Nonequilibrium partitioning during rapid solidification of Si–As alloys

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Abstract

The velocity dependence of the partition coefficient was measured for rapid solidification of polycrystalline Si–4.5 at% As and Si–9 at% As alloys induced by pulsed laser melting. The results constitute the first test of partitioning models both for the high velocity regime and for non-dilute alloys. The continuous growth model (CGM) of Aziz and Kaplan fits the data well, but with an unusually low diffusive speed of 0.46 m/s. The data show negligible dependence of partitioning on concentration, also consistent with the CGM. The predictions of the Hillert–Sundman model are inconsistent with partitioning results. Using the aperiodic stepwise growth model (ASGM) of Goldman and Aziz, an average over crystallographic orientations with parameters from independent single-crystal experiments is shown to be reasonably consistent with these polycrystalline partitioning results. The results, combined with others, indicate that the CGM without solute drag and its extension to lateral ledge motion, the ASGM, are the only models that fit the data for both solute partitioning and kinetic undercooling interface response functions. No current solute drag models can match both partitioning and undercooling measurements.

1. Introduction

Much of our understanding of nonequilibrium interface kinetics during rapid solidification has come as a result of pulsed laser melting (PLM) experiments in doped silicon [1–3]. The dilute alloy limit of the continuous growth model of Aziz and Kaplan [4] has been shown to describe the velocity, \( v \), dependence of the partition coefficient, \( k \) (ratio of solid, \( X_S \), to liquid, \( X_L \), solute concentrations at the interface), for several dopants in Si [1,2,5], as well as for several alloying elements in Al [6,7]. The dilute CGM expression for \( k(v) \) is given by

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

where the "diffusive speed" \( v_D \) is the ratio of solute diffusivity at the interface to the interatomic distance. In the CGM, as \( v \) approaches \( v_D \), solute atoms no longer diffuse rapidly enough to avoid engulfment by the advancing crystal/melt interface. Because an independent physical mea-
measurement of \( v_D \) is not possible \(^1\), it is treated as a free parameter in the model. At \( v = v_D \), \( k \) is in mid-transition between its equilibrium value (\( k_e \)) and unity. Pulsed laser melting has provided ready access to the velocity regime of about 1–10 m/s, over which \( k \) in these systems has been measured in transition from local interfacial equilibrium to complete solute trapping (\( k \rightarrow 1 \)). In no case, however, has the entire transition been accessed experimentally. In several systems the CGM has been tested in the low-velocity regime (\( v \leq v_D \)) \([1,5]\), but it has never been tested quantitatively in the high-velocity regime (\( v \geq v_D \)). The Si–As system is a good candidate for such a test because early “laser annealing” experiments on this system at velocities of a few meters per second gave no evidence of partitioning; the amount, if any, of As swept to the free surface by the crystal/melt interface was undetectably small \([9–16]\). Additionally, Si–As is an excellent alloy system for a test of the CGM away from the dilute alloy limit, as the production by PLM of Si–As supersaturated solid solutions \([9–15]\) of up to 18 at% As \([16]\) has been reported.

Although many applications of rapid solidification processing involve polycrystalline materials, the consequences of an orientation dependence to solute trapping for polycrystalline samples has not been examined. It remains to be determined whether a polycrystalline sample can be described by an effective, orientationally-averaged partition coefficient. For single crystals at constant \( v \), the orientation-dependence of solute trapping in Si is sharply peaked at the \{111\} orientations \([3]\). This is accounted for in the aperiodic stepwise growth model (ASGM) of Goldman and Aziz \([3]\), an extension of the CGM to growth by the lateral passage of steps on \{111\} terraces. As the orientations approach \{111\}, steps are more sparsely distributed and must move faster to maintain a given interface velocity. The ASGM fits both the velocity and orientation dependence of \( k \) for Bi in Si \([3]\) with two free parameters, the diffusive speeds at the terrace (\( v_T^e \)) and at the ledge (\( v_L^e \)). In the ASGM the partition coefficient is given by

\[
k(v, \theta) = \frac{k_e + \beta_T(k_e + \beta_L)/(1 + \beta_L)}{1 + \beta_T},
\]

where \( \beta_T = (v / \cos \theta) / v_T^e \), \( \beta_L = (v / \sin \theta) / v_L^e \), and \( \theta \) is the misorientation from \{111\}. Its velocity dependence is virtually indistinguishable from that of the dilute CGM, so the latter is often used to characterize the velocity-dependence of \( k \) at fixed orientation because of its simplicity. In Si the ASGM also fits the orientation-dependence of other dopants \([17]\), including As, but the velocity-dependence has not been carefully tested except for Bi \([1,3]\) and Sn \([5]\).

