Solute Trapping: Comparison of Theory with Experiment

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The dependence of the nonequilibrium partition coefficient k of Bi in Si upon solidification velocity v has been measured with sufficient accuracy to distinguish between proposed solute-trapping mechanisms. For the range of measured velocities, 2–14 m/s, we observe a much more gradual increase in k with increasing v than those previously reported and no evidence for a "saturation" effect, i.e., $dk/dv \rightarrow 0$ at $k < 1$. The continuous-growth model of Aziz fits the data quite well; the Aziz stepwise-growth model and the two-level Baker model yield values of dk/dv that are too high.

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The departure from local compositional equilibrium at a rapidly moving solid-liquid interface has been demonstrated for splat-quenched metallic alloys[1] and for rapid solidification following pulsed-laser melting of doped semiconductors.[2,3] When the partition coefficient k, defined by the ratio between the impurity concentration in the growing solid and that in the liquid at the interface, departs from its equilibrium value k_e, defined by the ratio of the solidus and liquidus concentrations on the phase diagram, it can often be shown that the impurity has actually undergone an increase in chemical potential upon solidification.[1,4] This phenomenon is termed "solute trapping." A number of models[5-14] are in qualitative agreement with the existing data, showing the partition coefficient increasing from its equlibrium value and approaching unity as the interface velocity v increases.

The pioneering work of White and co-workers[2,15] and Baeri and co-workers[3,16] showed that k in Si can in fact increase several orders of magnitude above k_e at high interface speeds and demonstrated the velocity dependence of k by varying the laser and substrate parameters to cover a range of regrowth velocities. Compared in detail, however, the results of the two groups were contradictory in some cases. Certain studies showed an effect termed "saturation," where $dk/dv \rightarrow 0$ at some value of $k < 1$. This effect was reported for Bi,[16] In,[17] and Sb[18] in Si. In a separate study of Bi in Si, however, the effect was not observed.[15] This saturation phenomenon is intriguing because it cannot be explained by any simple model; if correct, it indicates that more complicated solute-trapping models[8,13,19] are necessary.

The present study was undertaken to examine the saturation phenomenon in detail and to determine whether any of the existing models could yield quantitative agreement. The data collection and analysis procedures were improved in two important ways over previous studies. First, we used the transient-conductance technique to measure the interface velocity directly.[20] This approach eliminated many of the errors that arose in the previous studies in which v was estimated from heat-flow calculations. Uncertainties in the measured laser energy and pulse duration, and in the optical and thermophysical parameters of the crystal, the liquid, and especially the amorphous phase of Si (which were not well known at the time) created large uncertainties in the velocity and melt duration in previous studies. Second, our current numerical simulations use the measured melt histories and as-implanted impurity distributions, rather than approximating v as infinite during melting and constant during regrowth and approximating the as-implanted impurity profile as a Gaussian. While these errors were not significant for the purpose of the original work, they create errors in the analysis of k that are unacceptable if one desires to distinguish quantitatively between qualitatively similar models.

Wafers of 0.5-μm-thick Si(100) on sapphire were patterned for transient-conductance measurements[20] and implanted with 100-keV $^{209}\mathrm{Bi}^{++}$ to a dose of $5 \times 10^{14}/\mathrm{cm}^2$. The dose rate was 3 $\mu\mathrm{A/cm}^2$ and the samples were held at $\sim 250\,°\mathrm{C}$ during implantation. Ion channeling measurements showed a resulting amorphous surface layer 80 nm thick. The samples were melted by use of a pulsed ruby laser ($\lambda = 0.69$ μm) with a pulse duration of 30 ns or 3 ns FWHM and pulse energy densities between 1.16 and 0.56 J/cm^2 to yield solidification velocities between 2 and 14 m/sec. The time evolution of the melt depth was measured with $\sim$1-ns time resolution with the transient-conductance technique. In all cases the melt front penetrated through the amorphous layer but did not reach the sapphire substrate. Initial and final Bi profiles were determined by Rutherford backscattering spectroscopy (RBS) carried out in glancing-angle geometry.

Analysis of the partition coefficient was performed by numerical simulation with a finite-element solution to the diffusion equation,[21] using the measured as-implanted profile and the measured melt depth as a function of time for each sample. Impurity diffusion was assumed to occur in the liquid phase but neglected in the solid phase. During solidification a fraction k of the impurity in the liquid at the interface was incorporated into the crystal. The bulk liquid-phase diffusivity D_L and the partition coefficient during solidification k were allowed to vary to fit the measured Bi profiles. Impurity profiles predicted by the various simulations were convoluted with the measured detector resolution of 19 keV, and comparisons with the measured Bi profiles yielded unique values for both D_L and k.

