation coefficient. Based on our simulations, we have developed an analytical model which fits the simulation results and for the first time provides some predictive capability for other alloy systems. The modeling suggests that it is the departure from equilibrium, for example as measured by the undercooling, rather than the absolute growth rate which is responsible for these effects. The experimental results and the Monte Carlo modeling imply that there is a kinetic phase diagram which differs signifi-

cantly from the equilibrium phase diagram.

### 2. Monte carlo simulations

Our computer simulations are based on the Monte Carlo scheme which has been so successful in modeling the growth of pure materials [1-5], and which has played a major role in the development of our present understanding of crystal growth processes. It incorporates implicitly the surface roughening transition, the effects of step density and surface configuration on growth. The Monte Carlo model used for the growth of pure materials has been modified only by the introduction of two species of atom in order to model alloy growth [6-9]. The assumptions about the interactions between the atoms is the same except that input data for both species are needed, and these are based on the equilibrium thermodynamic properties of the alloy to be modeled. Although these assumptions are quite simple, the predictions can be quite complex. The modeling has provided an extra link in developing an understanding of these complex phenomena.

In the conventional quasi-equilibrium model for crystal growth, the growth rate of a crystal is written as:

$$v = v_0 \left[ \exp\left(-\frac{L}{k_B T_M} + \frac{E_L}{k_B T}\right) - \exp\left(\frac{E_S}{k_B T}\right) \right] \quad (1)$$

Here  $v_0$  is a temperature dependent prefactor,  $L$  is the latent heat of fusion,  $E_L$  and  $E_S$  are the internal energies of the liquid and solid respectively,  $T$  is the temperature in degrees Kelvin,  $T_M$  is the melting point and  $k_B$  is Boltzmanns constant. This form assures that

the growth rate is zero at  $T = T_M$ , since  $E_L - E_S = L$ . The internal energies should be replaced with enthalpies if that is appropriate. This expression is based on the implicit thermodynamic assumption that all growth sites are equivalent, and predicts that the growth rate is linear with undercooling near  $T_M$ .

An expression for the growth rate which is very similar in spirit can be written as:

$$v = v_0 \left[ \exp \left( -\frac{L}{k_B T_M} + \frac{\sum \phi_L^i}{k_B T} \right) - \exp \left( \frac{\sum \phi_S^i}{k_B T} \right) \right] \quad (2)$$

where the  $\phi$ 's are bond energies given by  $L = E_L - E_S = (\phi_S - \phi_L)Z/2$ , where  $Z$  is the number of nearest neighbors in the solid. The summation is over the nearest neighbors for each of the atoms at the interface, and then the rates are averaged over all the atoms at the interface. Eqn. 2 is conceptually very simple, and it is an embodiment of the classical Kossel-Stranski model for crystal growth.

Eqns. 1 and 2 look similar, but the similarity is deceptive. For example, when  $L/k_B T_M$  is large, the surface will be smooth, and there will only be isolated adatoms on the surface of the crystal, so the growth rate will depend on the rate of nucleation of new layers. This behavior is captured by Eqn. 2, but not by Eqn. 1. However, the summations in Eqn. 2 cannot be performed analytically except for special cases, because the distribution of nearest neighbors depends in detail on the configuration of the atoms at the interface. The physics of Eqn. 2 can readily be treated by Monte Carlo computer simulation where the configuration of each atom at the interface is stored in the computer. For simulations of alloys, the  $\phi$ 's depend on both the species of the nearest neighbors as well as whether they are in the solid or liquid.

It is important to note that the Monte Carlo modeling incorporates the appropriate distribution of sites depending on the surface roughness, but of course it does not predict the location of the surface roughening transition. The location of the surface roughening transition must be scaled properly in the simulations [9].

Eqn. 1 has traditionally been corrected to fit experiment by multiplying it by a factor  $f$  which is the fraction of surface sites which are active growth sites. For growth without defects,  $f$  can be evaluated from simulations based on Eqn. 2. For rough surfaces,  $f$  varies somewhat with direction, but is relatively independent of undercooling. For smooth surfaces,  $f$  incorporates the temperature dependence of the nucleation rate.

