Germanium partitioning in silicon during rapid solidification

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Pulsed laser melting experiments were performed on Ge$_x$Si$_{1-x}$ alloys ($x \approx 0.10$) with regrowth velocities ranging from 0.25 to 3.9 m/s. Analysis of post-solidification Ge concentration profiles, along with time-resolved melt depth measurements, allowed determination of the liquid-phase diffusivity $D_l$ for Ge in Si and the dependence of the Ge partition coefficient $k$ on interface velocity $v$. A $D_l$ of $2.5 \times 10^{-4}$ cm$^2$/s was measured. The $k$ vs $v$ data were analyzed using various models for partitioning, including both the dilute and nondilute Continuous Growth Models (CGM). Extrapolating to zero velocity using the partitioning models, an equilibrium partition coefficient of approximately 0.45 was obtained. Best fitting of partitioning data to the nondilute CGM yields a diffusive speed of 2.5 m/s. These measurements quantify previous indications of partitioning observed in other studies of pulsed laser processed Ge$_x$Si$_{1-x}$ alloys. © 1995 American Institute of Physics.

I. INTRODUCTION

The behavior at the solid/liquid interface during rapid solidification of binary alloys can be substantially different than during conventional solidification processing. Under normal conditions, solute partitioning at the interface is in accordance with the equilibrium phase diagram, even when significant concentration and temperature gradients exist in the adjacent phases. This condition of local interfacial equilibrium, however, can be violated during rapid solidification. In this case solute atoms have insufficient time for equilibrium partitioning before being engulfed by the solidifying matrix. Solute segregation is characterized by the partition coefficient $k$, defined as the ratio of the atomic fraction of solute in the solid $X_s$ to that in the liquid $X_l$ at the interface ($k = X_s/X_l$). In general $k$ is a function of interface velocity $v$ and ranges from its equilibrium value $k_e$ during slow solidification to a value thought to approach unity at sufficiently high solidification velocities.

Several models have been proposed for the velocity dependence of solute partitioning, but the Continuous Growth Model (CGM) has proved particularly successful in describing the $k(v)$ relation in a number of systems. For Henrian solutions, the nondilute CGM expression for $k$ may be written as

$$k(T,X_s,v) = \frac{K_s(T)\left[1-K_s(T)\right]X_s+v/v_D}{1+v/v_D},$$

where $T$ is the interface temperature, $K_s$ is the equilibrium partition coefficient for the solute (Ge) divided by that for the solvent (Si), and $v_D$ is the “diffusive speed” conceptually defined as the ratio of the solute diffusivity at the interface to the interface width. This expression is most typically used in its dilute limit, where it simplifies to

$$k(v) = \frac{k_e + v/v_D}{1 + v/v_D}.$$

At $v = v_D$, $k$ is in mid-transition between $k_e$ and unity. In addition to a velocity dependence, nonequilibrium partitioning has been observed to depend upon the crystallographic orientation of the growing solid. In the Aperiodic Stepwise Growth Model (ASGM), Goldman and Aziz extended the CGM to include these orientational effects and described the behavior of $k$ for Bi impurities in Si. The model has since been successfully applied to the orientational dependences of several other impurities in Si.

Technological applications employing rapid solidification often exploit the solute trapping behavior at high velocities to achieve structures not readily attainable with conventional processing. Pulsed laser crystallization of Ge$_x$Si$_{1-x}$ alloys ($x \approx 0.2$) is one such application and has been studied by many groups for producing device-quality thin films. In these studies, an initially amorphous layer of either pure Ge or GeSi alloy on Si is laser melted and rapidly solidified, resulting in strained heteroepitaxial growth of Ge$_x$Si$_{1-x}$/Si under appropriate conditions. Despite the short duration of the melt (typically 50 – 100 ns), Ge diffusion in the liquid is significant and, in fact, critical for homogenization in most of the reported works. While liquid-state diffusion is often beneficial, Ge partitioning at the interface during solidification is invariably detrimental. In reported pulsed laser crystallization experiments, qualitative indications of segregation have been observed in the Ge/Si system with segregation effects quite dramatic in some cases. Proper interpretation and understanding of these results require quantitative measurements of both the Ge diffusion co-
efficient in the liquid phase $D_l$ and the velocity dependence of Ge partitioning $k(u)$. 