In this work we address these issues by measuring \( k(v) \) for polycrystalline Si–4.5 at% As and Si–9 at% As alloys at interface velocities ranging from 0.25 to 2 m/s. These measurements span the largest range of \( k \) and log \( v \) to date and are the first to quantitatively test partitioning models in the high \( k \) regime. The solute trapping results also provide the first test of the CGM away from the dilute alloy limit for the velocity dependence of \( k \). In addition, measurements presented here complement those of the velocity–undercooling relation for the same alloys \([18]\), resulting in the first complete experimental determination of both interface response functions for rapid alloy solidification. The results permit us to settle the controversy on solute drag effects in solidification \([18]\). The version of the CGM “without solute drag” fits the velocity-undercooling and solute trapping measurements quite well, whereas the version of the CGM “with solute drag” and all other solute drag models do not fit the data. A solute drag model due to Hillert and Sundman (HS) \([19,20]\) which also predicts negligible drag, in agreement with our measured undercoolings \([18]\), is also considered here. Finally, using an orientational average of the ASGM, we compare our results on polycrystalline samples with the single crystal results of Reitano et al. \([17]\) and show that polycrystalline material can be treated

\(^1\) Cook and Clancy \([8]\) have determined \( v_D \) in a molecular-dynamics experiment and confirmed the basic hypothesis of the CGM, namely that the velocity about which the solute trapping transition is centered is indeed related to the interface diffusivity.
with an effective, orientationally-averaged partition coefficient that follows the simple velocity-dependence of the CGM.

2. Experimental techniques

Samples were irradiated using a 30 ns FWHM pulsed excimer (XeCl, 308 nm) laser. The laser beam was spatially homogenized (with a homogenizer obtained from XMR Inc.) to obtain laterally uniform illumination of the samples (to within approximately ±5%). As shown in Fig. 1, the samples consisted of a Si–As film electrically insulated from the Si substrate by a thermally grown SiO$_2$ film and an 80 nm thick Si$_3$N$_4$ film grown by plasma enhanced chemical vapor deposition [15]. The thin film geometry, which results in samples with optically smooth surfaces, and the spatial uniformity of the laser beam ensure planar melting and solidification fronts. The Si–As alloys were prepared by implanting As$^+$ at four different energies into e-beam deposited, 250 nm thick Si films. Approximately flat As profiles in the top 150 nm of the films were obtained. Alloys with 4.5 at% As (in the top 150 nm) were prepared with doses of $2.2 \times 10^{16}$ cm$^{-2}$ at 200 keV, $9.2 \times 10^{15}$ cm$^{-2}$ at 100 keV, $5.0 \times 10^{15}$ cm$^{-2}$ at 50 keV and $3.0 \times 10^{15}$ cm$^{-2}$ at 40 keV. Twice these doses were used for Si–9 at% As alloys. Samples were annealed for 10 min at 700°C in flowing Ar to crystallize the Si–As layer. The As distribution was further homogenized during pulsed laser melting. Each sample was irradiated only once and peak melt depths were kept between 130 and 160 nm. This ensured a uniform As concentration profile in the molten alloy, and sufficient time for the interface to approach steady state conditions during solidification. As an exception, samples used to determine liquid diffusion coefficients of As in Si were melted to ~240 nm.