For a smooth surface with steps created by dislocations,  $f$  depends on the density of growth sites generated by the dislocations, which often depends linearly on undercooling.

### 2.1. Growth on (111) silicon

The difference between growth on rough and smooth interfaces is illustrated by the difference between growth on the silicon (111) plane and the other planes of silicon. It is well known that the (111) plane of silicon facets during growth from the melt, whereas the other planes do not. From measurements of the interface undercooling in the [100] direction at very high growth rates [10] and from molecular dynamics simulations [11] (which are in reasonable agreement) the interface undercooling at Czochralski growth rates is estimated to be about  $3 \times 10^{-4}$  degrees. The undercooling will vary somewhat for other directions but by less than a factor of 2, and so the interface for all these directions is very close to the equilibrium isotherm. But for the (111) plane, the undercooling is much greater at the coolest part of the facet. We have estimated this undercooling from simulations based on Eqn. 2.

The Monte Carlo computer simulations were been performed using the crystal structure of silicon. In order to compare these results to the experimental data, it is necessary to correlate the growth rate in the simulations with the experimental growth rate. This was done by comparing the temperature dependence of the growth rate for the [100] direction in the simulations with molecular dynamics simulations [11] and with experimental measurements results [10].

At small undercoolings the growth rate normal to the (111) face of silicon is governed by the nucleation of new layers. Figure 1 presents the results of simulations of the growth on the (111) face as a function of time at several different temperatures. The growth is characterized by a time interval of no growth, followed by a nucleation event which starts a new layer and results in the rapid addition of a layer of atoms. The time interval between nucleation events increases with decreasing undercooling. The time scale was compared directly with experiment by matching growth rate in the [100] direction to the measured solidification rate in the same direction. Using the data from this curve, the mean time between nucleation events can be determined. A nucleation rate per unit area can be

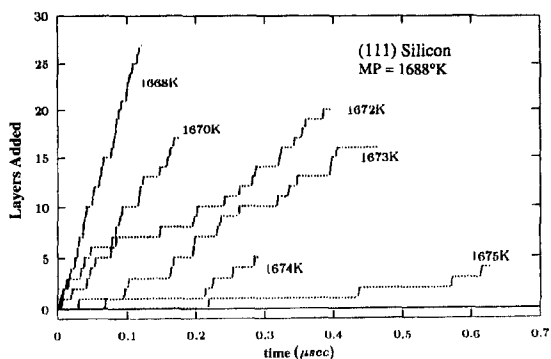


Fig. 1. Number of layers added as a function of time for Monte Carlo simulations of growth on the (111) face of silicon.

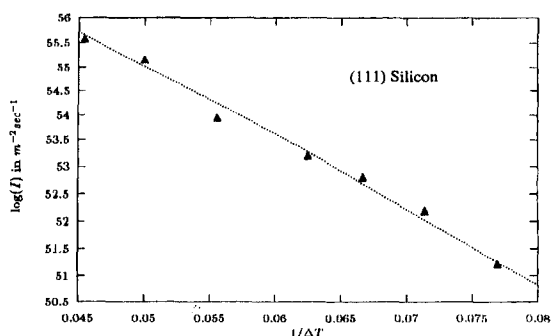


Fig. 2. Nucleation rate vs.  $1/\Delta T$  for the data of Fig. 1.

determined from this, since the area of the simulation surface is known. The logarithm of the nucleation rate (in  $\text{m}^2\text{sec}^{-1}$ ) versus the reciprocal of the undercooling is plotted in Fig. 2. The straight line indicates nucleation controlled growth. From these data, the effective free energy of the step riser per unit area can be calculated, and it is found to be about one tenth of specific surface free energy of the flat, two dimensional surface. This result is not surprising, because the step free energy is significantly reduced by the entropy associated with the roughening of the step. The growth data fit a nucleation model, but the step free energy, which can readily be determined from the simulations, must be used. Using a poly nuclear growth model [12] to extrapolate these data to the growth conditions of Czochralski silicon results in an undercooling of the facet where the nucleation of new layers occurs to be about 5 degrees. This compares with estimates based on experiment of 1.5 degrees by Edwards [13], 5 degrees by Ciszek [14], and 9 degrees by Abe [15].