A comparison of simulations to our RBS data for a sample with a relatively slow regrowth speed of 3.2 m/s is shown in Fig. 1, illustrating the sensitivity of our analysis. The solid and broken curves result from simulations with $k=0.07$ and 0.12, respectively, and $D_L=2\times10^{-4}$ cm^2/s. They bracket the best-fit value of $k=0.10$. If we choose D_L to be 1×10^{-4} cm^2/s, the simulated profiles do not penetrate far enough into the bulk to match the data for any value of k. Likewise, if D_L is chosen to be 3×10^{-4} cm^2/s the simulated profiles penetrate too deeply into the bulk. Most of the Bi in this sample was zone refined to the surface and appears as a large surface peak that goes off scale. The area under the measured surface peak does indeed fall between the areas in the two simulations. Since the total Bi content is the same in the simulations and in the measurements, we guaranteed that the areas of the simulated and measured surface peaks match by matching the areas of the profiles beneath the surface.

Higher-velocity results are shown in Fig. 2. Again, a liquid-phase diffusivity of 2×10^{-4} cm^2/s is necessary to reproduce the observed broadening of the Bi profile. The solid and broken curves result from simulations at $k=0.35$ and 0.20, respectively. The former value predicts too little accumulation of zone-refined Bi at the free surface whereas the latter simulation predicts too much. The best-fit value was taken to be 0.28.

The results of analysis of a number of samples, along with predictions of three simple solute-trapping models, are shown in Fig. 3. In the stepwise-growth model of Aziz,[11] in which diffusionless crystallization of a monolayer and solute-solvent redistribution alternate in time, the partition coefficient is given by $k=k_e+(1-k_e)\exp(-1/\beta)$. The dimensionless speed β is given by v/v_D, where the diffusive speed v_D is the ratio of the interface diffusion coefficient to the interface width. v_D is the only free parameter in the three models considered; it was chosen in each case to yield the best overall fit to the data. In the dilute-solution limit of the continuous-growth model of Aziz,[12] expected to apply if the increase in solute potential occurs simultaneously with a steady-state advance of the interface, the partition coefficient is given by $k=(\beta+k_e)/(\beta+1)$. In the two-level Baker model,[8,11,22] in which the impurity is treated as diffusing in a continuum down a steep energy gradient at the interface,

$$k=\{\beta+\ln k_e\}/\{\beta+[(1/k_e)(\ln k_e)\exp(-\beta)]\}.$$

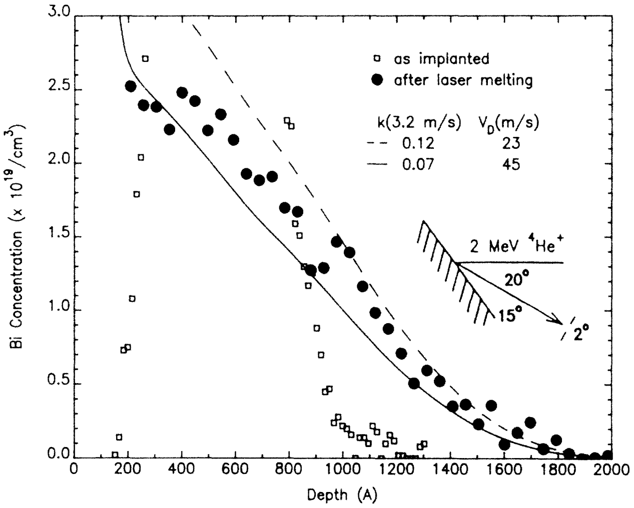

FIG. 1. Partitioning of Bi in Si at 3.2 m/s. Specimen irradiated with 0.94-J/cm^2, 30-ns pulse. Maximum melt depth 250 nm. Bi depth profiles before and after pulsed laser melting taken in RBS scattering geometry shown. Simulations with $D_L=2\times10^{-4}$ cm^2/s.