The SiO$_2$ and Si$_3$N$_4$ layers act as thermal barriers and control heat diffusion into the substrate, thereby controlling the solidification velocity. Samples were fabricated with SiO$_2$ layers of 110 nm and 1 μm, yielding solidification velocities of ~1 and 2 m/s respectively. To obtain a wider range of solidification velocities, samples were preheated using an 80 W, continuous-wave CO$_2$ laser (10.6 μm), for a few seconds immediately before firing the excimer laser; the back of the sample was coated with graphite paint to improve the coupling to infrared radiation. With preheating to ~900 K we obtained reductions in solidification velocities by a factor of ~3 to velocities below 0.3 m/s.

We determined time-resolved melt depths during and following PLM by performing nanosecond-resolved measurements of the transverse electrical conductance of the Si–As layer [15,21]. These transient conductance measurements (TCMs) exploit the large increase in electrical conductivity that accompanies melting. Photolithographic techniques were used to pattern resistors with length-to-width ratios of 65 in the Si–As film. Al contacts were then deposited by thermal evaporation. The melt depth dependent resistance of the Si–As resistor was measured using a traveling pulse configuration to suppress signal reflections [22]. Surface melting and solidification were identified by monitoring the reflectivity of a low-power continuous-wave Ar$^+$ ion probe laser.

Arsenic concentration profiles before and after PLM, as well as layer thicknesses, were deter-
mined by Rutherford backscattering spectrometry (RBS) using 2 MeV He\textsuperscript{++} ions. A grazing exit angle geometry (75° from surface normal) was used to obtain a depth resolution of ~ 9 nm.

Plan-view TEM analysis was performed using a Philips 420 electron microscope at 120 keV. The samples were thinned to electron transparency by chemically etching the Si substrates in a solution of 20% HF in HNO\textsubscript{3}, followed by ion milling with 3 keV Ar\textsuperscript{+} ions. X-ray diffraction studies were performed on the films in a θ–2θ geometry with Cu K\textsubscript{α} radiation.

### 3. Data analysis

During planar-interface PLM and solidification, the electrical conductance of the Si-As resistor is the sum of the conductances of the liquid and solid layers, which are proportional to their respective thicknesses. This permits the time-resolved determination of melt depths from TCM data [15,21]. The conductivities of the liquid alloys were determined by fully melting ~ 160 nm Si–As films and observing the peak conductance recorded by TCM. Because As is electrically activated in the crystal formed by PLM, the electrical conductivity of the solid was taken into account when analyzing the solidification portion of the TCM (it was negligible during melting of the amorphous solid). In the analysis, we assumed that at after solidification the electrically active As was uniformly distributed in the solidified layer up to the maximum melt depth reached during PLM.

Partition coefficients were determined by comparing solute concentration profiles after solidification with numerical simulations of diffusion in the liquid and interfacial partitioning. Full finite-element numerical solutions of the 1D diffusion equation for the liquid with a moving boundary (solid–liquid interface) were performed to determine time and depth dependent concentration profiles during PLM and rapid solidification [1]. Measured melt-depth history and initial concentration profiles were used as inputs, and diffusion in the solid was neglected. For the interface boundary condition the composition ratio was forced to the value \( k \), which was treated as a free parameter. Because the solidification rate is not constant, but decreases slightly over the depth range relevant for determination of \( k \), an assumption must be made regarding \( \frac{dk}{dv} \) over the limited range of \( v \) sampled by each experiment. Assuming \( \frac{dk}{dv} = 0 \) results in reasonable fits between the simulated and measured depth profiles. However, better fits result by assuming a \( \frac{dk}{dv} \) equal to the derivative of Eq. (1), the CGM expression for \( k(v) \). This provides a more accurate computation than simply assuming a constant \( k \) during solidification but does not result in any bias on the global \( k(v) \) relation [1]. The final concentration profiles from simulations were convolved with a Gaussian to account for RBS depth resolution (typically 9 nm), before comparison to the data. The \( k(v) \) data reported in the next section correspond to solidification velocities and partition coefficients at melt-depths of 30 nm.