In addition to its interest for technological applications, GeSi alloys are also a nearly ideal system to study laser-induced phase transformations and to examine theories of rapid solidification. For example, early measurements of solute partitioning performed on both the Si and Ge rich sides of the phase diagram were used to distinguish between two theories with identical predictions (under certain assumptions) for the velocity dependence of $k$, but different predictions for composition dependence. These early experiments were performed at high velocities (with little partitioning) where accurate, quantitative measurements are difficult. More recently, Reitano et al. 8,9 studied the partitioning of Ge and other impurities in single-crystal Si. They found $k$'s consistent with the ASGM7 for As, Ga, In, Sb, and Si impurities in silicon, but inconsistent for Ge in Si. Thus, this work also serves to provide quantitative $D_l$ and $k(u)$ data for this important model system and to explain the anomalous result for Ge in Si observed by Reitano.9

In this paper, we present our measurements of $D_l$ and $k(u)$ for Ge in Si. The $k(u)$ data are fit to many of the partitioning models in the literature, including both the dilute and nondilute CGM. With the CGM models, we find a diffusive speed of approximately 2.5 m/s and compare this to values for other impurities in silicon. We also extrapolate to zero velocity the fits of the $k(u)$ data to obtain an equilibrium partition coefficient of approximately 0.45. To our knowledge, this is the first time partitioning models have been extrapolated to equilibrium conditions to determine $k_e$. Additionally, we provide estimates of $k$ during pulsed laser assisted heteroepitaxy of GeSi$_{1-x}$/Si, and we report results of a revised analysis of data from Reitano and co-workers.9

II. EXPERIMENT

Laser melting and solidification experiments were performed with a variety of silicon-on-insulator (SOI) and silicon-on-sapphire (SOS) samples. The SOI substrates consisted of (100) oriented Si on about 1 μm of thermally oxidized silicon while SOS substrates were (100) Si on (1102) Al$_2$O$_3$. The Si film thicknesses ranged from 0.2 to 0.6 μm. For low Ge concentrations, SOI and SOS substrates were ion implanted with $^{76}$Ge at 80 keV, a 7° tilt, and a $5 \times 10^{15}$ cm$^{-2}$ dose. Rutherford backscattering spectrometry (RBS) showed the implant to be well-described by an Edgeworth distribution using a projected range of 59 nm, a straggler of 22 nm, a skewness of 0.45, and a kurtosis of 3.1. This corresponds to a peak Ge concentration of 1.8 at.% at a depth of 53 nm. Higher Ge concentrations were obtained with deposited films. SOS substrates with 50 nm epitaxial Ge$_x$Si$_{1-x}$ ($x=0.04$ and 0.10) films were grown by Molecular Beam Epitaxy (MBE) at a deposition pressure below $5 \times 10^{-10}$ Torr. The Si was evaporated from an electron beam source and the Ge was coevaporated from a Knudsen cell. An additional SOS substrate had a 50 nm amorphous Ge$_{0.04}$Si$_{0.96}$ layer grown by electron beam evaporation at a pressure of $5 \times 10^{-7}$ Torr.

FIG. 1. (a) Top view of TCM sample. (b) Schematic of SOI sample irradiation and TCM data collection. A bias voltage $V_S$ of 25 V, and 50 Ω source $R_s$ and load $R_l$ resistors were used. Figure for SOS sample irradiation is similar, except the SiO$_2$/Si substrate/graphite paint is replaced by the sapphire substrate.

Using microelectronics fabrication techniques, the samples were processed for transient conductance measurements (TCM) to provide time-resolved melt depth information. The implanted samples were first patterned with 350 nm thick Al contact pads and then implanted under the prescribed conditions. The Si(Ge) layer was patterned with photoresist and reactively ion etched (SF$_6$/O$_2$ plasma) into a meandering path resistor with a length-to-width ($L/W$) ratio of 65 and a confined area of 1×1 mm$^2$. Following Si(Ge) patterning, the samples were annealed at 500 °C for 30 min to minimize contact resistance to the Al pads. The samples with deposited Ge$_x$Si$_{1-x}$ films on SOS were processed similarly, but with the Al deposited after the Ge$_x$Si$_{1-x}$ deposition and patterning.

The patterned samples were irradiated with a single pulse from a XeCl excimer laser (308 nm, 30 ns FWHM) with simultaneous measurements of transient sample conductance [Fig. 1(b)]. The TCM technique exploits the large conductivity difference between the semiconducting solid and the metallic liquid to determine time-resolved melt depths during laser processing. The small amount of conductance from the hot solid was subtracted before using the TCM data in subsequent analysis. Laser fluences were chosen to give melt depths of typically 150 to 200 nm. To access slower regrowth velocities, some samples were preheated from the backside for a few seconds with a CO$_2$ laser (10.6 μm). To aid coupling of infrared laser energy to sample heating, the backsides of the SOI wafers were coated with carbon paint; such coating was unnecessary for the SOS substrates. During regrowth, velocities were not constant but slowed as the interface approached the surface. For consistency, veloc-
laser irradiated, ion implanted SOS sample are shown in Fig. 2(a). The RBS spectra show only scattering events from the simulated RBS spectra were compared with experimental information was obtained. The expression for $k(v)$. To reflect the $v$ dependence of $k$, Eq. (2) was used with $k_0$ set to a nominal value of 0.4 and the value of $v_D$ allowed to vary. Because each experiment samples only a small range of velocities, the exact analytical form of $k(v)$ is not significant. To a large degree, the use of the dilute CGM equation simply guarantees a reasonable estimate for $dk/dv$ about the average $v$ (and thus, $k$) for a particular regrowth experiment. These diffusion and partitioning simulations produced final Ge concentration profiles that were compared to experimental RBS data using the analysis program RUMP.24