## 2.2. Growth of doped crystals and alloys

The compositions, structure and properties of multi-component materials produced by phase transformations which occur under conditions which are far from equilibrium are often quite different from those predicted by equilibrium thermodynamics. Quantitative data are available for the dependence of the distribution coefficient ( $k$ -value) on growth rate during the very rapid recrystallization of laser-melted, ion-implanted silicon [16-25], and more recently for aluminum alloys [26, 27]. The  $k$ -value in these experiments has been observed to increase by more than two orders of magnitude over the equilibrium value. The growth rate dependence of the  $k$ -value is also responsible for the so-called "facet effect" observed in the growth of semiconductor crystals [15, 28] which is an increased incorporation of most dopants at a faceted region of the interface during growth at normal laboratory or production growth rates. Our recent computer modeling [6-9] has reproduced all of the main features of this data, including the orientation dependence of the  $k$ -value. In addition the modeling has provided a definitive explanation for the orientation dependence.

We have reported [6] simulations for a "diffusionless" transformation, where the transformation takes place by the motion of the interface, but the atoms do not move: their positions are fixed on lattice sites. These simulations correspond, for example, to a "shear" or martensite-type transformation where the interface moves very rapidly, at rates approaching the speed of sound, so that the atoms do not have sufficient time to diffuse as the transformation front passes. The growth rate in these simulations was found to be zero on the  $T_0$  line for the alloy. On this line, the free energy of the solid alloy is equal to the free energy of the liquid alloy with the same composition. This is clearly the expected behavior for a diffusionless transformation since the kinetics of a diffusionless transformation should depend on the difference between the free energies of the two phases, rather than on the difference between the chemical potentials in the two phases of the species present. For the diffusionless case, "freezing" or "melting" should be reversible at  $T_0$ , depending on which phase has the lower free energy. These results provided the first clear-cut confirmation of this expectation.

Data from simulations have been accumulated for a variety of different growth temperatures and with various diffusion coefficients [8]. The thermodynamic pro-

properties of bismuth in silicon have been used as a model system for many of these simulations since bismuth is a typical dopant in silicon and these alloys have been studied extensively experimentally [17-20, 22, 23]. For the simulations, a growth temperature is chosen and a normalized growth rate is calculated from the net number of atoms added to the crystal during the simulation. The growth rate dependence of the distribution coefficient has been found to depend on a dimensionless parameter  $\beta$  given by:

$$\beta = \frac{av\Delta\mu}{Dk_B T} \quad (3)$$

where  $a$  is the interatomic spacing,  $v$  is the growth rate,  $\Delta\mu$  is the overall driving force for the crystallization process, and  $D$  is the diffusion coefficient. For a rough interface, the growth rate  $v$  is proportional to the driving force,  $\Delta\mu$ , so that the  $k$ -value for a rough interface depends on the square of the growth rate, divided by the diffusion coefficient. The diffusion coefficient in the simulations was changed by a factor of 100 for various runs, but the data all coincide when plotted against  $\beta$ .

$\beta$  was first defined by Temkin [29] and derived from a crystallization time,  $\tau_{CR}$ , which is given by:

$$\tau_{CR} = \frac{\lambda}{v} = \frac{ak_B T}{v\Delta\mu} \quad (4)$$

where  $\lambda$  is a characteristic distance associated with fluctuations of the interface given by:

$$\frac{\lambda\Delta\mu}{a} = k_B T \quad (5)$$

$\beta$  is the ratio of the diffusion jump time to the crystallization time,  $\tau_{CR}$ .