### 4. Results and discussion

TEM studies of samples solidified at 1.9 m/s showed that the resulting Si–As alloys were polycrystalline and homogeneous, with an average grain size of ~ 300 nm [15]. Diffraction rings indicated random orientations in the plane of the film, with no allowed orders of diffraction missing (indicating no strong texture in the direction normal to the substrate). X-ray studies showed good agreement between the relative intensities of the three most intense peaks and those expected for randomly oriented polycrystalline films, as shown in Table 1. Time-resolved reflectivity measurements confirmed that the solid-liquid interface was approximately planar, with a lateral variation in depth of ~ 15 nm at the end of solidification over the ~ 100 μm sampled by the reflectivity probe beam [15]. Room temperature conductivities after PLM were independent of solidification velocity and indicated that As was quenched into electrically active sites. In addition, excellent matching was obtained between measured concentration profiles and results of solute liquid diffusion and partitioning simulations assuming...
Table 1

Distribution of grain orientations along surface normal, from \( \theta - 2 \theta \) X-ray diffraction scan; 400 peak from single crystal substrate prevented measurement of 400 peak from polycrystalline film.

<table>
<thead>
<tr>
<th>X-ray reflection, ( hkl )</th>
<th>Relative intensity excepted for random distribution of orientations (%)</th>
<th>Observed relative intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>220</td>
<td>55</td>
<td>59</td>
</tr>
<tr>
<td>311</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>400</td>
<td>6</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Planar interface motion. These observations indicate that the interface was stable against Mullins–Sekerka type shape instabilities [5,23].

Diffusion coefficients \( (D_L) \) in the liquid Si–As alloys were determined by fitting simulated profiles for samples that underwent deep melts. For both Si–4.5 at% As and Si–9 at% As alloys, \( D_L \) was determined to be \( (1.5 \pm 0.5) \times 10^{-4} \) cm²/s. In Fig. 2 we show arsenic concentration depth profiles before and after PLM for a Si–9 at% As sample with a peak melt depth of 240 nm. Results of the corresponding liquid diffusion and partitioning simulation are also shown.

In Fig. 3 we show measured melt-depth histories (Fig. 3a) and measured and simulated concentration profiles (Fig. 3b) for three Si–9 at% As samples with different solidification velocities. (The abrupt apparent decrease in \( v \) in the last \( \sim 20 \) nm of solidification is an artifact due to electrical conduction by the solid phase; it was subtracted off before performing diffusion simulations.) No evidence of a surface peak is observed for the sample solidified at 1.9 m/s. This resulted in a much larger uncertainty in the partition coefficient than for samples that exhibited a surface peak. \( k(v) \) results for Si–4.5 at% As and Si–9 at% As alloys are shown in Fig. 4.

![Fig. 2. Arsenic concentration depth-profiles, before and after PLM and solidification, for a sample with peak melt depth of 240 nm.](image)

![Fig. 3. (a) Measured melt depth versus time for three samples with different solidification velocities, and (b) corresponding As concentration depth profiles after PLM and solidification. In (b) data are represented by symbols and results of numerical simulations by lines.](image)
We compared the \( k(v) \) data to predictions of the CGM without solute drag. A subregular solution model was used to compute the thermodynamic functions for the solid and liquid alloys, with the Gibbs free energy given by

\[
G = XG_{A_5}^0 + (1 - X)G_{Si}^0 + RT[(1 - X)\ln(1 - X) + X\ln X] + X(1 - X)\Omega, \tag{3}
\]

where \( \Omega \) is an interaction parameter that can depend linearly on temperature, \( R \) is the gas constant, and \( G_{Si}^0 \) and \( G_{A_5}^0 \) are the Gibbs free energies for pure Si and pure As respectively (with diamond structure for the solid in both cases). The thermodynamic parameters used in the calculations are given in parameter set 1 of Table 2. The interaction parameters for the solid and liquid phases were chosen to fit the equilibrium liquidus data [24] and the assessed equilibrium solidus [24] (which corresponds in practice to the maximum reported equilibrium solubilities). The choice of \( G_{As}^0 \) is somewhat arbitrary. It was chosen to fall within a range of reasonable values as is discussed elsewhere [16]; our conclusions are insensitive to the value within this range.