A nonlinear least squares search algorithm was used to obtain best fit values for $D_l$ and $v_D$ for each irradiated sample. The difference between the experimental and simulated RBS profiles at each channel was divided by the statistical uncertainty ($\sqrt{\text{Counts}}$) and then squared. These squares were summed over the channels in the RBS data for the Ge peak, and this sum was minimized by appropriately varying $D_l$ and $v_D$. Occasionally, poor fitting resulted when using our TCM data directly for melt depth profiles. To improve the fit for these cases, we scaled the melt depths obtained from TCM by up to 10% of the original values. This represents the magnitude of the uncertainty in the conductance measurements. Such scaling was found to have a minimal, but beneficial effect on overall fitting results. After initially fitting all the data with both $D_l$ and $v_D$ free to vary, the $D_l$ values were averaged (result: $D_l=2.5\times 10^{-4}$ cm$^2$/s), and the simulations were performed again with $D_l$ fixed and $v_D$ allowed as a fitting parameter. The $k(v)$ data presented in this work correspond to the fixed $D_l$ simulations.

In making these measurements, an accurate RBS detector calibration is critical.10 For large values of $k$, a small Ge surface peak results and small errors in calibrating the RBS channel number for backscattering from surface Ge can lead to non-negligible errors in $k$. Fortunately, the presence of surface Si and Ge allows the samples to be essentially self-calibrating. The Ge peak “leading edge” from optimized simulated RBS spectra were compared with experimental spectra to verify proper detector calibration. If necessary, the calibration was adjusted and the analysis was performed again to find new optimized $D_l$ and $v_D$ values. This process was repeated until a reliable, self-consistent detector calibration was obtained.

III. RESULTS

Typical segregation measurements and simulations for a laser irradiated, ion implanted SOS sample are shown in Fig. 2(a). The RBS spectra show only scattering events from the liquid Ge and correspond to a total depth of approximately 200 nm. An Edgeworth distribution was fit to the as-implanted RBS spectrum (collected with a different scattering geometry) and is shown in the figure for reference.

In Fig. 2(b) the raw conductance data (converted to an equivalent liquid thickness) and the actual liquid thickness (corrected for solid conduction and smoothed for numerical stability) are shown. These example data correspond to a sample preheated by a CO$_2$ laser and irradiated at a fluence of 0.50 J/m$^2$.

Following irradiation, the Ge profile broadens by diffusion and is segregated to the surface as shown by the experimental data points in Fig. 2(a). Using the measured initial concentration profile [Fig. 2(a)] and corrected melt history [Fig. 2(b)] as inputs, a best fit simulation to the post-solidification spectrum yielded a $D_l$ of $2.19\times 10^{-4}$ cm$^2$/s with a $v_D$ of 2.88 m/s. This simulation is shown by the solid curve in Fig. 2(a).

For all samples, the liquid diffusivities were determined in a similar manner, and Fig. 3 summarizes these data. Given

![FIG. 2. (a) Experimental and simulated RBS spectra for an implanted SOS sample with a peak melt depth of 190 nm and a regrowth velocity of 1.52 m/s. Solid curve: best fit obtained varying $D_l$ (2.19$\times 10^{-4}$ cm$^2$/s) and $v_D$ (2.88 m/s). Dashed curve: best fit obtained with $D_l$ fixed (2.5$\times 10^{-4}$ cm$^2$/s) and varying $v_D$ (2.81 m/s). (b) Raw melt history (dashed) and data corrected for hot solid conduction (solid).]
FIG. 3. Ge diffusivity in the liquid for different sample types. The average value is $2.5 \times 10^{-4}$ cm$^2$/s with a standard deviation of $0.5 \times 10^{-4}$ cm$^2$/s.

FIG. 4. Partition coefficient plotted vs velocity. The arrows on the points of Reitano et al. (See Ref. 9) and Aziz et al. (See Ref. 19) indicate values for $k$ measured at a $D_1$ of $2.5 \times 10^{-4}$ cm$^2$/s according to Eq. (4). The curve for $k_\text{CGM}$ is a fit of the dilute Continuous Growth Model to the data in this work.

