A TEST OF TWO SOLUTE-TRAPPING MODELS


ABSTRACT

Two solute trapping models are compared. They are shown to predict identical behavior at any given end of a phase diagram but different behavior as the phase diagram is traversed. The segregation behavior of dilute solutions of Ge in Si (k_e < 1) and of Si in Ge (k_e > 1) during regrowth from pulsed-laser melting is being studied using transient conductance, high resolution RBS, and SIMS. Our results to date suggest a significant amount of solute trapping (k_e > 1) of Ge in Si and of Si in Ge. Such a result would be inconsistent with the predictions of one of the models.

INTRODUCTION

One of the most exciting aspects of pulsed-laser melting is that it allows, for the first time in high-mobility systems, a quantitative study of the kinetics of the fundamental atomic processes occurring at the solid-liquid interface. Such a study is possible because these experiments have reached the regime where, due to kinetic limitations, deviations from local thermodynamic equilibrium are obvious and crystal growth is no longer heat-flow limited. In this paper we describe an experimental test of models for the departure from local compositional equilibrium at the interface — so-called solute trapping models.

There are a number of models [1-9] of the kinetics of the solidification reaction of a two-component system. A complete description of the process requires the derivation of the two "interface response functions" [10]; they predict (a) how fast the interface will move, and (b) the composition of the growing solid, in terms of the local conditions at the interface, namely temperature and liquid composition.

We will concentrate on two models for the following reasons. They are "complete", in that they propose forms for both of the above response functions and can therefore form a basis for our understanding of the entire solidification process. They can also be readily applied by the experimentalist to the particular problem at hand. In both of these models two simultaneous, coupled reactions occur at the interface. In the model of Jackson, Gilmer and Leamy [6,11], the two reactions are the solidification of host atoms and that of impurity atoms. The barriers to solidification of each species, Q_A and Q_B, respectively, are unknown constants that influence the respective reaction rates. In the continuous growth model of Aziz [7,12] the pair of reactions are a net alloy crystallization reaction across a barrier Q_C, and a diffusive solute-solvent redistribution reaction across a barrier Q_G. This pair of reactions is essentially a linear combination of the aforementioned pair. The differences between the models arise from the choice of which barriers are the constant ones and the manner in which the reactions are coupled. Solute trapping occurs in the

former model (which we shall call "AB", for the two species) when \( Q_A \ll Q_B \). Solute trapping occurs in the latter model (which we shall call "CD", for "crystallization and diffusion") when \( Q_C \ll Q_D \).

Given a free choice of barrier heights, the models can predict virtually identical behavior for a dilute solution of any single dopant in any single host. This can be seen by the form of the resulting equations relating the segregation coefficient \( k \) to the growth velocity \( v \). The CD model yields

\[
k = \frac{(v/v_D) + k_e}{(v/v_D) + 1}, \tag{1}
\]

where \( k_e \) is the equilibrium segregation coefficient at the temperature \( T \) of the undercooled interface and \( v_D \) is the diffusive velocity, which depends upon the height of the barrier to redistribution \( Q_D \). The prediction of the AB model can be put into the form

\[
k = \frac{(v/v') + k_e}{(v/v') + 1}, \tag{2}
\]

where

\[
v' = \exp \left( \frac{Q_B - Q_A}{RT} - \frac{\Delta S_f^B}{R} \right) / K_{A^*} \tag{3}
\]

The entropy of fusion \( \Delta S_f^B \) of species B is a positive number and \( K_{A^*} \) is the velocity of the forward reaction alone across the barrier \( Q_A \). (A lower limit on the magnitude of \( K_{A^*} \) for Si (100) is 15 m/s, the largest measured crystal growth rate [13]; \( K_{A^*} \) is probably significantly larger than this.) We see that in this form the AB model predicts a maximum value of \( k \) that should not be termed "saturation" but rather "truncation"; i.e. \( dk/dv \) does not approach zero at \( k < 1 \), but there is an upper limit to \( k \) which occurs at the maximum allowed velocity, \( v = K_{A^*} \). Past confusion over apparent differences between the models on the dependence of \( k \) upon orientation and velocity has arisen due to the different assumptions for \( v(T) \) that were put into the models. With suitable choices of the pairs of fitting parameters (the \( Q_i \)'s), the models give identical predictions if the same \( v(T) \) is input.