The two kinetic parameters in the CGM [4] are the diffusive speed \( (v_D) \) and \( v_0 \), the maximum speed of crystallization at infinite driving force. The parameter \( v_0 \) has negligible effect on the \( k(v) \) relation and was taken from the velocity–undercooling relation for pure Si (\( \Delta T_{\text{kinetic}}/v = 15 \) K s/m) to be \( v_0 = 31 \) m/s [15,25,26]. We determined \( v_D \) by fitting the \( k(v) \) data, obtaining \( v_D = 0.46 \) m/s. The \( k(v) \) relations predicted by the CGM for Si–As alloys of three different concentrations are shown in Fig. 4. The CGM without solute drag describes the data very well, and predicts the observed negligible concentration dependence of the \( k(v) \) relation. In the analysis, the same value of \( v_D \) was used for both As concentrations. It should be noted, however, that the diffusive velocity is defined theoretically in terms of a thermally activated diffusive jump across the interface [4]. Because interface temperatures for the Si–9% As alloys are \( \sim 1450 \) K, while those for the 4.5% As alloys are \( \sim 1565 \) K [15,18], a slightly smaller value of \( v_D \) might be expected for the more concentrated alloy. This could explain the slight trend observed in the data which suggests that an increase in concentration results in a shift towards decreasing velocities. Additionally, we note that no concentration-dependence of partitioning of Sn (up to 2 at%) was observed in previous work [27], although the concentrated-alloy CGM was not tested.

The diffusive velocity determined for the Si–As system is nearly two orders of magnitude lower than that determined for the Si–Bi system (\( v_D = 32 \) m/s) [1]. This is consistent (although as an extreme) with a trend observed for several Si as

![Graph showing measured partition coefficient versus interface velocity and predictions of models. CGM: continuous growth model, \( v_D = 0.46 \) m/s; ASGM: angular average of the aperiodic stepwise growth model, \( v_{SL} = 0.038 \) m/s, \( v_{LD} = 0.66 \) m/s; and Hillert–Sundman diffuse-interface model, \( \delta = 6.2 \) nm.](image)

**Table 2**

<table>
<thead>
<tr>
<th>Parameter set</th>
<th>Solid (diamond cubic)</th>
<th>Liquid (diamond cubic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{Si}^0 ) (J/mol)</td>
<td>0</td>
<td>-14226.6 – 7.2( T )</td>
</tr>
<tr>
<td>( G_{As}^0 ) (J/mol)</td>
<td>0</td>
<td>-160000 + 99T</td>
</tr>
<tr>
<td>( \Omega ) (J/mol)</td>
<td>0</td>
<td>-195500 + 151T</td>
</tr>
<tr>
<td>Parameter set 2</td>
<td>Liquid (diamond cubic)</td>
<td>0.5</td>
</tr>
<tr>
<td>( G_{Si}^0 ) (J/mol)</td>
<td>0</td>
<td>140000 + 87.5T</td>
</tr>
<tr>
<td>( G_{As}^0 ) (J/mol)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \Omega ) (J/mol)</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
well as Al alloys, for which an inverse correlation is found between the diffusive velocities and the equilibrium partition coefficients \([6,7,17]\). It has been suggested that kinetic barriers for solute–solvent redistribution across the interface are smaller for systems with steep potential gradients and that the quantity \(v_D \times k_e^{1/2}\) is approximately the same for different solutes in the same solvent \([7]\). This relation is approximately followed in the existing data for (001) oriented Si alloys \([1,5,17]\).

We also compared our data with predictions of the Hillert–Sundman model. This model assumes a finite interface width \(\delta\). The continuum 1D diffusion equation is solved across the interface, with a diffusivity that varies exponentially across the interface matching the values for the liquid and the solid at the corresponding interface boundaries. The parameters \(\Omega, G_{Si}^e\) and \(G_{As}^e\) in Eq. (3) are assumed to vary linearly across the interface and match the corresponding solid and liquid values at the boundaries. Because the free energy dissipated by solute–solvent redistribution is calculated and subtracted from the free energy driving interface motion, in principle this is a solute drag model. However, the actual amount of solute drag computed from the model is negligible as a consequence of the steep rise in diffusivity coefficient across the interface. The steep rise in diffusivity results, for the partial solute trapping regime, in a region of the interface (close to the solid) where solute–solvent redistribution is kinetically frozen and a region (close to the liquid) that is in local equilibrium with the liquid. This leaves only a narrow zone within the interface where free energy can be dissipated by the solute–solvent redistribution, resulting in a negligible solute drag effect.