TABLE I. Results of fitting various partitioning models to the data in this work. Used $k_\text{CGM} = 0.4$ in fits with fixed $k_\text{CGM}$.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\chi^2$</th>
<th>Parameter (units)</th>
<th>Value</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dilute CGM a</td>
<td>1.002</td>
<td>$u_0$ (m/s)</td>
<td>2.03</td>
<td>0.13</td>
</tr>
<tr>
<td>dilute CGM</td>
<td>0.766</td>
<td>$v_D$ (m/s)</td>
<td>2.74</td>
<td>0.46</td>
</tr>
<tr>
<td>SGM b</td>
<td>3.75</td>
<td>$v_D$ (m/s)</td>
<td>1.16</td>
<td>0.05</td>
</tr>
<tr>
<td>SGM</td>
<td>0.915</td>
<td>$k_\text{SGM}$</td>
<td>1.99</td>
<td>0.20</td>
</tr>
<tr>
<td>Wood c</td>
<td>1.91</td>
<td>$v_0$ (m/s)</td>
<td>1.96</td>
<td>0.09</td>
</tr>
<tr>
<td>Wood</td>
<td>0.724</td>
<td>$v_0$ (m/s)</td>
<td>2.94</td>
<td>0.37</td>
</tr>
<tr>
<td>Baker: 2 level d</td>
<td>1.61</td>
<td>$D_1/D_0$ (m/s)</td>
<td>0.69</td>
<td>0.04</td>
</tr>
<tr>
<td>Baker: 2 level</td>
<td>0.790</td>
<td>$D_1/D_0$ (m/s)</td>
<td>1.08</td>
<td>0.16</td>
</tr>
<tr>
<td>Baker: 3 level e</td>
<td>1.16</td>
<td>$v_D$ (m/s)</td>
<td>2.49</td>
<td>0.18</td>
</tr>
<tr>
<td>Kurz-Fisher f</td>
<td>1.07</td>
<td>$v_D$ (m/s)</td>
<td>1.26</td>
<td>0.08</td>
</tr>
<tr>
<td>Kurz-Fisher</td>
<td>0.761</td>
<td>$v_D$ (m/s)</td>
<td>1.85</td>
<td>0.34</td>
</tr>
<tr>
<td>nondilute CGM g</td>
<td>0.745</td>
<td>$v_D$ (m/s)</td>
<td>2.49</td>
<td>0.18</td>
</tr>
</tbody>
</table>

*Continuous growth model (dilute limit), Eq. (2).
Stepwise growth model, see Ref. 7, Eq. (3).
*See Ref. 7, Eq. (3).
*Stepwise growth model, see Ref. 7, Eq. (3).
*Ref. 1, Eq. (A6.24).
*Nondilute continuous growth model (with $k_\text{CGM} = 0.44$), Eq. (1).

The data in this work have been fit to many of the models for partitioning, and the fit to the dilute CGM equation is shown in Fig. 4. Using $k_\text{CGM} = 0.40$ results in a best fit $v_D$ of $2.0 \pm 0.1$ m/s. Fits were also made to the partitioning models with a variable $k_\text{SGM}$ because the actual $k_\text{SGM}$ value is not well known (see Sec. IV B). From such a fit to the dilute CGM, a $k_\text{SGM}$ of $0.45 \pm 0.02$ and $v_D$ of $2.7 \pm 0.5$ m/s are found. Results of fitting our $k$ vs $v$ data to other partitioning models are summarized in Table I and discussed in Sec. IV C.

IV. DISCUSSION

A. Ge diffusivity in melt

To our knowledge, there are only three reported $D_1$ measurements in the literature. From solute segregation studies in Czochralski grown crystals, Romanenko and Smirnov extracted diffusivities for both Ge and Si in liquid Ge$_{0.5}$Si$_{0.5}$ near the liquidus temperature over the entire range of compositions. They report a $D_1$ for Ge of $6 \times 10^{-4}$ cm$^2$/s in nearly pure liquid Si; this value falls to $4.5 \times 10^{-4}$ cm$^2$/s at 10% Ge and $1.5 \times 10^{-4}$ cm$^2$/s at 30% Ge. They note, however, that such a strong dependence of $D_1$ on composition is not expected based upon calculations with the
Einstein–Stokes equation. Additionally, they indicate a large degree of uncertainty in their $D_I$ measurements. Considering the differences in regrowth velocities ($\sim 1$ vs $\sim 10^{-5}$ m/s) and techniques for measuring $D_I$, a factor of about 2.5 between the $D_I$ given here and by Romanenko and Smirnov is not surprising. Another reported $D_I$ is $4 \times 10^{-4}$ cm$^2$/s by Aziz et al.,\textsuperscript{19} using a similar technique to that used here. More recently, Reitano et al.\textsuperscript{9} contributed a $D_I$ of $3 \times 10^{-4}$ cm$^2$/s. Their experiments, conducted to determine the effect of crystallographic orientation on $k(v)$, used measured melt durations and heat flow calculations to estimate melt depth profiles and used a somewhat different analysis technique than that presented here.