### 2.3. Analytical model

Analytical expressions for the growth velocity have been developed [30] which closely match Monte Carlo simulation data for doped silicon. They were derived based on the notion that surface tension effects at the interface can transfer driving force for crystallization between species. The analysis is best summarized by the equations for the net growth rate of the two components of a binary alloy. For the **A** component:

$$v_A = v_A^0 \left[ C_A^L - C_A^S \exp\left(\frac{(1-P)\Delta\mu_A^0 + P\Delta F^0}{k_B T}\right) \right] \quad (6)$$

and similarly for the **B** component:

$$v_B = v_B^0 \left[ C_B^L - C_B^S \exp\left(\frac{(1-P)\Delta\mu_B^0 + P\Delta F^0}{k_B T}\right) \right] \quad (7)$$

The  $C$ 's are the concentrations of the A and B components in the solid, S, and liquid, L, at the interface,  $\Delta\mu^0$  is difference in chemical potential between the solid and the liquid for the corresponding species,  $\Delta F^0$  is the free energy difference between the solid and the liquid, and  $k_B T$  is Boltzmann's constant times the temperature. The superscript 0 on the chemical potential and free energy differences indicates that the explicit concentration terms are not present.

For  $P = 0$ , these equations reduce to the quasi-equilibrium model for alloy crystallization. Equilibrium occurs when  $v_A = v_B = 0$ , so that for  $P = 0$ , the equilibrium condition is given by the usual equality of chemical potentials in the two phases for each species:  $\Delta\mu_A = 0 = \Delta\mu_B$ , and so these equations reduce to the usual thermodynamic conditions at equilibrium.

$P$  approaches 1 when diffusion is very slow compared to the growth rate.  $P = 1$  for diffusionless growth ( $D = 0$ ), in which case  $C^L = C^S$  for both species because no redistribution occurs, and so the term

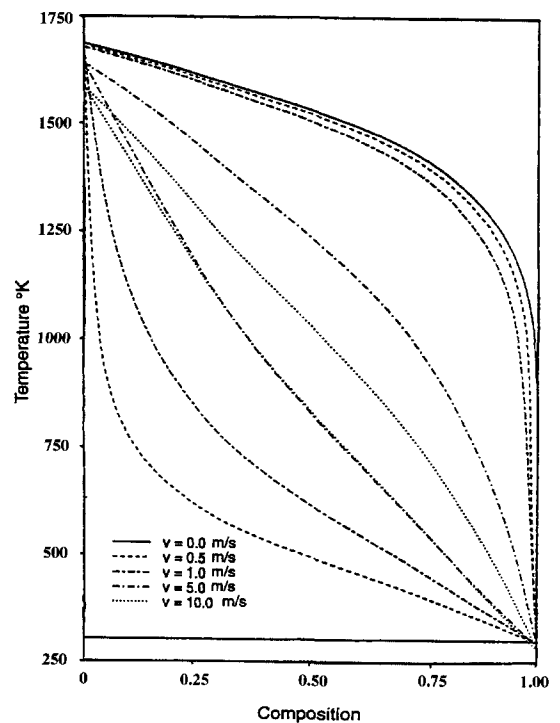


Fig. 3. Kinetic phase diagram calculated from Eqns. 6 and 7, based on an idealized bismuth-silicon equilibrium phase diagram.

in the square brackets in Eqns. 6 and 7 is zero at the temperature  $T_0$  which is defined as the temperature where  $\Delta F^0 = 0$ .

Eqns. 6 and 7 can thus be used to calculate a variety of phase diagrams, depending on the magnitude of  $P$ .  $P = 0$  gives the equilibrium phase diagram, and for  $P = 1$ , the solidus and liquidus lines collapse onto the  $T_0$  line. Intermediate values of  $P$  give a range of "kinetic phase diagrams" between these two limits, as illustrated in Fig. 3.

The quantity  $P$  is related to a trapping probability, and the Monte Carlo data indicate that  $P$  has the form:

$$1 - P \approx \frac{1}{1 + A\beta^g} \quad (8)$$

where  $A$  is a constant and  $g \approx 0.5$ . A simple approximate expression for the distribution coefficient for component  $B$  can be derived from Eqns. 6 and 7:

$$k \approx k_e^{1/(1+A\beta^{0.5})} \quad (9)$$

where  $k_e$  is the equilibrium distribution coefficient.