Calculations were performed using parameter set 1 of Table 2 and a solid diffusion coefficient \(D_s = 3 \times 10^{-13}\) cm\(^2\)/s \([28]\), which corresponds to measured interface temperatures for the 9 at% alloy \([18]\). The interface width was used as a fitting parameter and results are shown in Fig. 4 for \(\delta = 6.2\) nm. The calculated \(k\) versus \(v\) curve rises too slowly compared to the data. This value of 6.2 nm for \(\delta\) is unphysically large by at least an order of magnitude. Furthermore, a reduction of \(\delta\) by an order of magnitude to a physically reasonable value produces a shift of the curve to the right by an order of magnitude.

The thermodynamic parameters used in the calculations result in a substantial overestimate of measured congruent melting temperatures \((T_0)\) and an underestimate of measured enthalpies of fusion \((\Delta H_f)\) \([15]\). It is not possible within the framework of the subregular solution model to fit all existing thermodynamic data for the Si–As system. For this reason, calculations were also performed with a set of thermodynamic parameters, parameter set 2 of Table 2, that result in a good fit to the equilibrium liquidus, measured values of \(\Delta H_f\), and measured congruent melting temperatures. We used the same values of \(G_{Si}^e\) and \(G_{As}^e\) as before, but with new values of the interaction parameters. This alternative set of thermodynamic parameters, however, does not result in a good fit to the assessed equilibrium solidus. Nevertheless, it should be noted that there are large discrepancies in reported solidus data \([24]\). Parameter set 2 also gives an unlikely value, \(k_e = 7 \times 10^{-4}\), of the dilute limit of the equilibrium partition coefficient. Although the commonly accepted value of \(k_e = 0.3\) is based on scant experimental evidence \(2\), it is unlikely to be off by orders of magnitude. Calculations using the CGM with \(v_D = 0.37\) m/s and parameter set 2 result in very similar predictions for \(k(v)\) to those shown in Fig. 4 from the first parameter set. Calculations with the Hillert–Sundman model and parameter set 2 result in similar predictions to those obtained for the same model with the first parameter set, although with a somewhat steeper rise in \(k\) versus \(v\) \([18]\). However, in this case the only possible fit to the data corresponds to a physically unacceptable interface width of approximately 73 nm. Hence no matter which set of thermodynamic parameters is used, the Hillert–Sundman model with a physically plausible interface width does not fit the data.

We also compared our measurements with

\(^2\)Olesinski and Abbaschian \([24]\) report that the dilute limit of \(k_e\) is quoted by Burton \([29]\) as 0.3, citing Hall \([30]\) and J.D. Struthers, but that Hall actually reported a \(k_e\) smaller by a factor of five.
predictions of the ASGM, which predicts the orientation as well as the velocity dependence of the partition coefficient. Recently, Reitano et al. determined the orientation dependence of \( k \) in dilute Si–As alloys [17]. They determined partition coefficients in a similar manner to that used here, but rather than measuring melt histories directly, they estimated them by matching heat-flow simulations to measured melt durations. They obtained a good fit for the orientation dependence of \( k \) using the ASGM with \( v_D^L = 0.66 \) m/s and \( v_T^L = 0.038 \) m/s and assuming \( k_e = 0.3 \). In order to compare predictions of the ASGM to our measurements, performed in nondilute polycrystalline alloys, we assumed that individual grains were randomly oriented (as indicated by TEM and X-ray analysis). We also assumed that all grains solidified with the same interface velocity (as indicated by reflectivity measurements [15]) and solid composition (as expected for steady state conditions). The quantity that was assumed to vary from grain to grain, as a function of orientation, was the solute concentration in the liquid at the interface, \( X_e \). In Fig. 5 we show simulated non-steady-state As concentration profiles during solidification for four grains with different orientations. The profiles were computed using diffusion and partitioning simulations with partition coefficients predicted by the ASGM; they show that \( X_e \) varies substantially from grain to grain whereas \( X_s \) varies only slightly. For regrowth at higher \( v \), typical of most cases, the variations in \( X_s \) will be smaller still. Consequently, the quantity determined experimentally was an effective average partition coefficient \( \bar{k}(v) \), given by \( X_s/X_e \), where \( X_L \) is the orientational average of \( X_e \) and \( X_s \) can be assumed to be the same in all grains. We used the kinetic parameters \( v_D^T \) and \( v_T^T \) determined by Reitano et al. for dilute solutions and, because the experiment averages over \( X_L \) as discussed above, evaluated \( \bar{k}(v) \) as the reciprocal of the orientational average of \( 1/k \) for a fixed interface velocity. That is