A simple approximation can be made to show how an error in $D_I$ affects the measurement of $k$. In practice, the area of the surface peak in the solute concentration profile is experimentally observable [as, for example, in Fig. 2(a)], and $k$ is extracted primarily from the magnitude of this peak. For a smaller value of $k$, more solute is swept to the surface and a larger surface peak results. During steady-state solidification, the amount $A$ of excess solute in the surface peak for a growing solid of composition $C_s$ is simply\textsuperscript{1}

$$A = C_s \left( \frac{1}{k} - 1 \right) \frac{D_I}{v}. \quad (3)$$

From this equation, we find that for a fixed $C_s$, the same surface peak area will result by using either $k_1$, $D_I$, and $v_1$ or $k_2$, $D_2$, and $v_2$, provided that

$$k_2 = k_1 \left( \frac{D_2}{D_1} \right) \left( \frac{v_1}{v_2} \right) \left[ 1 + \left( \frac{D_2}{D_1} \right) \left( \frac{v_1}{v_2} \right) - 1 \right] k_1^{-1}. \quad (4)$$

Applying this equation to the data of Aziz,\textsuperscript{19} their $k$'s determined with a $D_I$ of $4 \times 10^{-4}$ cm$^2$/s can be approximately converted to $k$'s (at the same velocity) using the $D_I$ determined in this work. That is, their reported $k$'s of 0.78, 0.82, and 0.90 correspond to values of 0.69, 0.74, and 0.85 (see Fig. 4) for our $D_I$ of $2.5 \times 10^{-4}$ cm$^2$/s. With this correction, those earlier measurements are almost identical to results reported in this work. However, the 0.70 value reported by Reitano et al.\textsuperscript{9} with $D_I = 3.0 \times 10^{-4}$ cm$^2$/s is reduced only to a $k$ of 0.66 for our liquid diffusivity. While this brings it closer to our observed $k(v)$ curve, a significant difference is still apparent.

### B. Equilibrium partition coefficient

In previous sections, a value of 0.40 has been used for the equilibrium partition coefficient; this is higher than the values of 0.33 or 0.3 typically used.\textsuperscript{1,19} There is considerable uncertainty in $k_e$ with published values ranging from 0.25 to 0.45. The primary reference for a “direct” measurement of the phase diagram is the 1939 paper by Stöhr and Klemm,\textsuperscript{26} from which $k_e$ values of 0.25 at 10% Ge and 0.32 at 20% Ge may be extracted. However, their phase diagram is inconsistent with a general relation valid for all solutions in the dilute limit.\textsuperscript{1} The equilibrium partition coefficient in the dilute limit $k_0$ is related to the liquidus slope $m$, the solvent's enthalpy of fusion $\Delta H_f$, and the solvent's fusion temperature $T_f$ by

$$k_0 = 1 - \frac{m \Delta H_f}{R T_f}. \quad (5)$$

Taking a liquidus slope of $-185$ K at 10% Ge from Stöhr and Klemm’s GeSi phase diagram, a value of 0.60 is calculated for $k_0$, which is very different than their reported $k_e$ of 0.25. This discrepancy indicates the care that must be taken in choosing the value for $k_e$.

The GeSi phase diagram was reviewed by Olesinski and Abbaschian\textsuperscript{27} in 1984. In their review, they used free energy of fusion functions for the pure components and varied regular solution parameters to best fit the original Stöhr–Klemm data plus a few points measured in 1955 from the Ge rich side of the phase diagram. Their calculated phase diagram with this regular solution approximation matched experimental points well using liquid and solid interaction parameters, $\Omega_s$ and $\Omega_d$, of 6.50 and 3.50 kJ/mole, respectively. Our calculations with these parameters give a $k_0$ of 0.44, with the equilibrium partition coefficient not changing appreciably until the Ge composition in the liquid exceeds about 60%. This is very similar to the experimental results seen by Romanenko and Smirnov.\textsuperscript{25} They observed a nearly constant $k_e$ for Ge of about 0.45 with a scatter of about 0.05 over the composition range from 10 to about 60% Ge in the melt.

In light of the uncertainty concerning the Stöhr–Klemm data on the silicon rich side of the phase diagram and the above discussion, the assumption of $k_e = 0.4$ used in our analysis seems reasonable. Moreover, if we assume the validity of the dilute CGM equation in describing $k(v)$, the extrapolation of our data to zero velocity provides an independent measurement of $k_e$. This $k_e$ value of 0.45 ±0.02 is consistent with the $k_0$ of 0.44 calculated using published thermodynamic parameters.\textsuperscript{27} Extrapolations to $k_e$ for other models are given in Table I. All models except the Stepwise Growth Model give $k_e$'s between 0.45 and 0.48. The anomalous $k_e$ for the CGM is not surprising because this model poorly fits both our $k(v)$ data (high $\chi^2$) and data for Bi in Si.\textsuperscript{3}

Finally, we note that the extrapolation of $k(v)$ to a reasonable $k_e$ provides a good check on, and further verification of, the overall validity of our measured $k$ vs $v$ characteristic.