The two models differ substantially, however, in their composition dependence. If the barrier heights are constrained by forcing the models to predict the same behavior at one impurity concentration, then they need

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Fig. 1. Diffusion of Ge in Si. RBS spectra showing Ge profiles before and after pulsed laser melting. Solid line shows predicted spectrum for \( D_L = 4 \times 10^{-4} \) cm²/s; broken line shows predicted spectrum for \( D_L = 3 \times 10^{-4} \) cm²/s.
not predict the same behavior at other concentrations. In particular, the CD model predicts that if there is significant trapping of B in A then there should be significant trapping of A in B at a similar velocity. The AB model predicts that if there is significant trapping of B in A then there cannot be significant trapping of A in B at any velocity.

The presence of the diamond cubic crystal structure on both ends of the Si-Ge phase diagram allows a meaningful test to distinguish between these models. The solution behavior of both phases is well modelled, which reduces the likelihood of a chemical "surprise" and allows a surer test of the kinetics than has been previously attempted. The system exhibits complete miscibility of Si and Ge in both the liquid and solid phases. For a dilute solution of Ge in Si, $k_{Ge}^{Si} = 0.3$; for a dilute solution of Si in Ge, $k_{Si}^{Ge} = 6$. The phase diagram can be accounted for by ideal solutions in both the liquid and solid phases. This extremely simple solution behavior is not necessary for distinguishing between the models; it does, however, make the interpretation of results much easier. If we could obtain data for $k_{Ge}(v)$ at the Si-rich end of the phase diagram, fit the parameters of both models to these data, use these parameters to obtain predictions for $k_{Si}(v)$ at the Ge-rich end of the phase diagram, and distinguish between them experimentally, we could rule out at least one of the models.

EXPERIMENTAL

Ge was implanted at 150 keV into silicon-on-sapphire (SOS), Si was implanted at 100 keV into Ge layers deposited on SOS, and crystallinity was restored in a vacuum furnace anneal. The samples were then irradiated with a pulsed-ruby laser with a pulse duration of 30 ns FWHM. The regrowth velocity was varied by changing the pulse energy density. The time evolution of the melt depth was measured with nano-second time resolution by the transient conductance technique. The as-recrystallized and the final Ge impurity profiles were measured by glancing angle RBS and channeling. The Si impurity profiles were analyzed by glancing angle RBS and by SIMS depth profiling. To determine $k$ with high accuracy the bulk liquid diffusion coefficient $D_L$ must be known to high accuracy. For the case of Ge in Si, both were determined by numerical simulation. The measured as-implanted profile was broadened numerically using the measured melt depth as a function of time. Guesses were made for $D_L$ and $k$; they were assumed not to depend upon $v$ and $T$. The predicted final profile was convoluted with a 14 keV detector resolution and compared to the RBS data.

![Graph showing concentration vs depth](image)

**Fig. 2.** Segregation of Ge in Si at 2.3 m/s. Glancing angle RBS spectrum showing surface peak of zone refined Ge. Peak height and area match simulation for $k = 0.80$. Predicted peak for $k = 0.85$ is too small.
RESULTS

Figure 1 shows an example of an RBS spectrum used to determine $D_L$. The value $D_L = 4 \times 10^{-4}$ cm$^2$/s provides excellent agreement with the data; in contrast, the simulation with $D_L = 3 \times 10^{-4}$ cm$^2$/s simply does not provide enough broadening. It should be noted that the entire volume change upon melting will be taken up in the direction normal to the interface during pulsed laser melting. Numerical broadening programs like ours that do not account for the volume change will thus overestimate $D_L$. The resulting error is significant if a high precision determination is compared with the result from a conventional method of measuring $D_L$. This error does not affect our determination of $k$ and we did not correct for it.

Once we know $D_L$ we can determine $k_{Ge}$ to high accuracy by a careful examination of the surface peak of zone-refined material. As shown in Fig. 2, we can easily discern between $k = 0.80$ and $k = 0.85$ by this method. This sample was shot twice in order to allow enough broadening of the Ge implant that the final profile is essentially flat beneath the surface. Uncertainties in identifying the peak area are thus reduced. We note that this surface peak is not detectable by normal geometry RBS.

The results for $k_{Ge}(v)$ are plotted in Fig. 3. The horizontal error bars represent fluctuations in the transient conductivity signal during the final 500 A of regrowth. The vertical error bars represent our estimate of the uncertainties in the results at the 90% confidence level, considering only uncertainties in detector resolution, $D_L$, and eyeballing the fit. Other systematic corrections may apply. The curve drawn through the data is obtained from the CD model with a diffusive velocity of $v_D = 1$ m/s. The same curve results from the AB model with $Q_{Ge} - Q_{Si} = 1$ eV and reasonable choices for the other parameters, $k_A^+ = 30$ m/s, $T = 1645$ K.