\[
\bar{k}(v) = \left[ \frac{1}{\omega} \int \frac{1}{k(v, \theta)} \sin \theta \, d\theta \, d\phi \right]^{-1}, \tag{4}
\]

where \( \theta \) is the angle between [111] and the growth direction, and \( k(v, \theta) \) the partition coefficient predicted by the ASGM, Eq. (2). The average over \( \theta \) and \( \phi \) is performed over the octant, \( \omega \), of the sphere closer to [111] than to any other \( \langle 111 \rangle \) direction. The partition coefficient was assumed to be independent of azimuthal orientation \( (\phi) \), which we would not expect to be true if, say, ledges advanced solely by the lateral motion of kinks. In the absence of any experimental evidence about the \( \phi \)-dependence, the simplest assumption seems the most reasonable. The results of this calculation, shown in Fig. 4, are in reasonable agreement with predictions of the CGM using the thermodynamic parameters of parameter set 1 in Table 2 (which correspond to \( k_e \sim 0.3 \)) and \( v_D = 0.46 \) m/s, in the dilute limit. In Fig. 4, Eq. (4) predicts a \( \bar{k}(v) \) curve with the same slope as the CGM and the experimental data; however, the velocities appear to be too low by a factor of \( \sim 0.7 \).

There are a number of possible sources of the discrepancy between the orientational average of the ASGM with parameters measured for dilute alloys by Reitano et al. [17], and the result reported here for polycrystalline nondilute alloys. It does not appear to be due to uncertainties in the thermodynamic parameters (Table 2) alone; the
discrepancy appears no matter which parameter set is used. It is quite possible that a systematic error in regrowth velocity estimates for CO$_2$ laser preheated samples in Ref. [17] accounts for much of the discrepancy. These velocities, which were estimated from heat-flow calculations rather than measured, affect their determination of the values of $v_T^1$ and $v_T^2$ which were used here to compare the ASGM and the polycrystalline data. Due to incomplete literature for high temperature Si properties used in heat flow calculations, such errors are more likely for samples that underwent significant CO$_2$ preheating. A heat-flow predicted velocity that was too slow by a factor of approximately 0.7 would be consistent with recent findings of Brunco et al. [31] in the Si(Ge) system. (We note that velocity estimates in Ref. [17] are probably more accurate for room temperature irradiations because of more reliable materials parameters in calculations.) Additionally, if Reitano et al. underestimated the regrowth velocity and correspondingly the melt depth, their estimate of $D_L$ would need to be high to produce the same amount of solute spreading in the tails of the concentration profile. This could in part account for their $D_L$ value of twice ours. Alternatively, the discrepancy may reflect a real physical effect such as a variation of $D_L$ with composition or temperature: in our concentrated solutions the interface temperatures is close to 250 K lower during solidification than in the dilute solutions of Reitano et al. Finally, we note that the difference between the ASGM line in Fig. 4 and our data could reflect a $k$ that is not independent of azimuthal orientation, contrary to the assumption in Eq. (4), or a not truly random orientation in our polycrystalline samples. Considering the approximations involved in the modeling and the uncertainties in experimental results, there is quite reasonable agreement between our measurements of $k'(v)$ on nondilute polycrystalline samples and measurements of the orientation dependence of $k$ in dilute single-crystal samples by Reitano et al.