### C. Models for partitioning

Many models have been proposed for the dependence of $k$ on interface velocity. Table I presents fitting results for some of these models to the measured $k(v)$ data shown in Fig. 4. These fits were weighted by the error bars shown in the figure, and the reduced chi-squared values $\chi^2_r$ given in the table provide a measure of the “goodness” of the fit. Except for the nondilute CGM, fits for all models were done with both a presumed $k_0$ of 0.40 and with $k_e$ allowed to vary.

The fitting procedure for the nondilute CGM\textsuperscript{2} was considerably more involved, largely because an estimate for the interfacial temperature was required. The nondilute CGM has expressions for both the partitioning and velocity “interfacial response functions,” and the velocity expression comes in two versions: “with solute drag” and “without solute drag.” The theory without solute drag has recently been shown by Kittl et al.\textsuperscript{3} to model well the interface kinetics in
the Si/As system, whereas all tested models incorporating solute drag failed. Thus, the version of the CGM without solute drag was chosen here. As required by the Henrian approximation to the nondilute CGM, \( k_e(T) \) for both Ge and Si were obtained from the phase diagram calculations assuming regular solutions described in Sec. IVB. Using the velocity expression of the CGM without solute drag, the interface temperature was calculated from the composition, the measured \( k_e \), and the measured \( v \) for each laser-irradiated sample. Then, using this calculated \( T \), the composition, and the measured \( v \), a value for \( k_e \) was computed from Eq. (1) and compared to the experimental \( k_e \). The diffusive speed was varied in Eq. (1) to best match the measured \( k_e \) vs \( v \) data, resulting in a value of \( 2.49 \pm 0.18 \) m/s.

From Table I, we find that the nondilute CGM, the dilute CGM, and the Kurz–Fisher model all give reasonable fits when only a single parameter (\( u_D \)) is allowed to vary. When \( k_e \) is also varied, all models except SGM provide fits of CGM, and the Kurz-Fisher model all give reasonable fits from the small differences in \( x_e \), noted between models. First, \( k_e \) is not truly a fitting parameter in that it can be measured independently. Second, the Ge/Si system is less than ideal for distinguishing among models for \( k_e \); the rather small variation in \( k_e \) over the measured velocity range, coupled with the uncertainty in each point for \( k_e \) (including its equilibrium value) makes statistically significant tests difficult.

**D. Relation of \( v_D \) to \( k_e \)**

While no experimental correlation has been found between \( v_D \) and either the solute diffusivity in the solid or in the liquid, a negative correlation has been observed between \( v_D \) and \( k_e \).\(^\text{9,28}\) Here, \( v_D \) may be regarded as either a fitting parameter in the CGM equation for \( k \) or simply the velocity at which \( k \) is halfway between its equilibrium value and unity. Physically, the correlation suggests that the more strongly the solute atoms "want" to be in the liquid (lower \( k_e \)), the faster one must solidify to trap them in the solid (higher \( v_D \)). In Fig. 5, our \((k_e,v_D)\) point is plotted with other available data (see Table II) for solutes in rapidly solidified (100) oriented Si. A least squares fit to the data gives \( \log(v_D) = -0.30 - 0.61 \log(k_e) \), which can be used for a rough estimate of \( v_D \) for a solute in Si in the absence of experimental data. From the correlation, \( v_D \) for Ge is above the trend based on its \( k_e \) of about 0.45. While Fig. 5 indicates the likely existence of a negative correlation between \( v_D \) and \( k_e \), a definitive model for a priori predictions, of \( v_D \) remains elusive.

**E. Relation to heteroepitaxy experiments**

The segregation seen in this work is consistent with that observed in pulsed laser crystallization studies of Ge\(_{1-x}\)Si\(_x\) on Si.\(^{11-14,16}\) While none of the references give regrowth velocities, an approximate velocity can be calculated from the melt durations reported by Lombardo et al.\(^{15,16}\) Typical melt depths of 60 nm had \( \approx 50 \) ns melt durations, and the laser pulse duration is given as \( \approx 30 \) ns. Since approximately the first third of the pulse is required to induce melting and solidification commences at the end of the pulse, the average regrowth velocity can be estimated as \( \frac{(50 - 30 + 10) \text{ ns}}{2} \approx 2 \text{ m/s}. \) At this velocity, the dilute Continuous Growth Model [Eq. (2)] with \( k_e = 0.45 \) and \( v_D = 2.7 \) m/s gives a \( k \) of 0.68, slightly less than halfway to complete trapping. Although this is only an estimate and actual velocities will depend upon specific conditions, substantial segregation is to be expected during heteroepitaxial growth of Ge\(_{1-x}\)Si\(_x\).