![Graph](image)

Fig. 3. Segregation of Ge in Si. Curve arises from CD model with $v_D = 1$ m/s and from AB model with $Q_{Ge} - Q_{Si} = 1$ eV.

The AB model then predicts, with $Q_{Si} - Q_{Ge} = -1$ eV and $k_{Si}^+ = 6$, $k_{Si}(v) = 6$ at all velocities. (Recall $v < k_{Si}^+$.) This conclusion does not change even when all parameters are taken to their extreme limits of conceivability in order to maximize the predicted difference between $k_{Si}(v_{max})$ and $k_{Si}^+$. In contrast, the CD model predicts the familiar transition from equilibrium segregation to complete trapping centered at a diffusive speed which may be somewhat reduced due to a lower interface temperature on the Ge-rich side of the phase diagram. For $v_D = 0.7$ eV, the CD model predicts $k_{Si}^+(4 \text{ m/s}) = 1.1$. 


We examined pulsed laser melted Ge layers with Si implants to see whether we could distinguish between $k_{Si} = 1.1$ and $k_{Si} = 6$. For most impurities in most semiconductors, $k < 1$. Thus during regrowth from pulsed laser melting a steady-state spike of zone refined impurity is set up in front of the interface. If $C_s$ is the impurity concentration in the growing solid, the height of the spike above $C_s$ is $C_s^{[1/(k-1)]}$. Its 1/e width is $D/V$, and its area is $(D/V)C_s^{[1/(k-1)]}$. After solidification is completed, the spike appears at the free surface with a somewhat different shape; its area, however, is unchanged. The same analysis holds for Si in Ge where $k_{Si} > 1$, except that the Si spike becomes inverted, i.e. the liquid layer at the interface is purer in Ge than both the growing crystal and the bulk liquid. When this inverted spike reaches the free surface we are left with a surface deficit of Si, which can be examined in our samples by RBS. Figure 4 shows a high resolution glancing angle RBS spectrum of a Si-implanted polycrystalline Ge layer on SOS that solidified at approximately 4 m/s. The entire spectrum is shown in the inset at the right; the signal from Si at the free surface is shown in detail. The background counts presumably arise from dirt in the Ge layer; see that they do not interfere with the identification of the Si edge. In order to identify the backscattered energy corresponding to Si at exactly zero depth, we translated into the beam a piece of virgin Si adjacent to the sample without changing the scattering geometry. We see the Si edge in the same location in the two cases. Curve (a) is the spectrum predicted from our simulation with the following assumptions: $D = 4 \times 10^{-4}$ cm²/s, $k = 6$, detector resolution = 14 keV. If $k$ is changed to 1.1 we obtain curve (b). The important feature of these curves is the location of the Si edge. We see that the surface deficit predicted by the AB model would manifest itself as an apparent 100 A depression of the Si edge in the RBS spectrum. Within the resolution of our measurement, there is no evidence for such an effect. This result suggests that at 4 m/s $k_{Si}$ differs significantly from $k_{Si}$ for Si in Ge. Such a phenomenon, combined with a significant amount of trapping of Ge in Si, would rule out the AB model.

Fig. 4. Segregation of Si in Ge. Glancing angle RBS spectrum showing no surface deficit of Si. $E_1$: signal from surface Ge; $E_2$: surface Si; $E_3$: buried SOS. The virgin Si spectrum and the curves have been rescaled vertically. Depth scale for Si in Ge. Curve (a): AB model, $k_{Si} = 6$. Curve (b): CD model, $k_{Si} = 1.1$. 
Our results are suggestive but not yet conclusive. Although the dependence of $k$ upon orientation is expected to be small at these values near unity, the polycrystalline nature of the Ge layers introduces some uncertainty into our analysis. In addition, the presence of a surface oxide might obscure a surface Si deficit. Finally, the resolution of RBS is barely sufficient for these measurements. Before we draw a final conclusion, further work with better resolution on single crystal Ge in controlled atmospheres is desirable.

SUMMARY

High resolution RBS and SIMS measurements have been combined with the transient conductance measurement to determine the segregation coefficient for Ge as an impurity in Si and for Si as an impurity in Ge. We observe a significant degree of trapping of Ge in Si and of Si in Ge. Such a result is inconsistent with the model of Jackson and coworkers; it suggests that a superposition of an alloy crystallization reaction and a solute-solvent redistribution reaction might be a more appropriate basis for understanding binary alloy solidification.

REFERENCES