The combined results indicate that the ASGM adequately describes both the velocity and orientation dependence of the partition coefficient in the Si–As system. Conceptually it gives a highly satisfactory description of the solute trapping process for substitutional dopants in silicon.

Finally, it is evident that if one is interested only in the velocity-dependence of $k$ and not the orientation-dependence, the dilute CGM expression, Eq. (1), may be used as a good approximation. In light of the success of the ASGM [3,17], clearly the CGM gives only an approximate description of partitioning in Si; yet the approximate description works remarkably well. The CGM adequately describes the $k(v)$ relation in all systems in which it has been tested: single crystal Si, polycrystalline Si, and (111)-textured polycrystalline Al. Its advantage over the ASGM is its simplicity – it has only one instead of two free parameters – and its applicability to a wide range of materials systems. Additionally, although correlations have now been identified that help in estimating the values of the fitting parameters of both models in the absence of a solute trapping measurement [7,17], the correlation for the CGM has been established for a wider range of systems than those for the ASGM.

Combining the $k(v)$ measurements with those of the velocity-undercooling relation for the same alloys [18] results in the first complete experimental determination of the interface response functions for rapid alloy solidification and allows us to address the controversy on solute drag effects. The CGM without drag fits the data for both the $k(v)$ and $v(T)$ relations; no solute drag model fits all of these data. The predictions of the ASGM and the CGM will be indistinguishable for the $v(T)$ behavior as well as for the $k(v)$ behavior. This occurs because the ASGM postulates that lateral ledge motion follows CGM kinetics, so if the CGM without drag is used then solute–solvent redistribution at the step edge will dissipate no free energy. Subsequent solute–solvent redistribution through the terrace must dissipate free energy if it is independent of the ledge motion; however, the actual amount of free energy dissipation computed for this process turns out to be negligible in the velocity regime covered by the experiment. Consequently the ASGM is also consistent with the measured $v(T)$ relation, as well as with the measured velocity and orientation-dependence of $k$. 
5. Summary

(1) We measured the velocity dependence of the partition coefficient for polycrystalline Si–4.5 at% As Si–9 at% As alloys. These measurements provide the first test for interface kinetic models of \( k(v) \) away from the dilute alloy limit and the first test into the high velocity regime \((v \geq v_D)\). They also constitute a test of solute trapping models over the widest range of \( k \) and \( \log v \) to date.

(2) To within the accuracy of the measurements there is negligible concentration dependence in the results, which is consistent with the nondilute continuous growth model without solute drag.

(3) As is the case for other dopants in Si, the continuous growth model describes \( k(v) \) very well, with a diffusive velocity \( v_D = 0.46 \text{m/s} \). Because of this low value of \( v_D \), these results are consistent with previous measurements performed at \( v \gg v_D \) where the observed solidification behavior was indistinguishable from partitionless.

(4) Although the Hillert–Sundman model gives a conceptually plausible description of solidification at a diffuse interface, its predictions are in disagreement with our \( k(v) \) measurements, no matter which set of thermodynamic parameters is used.

(5) An orientational average of the aperiodic stepwise growth model, using independently measured values of \( v_B^L \) and \( v_D^L \), has been shown to describe \( k(v) \) in a similar manner to the dilute limit CGM and to fit the \( k(v) \) data reasonably well. Consequently, the ASGM provides a satisfactory description of both the orientation and velocity dependence of partitioning in the Si–As system.

(6) When only the velocity-dependence, and not the orientation-dependence, is of concern, the CGM provides a good approximation to the ASGM. This is true of \( k(v) \) for any particular orientation as well as for the orientational average. Because the CGM also fits the \( k(v) \) data in metals, for practical purposes it appears to offer a universal, though approximate, description of solute trapping.

(7) These measurements complement those of the velocity–undercooling relation for the same alloys, resulting in the first complete experimental determination of the interface response functions for rapid alloy solidification and allowing us to settle the controversy on solute drag effects. The CGM without drag fits the data for both the \( k(v) \) and \( v(T) \) relations; no solute drag model fits all of these data. If the ASGM uses the CGM without drag as a starting point, it also fits the \( v(T) \) measurements.

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