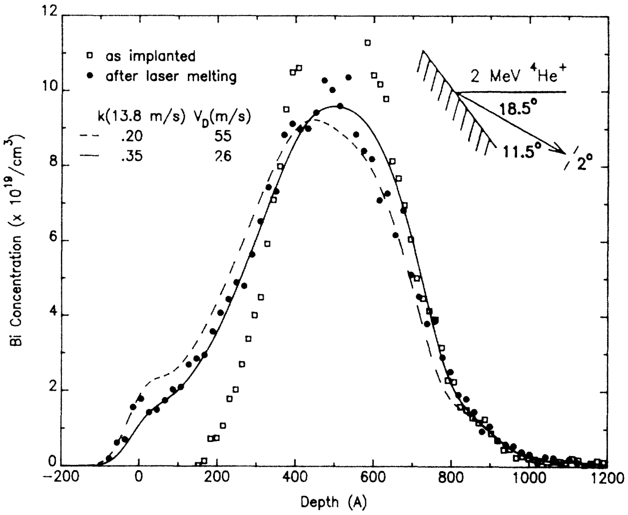

FIG. 2. Partitioning of Bi in Si at 14 m/s. Specimen irradiated with a 0.56-J/cm^2, 3-ns pulse. Maximum melt depth 80 nm. Bi depth profile after pulsed laser melting taken in RBS scattering geometry shown. As-implanted profile taken with geometry shown in Fig. 1. Simulations with $D_L=2\times10^{-4}$ cm^2/s.

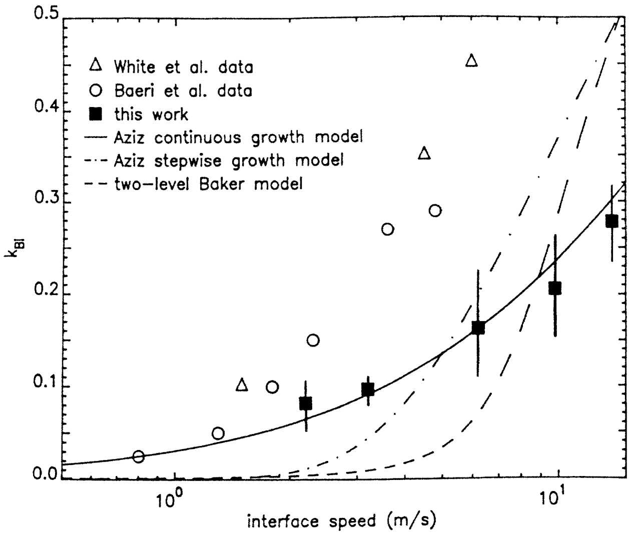

FIG. 3. Dependence of partition coefficient on velocity. Triangles and circles: velocity estimated from heat-flow calculations. Squares: velocity measured by transient conductance. Continuous-growth model: $v_D = 32$ m/s. Stepwise-growth model: $v_D = 10$ m/s. Baker model: $v_D = 1$ m/s.

Other solute-trapping models were not considered here. One model due to Jackson *et al.*[10] produces a $k(v)$ curve similar to that of the continuous-growth model, but has been rejected because it fails to account for solute trapping on both ends of a phase diagram.[23] Other models that involve complex computer calculations[9,13] have not been compared with our results.

For all three equations above, v appears only as the ratio v/v_D. Thus, in a plot of k vs $\log v$ (Fig. 3), a change in v_D produces only a rigid horizontal shift of the curves, with no change in slope. For the present data, the stepwise-growth model and the two-level Baker model produce curves that rise too steeply. These models yield a partition coefficient that is much too low at 3.2 m/s and much too high at 14 m/s. The continuous-growth model, on the other hand, fits the present data quite well with a diffusive speed of 32 m/s. Note that the interface diffusion coefficient of 10^{-4} cm^2/s, obtained by multiplying v_D by the (111) layer spacing of 3.1 Å, is close to the value we measure for D_L.

Data from the original work of Baeri *et al.*[16] and of White *et al.*[15] are also shown in Fig. 3. While sufficient to establish that k increases far beyond k_e as v increases, their data are not accurate enough to allow definite conclusions regarding appropriate models or the presence of "saturation." Note that there is no evidence in our data for the saturation effect.[24]

By combining transient-conductance and glancing-angle RBS measurements, nonequilibrium partition coefficients have been determined with much greater accuracy than previously possible. Partitioning of Bi in (100)Si for interface speeds between 2 and 14 m/s agrees well with the Aziz continuous-growth model. This result casts doubts on the existence of a saturation of the partition coefficient at values less than unity. It supports a description of solute trapping with atomic fluxes that are steady state, rather than oscillatory with the period of a crystal monolayer.

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[24]After discussions with the authors of the earlier work, it appears that the main source of the disagreement is the use in the original heat-flow calculations of an assumed value for the thermal conductivity of amorphous Si that is much greater than measurements [T. Papa, F. Scudieri, M. Marinelli, U. Zammit, and G. Cembali, J. Phys. (Paris), Colloq. **44**, C5-73 (1983)] eventually indicated.