Pulsed laser heteroepitaxy experiments are typically done with higher Ge concentrations (\( \leq 20\% \)) than considered in this work (\( x \approx 0.10 \)). Using the nondilute CGM with the measured \( v_D \) of 2.49 m/s, our \( k_e \) vs \( v \) data can be extrapolated to higher Ge concentrations. Calculations of Ge partitioning behavior in (100) oriented Ge\(_{1-x}\)Si\(_x\) for Ge concentrations in the solid ranging from 0% to 40% are shown in Fig. 6. Between 0% and 20% Ge, the maximum change in \( k \) at any velocity is less than 0.02, which is much smaller than the error bars reported in Fig. 4. This indicates that the dilute CGM is a good approximation to nondilute theory for Ge compositions up to approximately 20%. At higher Ge con-

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**TABLE II. Summary of CGM fitting for solutes in Si(100).**

<table>
<thead>
<tr>
<th>Solute</th>
<th>( k_e )</th>
<th>( v_D ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(^{11})</td>
<td>0.11</td>
<td>0.40</td>
</tr>
<tr>
<td>Bi(^{12})</td>
<td>0.0007</td>
<td>32</td>
</tr>
<tr>
<td>Gb(^{13})</td>
<td>0.008</td>
<td>41</td>
</tr>
<tr>
<td>In(^{14})</td>
<td>0.0043</td>
<td>74</td>
</tr>
<tr>
<td>Sb(^{15})</td>
<td>0.023</td>
<td>0.97</td>
</tr>
<tr>
<td>Sn(^{16})</td>
<td>0.016</td>
<td>17</td>
</tr>
</tbody>
</table>

\(^{11}\)Dilute CGM fit to data in Ref. 6 using \( k_e \) estimated from R. W. Olesinski and G. J. Abbaschian, Hull. Alloy Phase Diagr. 6, 254 (1985).

\(^{12}\)Ref. 3.

\(^{13}\)CGM fitting to the ASGM parameters found in Ref. 9.

\(^{14}\)Nondilute CGM fit to data in this work. Listed value for \( k_e \) corresponds to dilute limit \( k_0 \).

\(^{15}\)Ref. 4.

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FIG. 5. Log–log plot of \( k_e \) vs \( v_D \) for impurities in (100) oriented crystal Si.

At \( u = u_0 \), \( k_e \) is halfway between its equilibrium value and unity.
centrations, deviations from the dilute limit become more apparent.

It is important to consider the validity of extending these measurements using SOI and SOS substrates (with relatively high defect densities) to heteroepitaxial growth on essentially perfect Si(100) substrates. Possible differences due to Si seed material for regrowth are addressed by some extent by using both SOS and SOI substrates, for which the crystal quality of the Si layers differ. (Si substrates were not used because direct measurements of melt history via TCM are not possible.) To within the scatter of the data in Fig. 4, no dependence on seed material was observed in the $k$ vs $v$ data. Also, three different sources of Ge were used in this work: a $^{76}$Ge implant (clean), MBE grown Ge$_{x}$Si$_{1-x}$ (clean), and e-beam Ge$_{x}$Si$_{1-x}$ grown in a multi-user chamber in which evaporants can change on a daily basis (some contamination likely). Still, no significant differences were seen in the $k$ vs $v$ data.

A second concern is the effect of stress on equilibrium partitioning. To examine this, the phase diagram for strained, heteroepitaxial Ge$_{x}$Si$_{1-x}$ on Si(100) was calculated. For these calculations, the strain energy due to heteroepitaxy, $E = [c_{11}(2\epsilon_{1}^{2} + \epsilon_{2}^{2}) + 2c_{12}(\epsilon_{1}^{2} + 2\epsilon_{1}\epsilon_{2})]$, was added to the free energy of the solid where the elastic constants $c_{ij}$ were obtained from Horstma and Bartels$^{29}$ and $\epsilon_{1}$ and $\epsilon_{2}$ are the parallel and perpendicular strain components in the GeSi film. While $k_{s}$ did decrease for strained Ge$_{x}$Si$_{1-x}$, as compared to unstrained material, the decrease was comparatively small. For example, less than a 9% drop in the value of $k_{s}$ was found at $X_{s}$,Ge=0.25, with lesser effects at lower compositions. For more details on these calculations, consult Appendix A of Ref. 10.