#### 2.4. Comparison with experiment

The critical experiments to explore the solute trapping phenomenon were performed by laser melting of a thin layer on the surface of a silicon single crystal which had been ion implanted with a dopant [16-25]. An area of a square centimeter is melted uniformly to a depth of a micron or so with a single short pulse from a laser. The layer of liquid silicon then crystallizes very rapidly as the heat is extracted into the underlying crystal. In a typical experiment on bismuth implanted into silicon [20], the final distributions of bismuth could only be fitted with a  $k$ -value of 0.1, but the equilibrium  $k$ -value is  $7 \times 10^{-4}$ .

Monte Carlo computer simulations have been performed using the crystal structure of silicon. The growth rate in the simulations and the experimental growth rate were correlated as described above for pure silicon. The agreement of the simulation results with experimental data of both Baeri *et al.* [17, 20] and White *et al.* [18, 19] for the  $k$ -value for bismuth in (100) silicon as function of growth rate as observed in laser annealing experiments is surprisingly good [7, 8]. The velocity dependence of similar data of Aziz *et al.* [21] differs from both of the other sets of data as well as from the simulation results, but the reason for this discrepancy is not clear at present.

It is well known that the  $k$ -value of dopants in sili-

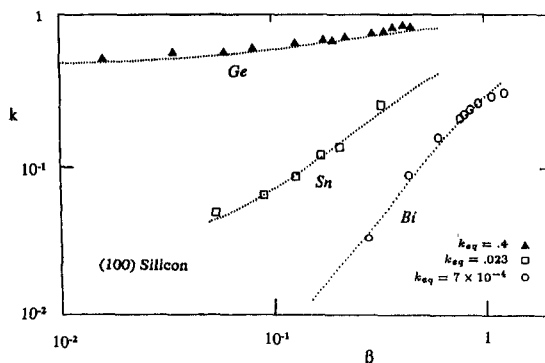


Fig. 4. Simulation data for the growth rate dependence of the  $k$ -value for silicon doped with germanium, tin and bismuth. The solid lines are Eqn. 9 with  $A = 8$ .

con, as well as in compound semiconductors, is orientation dependent. In order to investigate this, an extensive set of simulations were carried out in three dimensions using the crystal structure of silicon, with various orientations of the interface [9]. Nothing was changed in these simulations except the orientation of the growth front. The growth rates for the simulations using the crystal structure of silicon were correlated to experimental growth rates as outlined above. The data agree well with experimental measurements of the orientation dependence of Bi incorporation into laser-melted silicon wafers [9]. For growth which is controlled by the movement of steps, as is the case for a faceted interface such as the (111) interface of silicon, the growth velocity is the product of the rate of addition of atoms at kink sites, and the kink site density. (A kink site is an active growth site formed by a kink in a step on the surface.) On smooth surfaces the kink sites (and steps) must move faster to maintain a given growth velocity. It has been suggested [15] that differences in step velocity are responsible for the "facet effect". The normalized rate of addition of atoms at a kink site,  $u_k$ , should be given by  $u_k = \Delta\mu/k_B T$ . This was confirmed by determining the kink site density as a function of temperature and interface orientation in the simulations.

In Fig. 4, simulation data are presented for the growth rate dependence of the  $k$ -value for silicon doped with germanium, tin and bismuth. The simulations were performed changing only the dopant-silicon bond energies to give the appropriate equilibrium  $k$ -value. The dotted lines are Eqn. 9 with  $A = 8$ . The data for all three dopants fit with the same value of  $A$ .

### 3. Conclusions

These comparisons between the experimental results and the simulation data suggest that the non-equilibrium segregation behavior is being correctly modeled by the simulations. Furthermore, the analytical model outlined above is apparently capable of fitting both the simulation data and the experimental data reasonably well using the same fitting parameter. This suggests that it can be used for predicting non-equilibrium behavior.

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