Strain may additionally influence $k$ through its potential effect on interface morphology. For a planar interface, strain can be destabilizing because interface roughening allows for partial relaxation in the peaks of the roughened regions.$^{30-32}$ Such roughening has been observed for both solid phase epitaxy$^{33,34}$ and molecular beam epitaxy$^{35,36}$ of GeSi alloys on Si. There is also some evidence of roughening during solidification of SiGe alloys.$^{10}$ However, there is currently no detailed theoretical or experimental work characterizing the role of strain on interface morphology during rapid solidification, and it is not yet possible to estimate the degree of roughening, if any, that occurs during our laser-induced rapid solidification experiments.

In the event of substantial interface roughening, a slight re-interpretation of our analysis may be necessary because the solute diffusion and partitioning simulations used to determine $k$ assumed planar interfaces. However, even for a rough interface, our reported values for $k$ still do characterize the net redistribution of Ge resulting from rapid solidification, regardless of the nature of the interface. Thus for calculations of post-solidification profiles resulting from laser melting, the $k$’s reported here are the relevant values.

**F. Discrepancy with the data of Reitano et al.**

There is substantial discrepancy between our $k$ vs $v$ characteristic and the ($k=0.70,v=0.23$ m/s) point of Reitano et al.$^{9}$ We reviewed Reitano’s raw experimental data$^{37}$ in an attempt to resolve this difference. The RBS detector in the original spectrum was recalibrated using the method discussed in Sec. II, resulting in a slightly different calibration. Also, there was some uncertainty in the original melt profile. Because direct measurements of melt history via TCM$^{22}$ are not possible with single-crystal Si substrates, Reitano et al. estimated the melt profile by matching numerical heat flow calculations to the measured melt duration. The significant CO$_2$ laser preheating for their Ge-implanted Si sample resulted in a less reliable melt profile estimate due to the less well-known Si properties at high temperatures used in calculations. We determined the melt history in a different fashion. Heat flow calculations were used to generate the shape of the melt profile. Simulations of liquid phase diffusion and interfacial partitioning were then carried out with Reitano’s measured melt duration and our $D_{L}$ of 2.3X$10^{-4}$ cm$^2$/s. Melt depth and $v_{D}$ were varied to best fit the experimental post-melt Ge concentration profile. From these simulations, a $k$ of 0.63 was obtained for the regrowth velocity of 0.34 m/s. This can be compared to the CGM fit to our data ($k_{s}$=0.45, $v_{D}$=2.74 m/s), which yields a $k$ of 0.51 at 0.34 m/s.

While the difference between $k$’s of 0.63 and 0.51 remains significant, it is no longer irreconcilable. The necessity of estimating the melt profile for Reitano’s work could, in large part, account for the discrepancy. Additionally, as noted in Sec. IV E, there may be small effects due to differences between growth from a Si(100) wafer and growth from SOS and SOI materials.

**V. CONCLUSIONS**

We report the most detailed study to date of nonequilibrium partitioning in Ge$_{x}$Si$_{1-x}$ alloys. Three different sources for Ge, compositions up to 10%, and a number of sample types were employed in this study. To within the resolution of these experiments, our results can be summarized by a liquid diffusivity for Ge of 2.5X$10^{-4}$ cm$^2$/s and a $k(v)$ given by the dilute CGM with a diffusive speed of 2.7+0.5 m/s and a $k_{s}$ of 0.45+0.02. These data are consistent with previous measurements of $k(v)$, and the extrapolation...
lation of $k(v)$ to zero velocity is nearly identical to $k_e$ estimated from thermodynamic calculations. To our knowledge, this is the first time partitioning measurements away from local equilibrium conditions have been extrapolated to zero velocity for a determination of $k_e$. For the nondilute CGM, a $v_D$ of $2.5 \pm 0.2$ m/s was obtained from these measurements and the thermodynamic data of Olesinski and Abbaschian \(^{(27)}\) ($k_0 = 0.44$).

This work also addresses the anomalous behavior for Ge in Si seen by Reitano et al. \(^{(9)}\) With respect to the CGM, Ge in Si(100) is well-behaved, and the discrepancy between our results and those in Ref. 9 is likely due to uncertainties in melt profiles for CO$_2$ laser preheated samples in the absence of direct melt history measurements.

Finally, these experiments confirm and quantify the Ge segregation seen by a number of investigators during pulsed laser assisted heteroeutectic growth of Ge$_x$Si$_{1-x}$ alloys. \(^{(11-16)}\) Both Leamy et al. \(^{(11)}\) and Lombardo et al. \(^{(16)}\) attributed defective growth at high Ge concentrations to segregation-driven interface instabilities. \(^{(38)}\) With the $D_v$ and $k(v)$ presented here, numerical calculations of interfacial stability using various stability models have been undertaken. The results of these calculations, along with limitations and extensions of current stability theories are discussed separately. \(^{(10,36,40)}\)

**ACKNOWLEDGMENTS**

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