International Journal of Thermophysics, Vol. 28, No. 4, August 2007 (© 2007)
DOI: 10.1007/s10765-007-0205-z

New Determinations of Diffusion Coefficients for Various Dopants in Liquid Silicon

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Received May 11, 2006

The objective of this article is to propose new determinations of the diffusion coefficients of various dopants in liquid silicon. The approach of this work is based on an analysis of the effective segregation coefficients obtained by Kodera in Czochralski growth of silicon-based alloys. However, it will be shown that the solidification model used by Kodera presents some serious deficiencies as it does not account for (i) the dependence of the solute boundary layer thickness on the interface velocity and (ii) the effect of density change upon freezing. In addition, the values of the thermophysical parameters used by Kodera can be questioned in view of recently published data. The approach proposed in the present work can be used to provide a much sounder physical basis for the analysis of the data, but it should be stated that the uncertainty on the partition coefficients is such that a measurement technique based on solidification experiments cannot be expected to be very accurate. In this respect, the scatter of the data, hardly avoidable in Czochralski growth experiments, is also discussed. To put things on a quantitative basis, an error analysis is carried out to quantify the error bar attainable by such a measurement technique.

KEY WORDS: Czochralski growth; error analysis; liquid-phase solute diffusion coefficients; Si–Al system; Si–As system; Si–B system; Si–Ga system; Si–In system; Si–P system; Si–Sb system.

1. INTRODUCTION

In many instances, doped solid-state silicon is produced from a liquid-phase process. One can of course think of single crystal growth by the

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Czochralski or float zone methods with applications as substrates for the semiconductor industry [1], and of polycrystalline solidification of materials for applications in the photovoltaic solar cells business [2]. Laser processes, such as laser thermal processing [3,4], also feature the formation of a liquid phase in which the kinetics of solute transport are a very important issue.

Whatever the growth configuration, solute diffusion is a key issue in many aspects of the process; it controls species transport in the melt, and thus the distribution of the dopants and the purification of the impurities. Liquid-state diffusivity is also an important ingredient in the criteria governing the morphological stability of the solidification interface (planar to cellular and dendritic transitions), and the kinetics of nucleation and growth at the atomic scale.

Molten silicon is known to be an extremely reactive material, which makes the realization of dedicated solute diffusion coefficient measurements a very difficult task. As a consequence, solute diffusion coefficients have often been estimated from dopant segregation in solidification experiments (see, e.g., Refs. 5–7). Our opinion, as expressed in a former article [8], is that the interpretation of such indirect measurements is always questionable, but one should at least make the best of what is available.

The purpose of the present manuscript is to re-examine the diffusivity data obtained by Kodera [5] in his seminal work on solute segregation of various dopants (Al, As, B, Ga, In, P, Sb) in silicon Czochralski growth. In such experiments, a crystal growing in contact with the melt is slowly pulled upwards while being rotated to ensure radial symmetry of the thermal distribution. Apart from the resulting forced flow, the fluid is also subject to buoyancy and surface driven convection, as well as a possible crucible rotation, which makes the hydrodynamic problem very complex [1].

Nevertheless, segregation data in alloys are often interpreted assuming that forced convection dominates in the vicinity of the growing crystal, and it is thus possible to relate the effective partition coefficient to the solidification conditions, namely, the interface velocity and the rotation rate. Of particular interest for our present purposes is the fact that the diffusion coefficient of the dopant is an important factor in the fitting procedure, and can thus be estimated from segregation data. Our objective in the present work is to show that the model used by Kodera for the interpretation of his experimental data is not appropriate, and that a better physical picture (and thus hopefully more reliable data) can be proposed.

As in all indirect measurement techniques, a number of other thermophysical parameters are involved in the derivation of the diffusion coefficients. In the present case, these auxiliary variables are the solid- and liquid-state mass densities, fluid viscosity, and dopant equilibrium partition coefficients. Regarding viscosity, in the absence of available experimental data, Kodera used an estimate that now appears questionable. We shall discuss how recently published data can be considered sufficiently reliable for our present purposes. We shall see that this is also true of mass densities.

Such is not however the case for the partition coefficients, where it seems that no new experimental data have been published since the review of Trumbore [9] in 1960. Trumbore himself was very conscious of the accuracy of his data, which he estimated "never better than 10%." Since 1960, Trumbore's data has been used in a number of articles, including Kodera's, without being questioned. Nevertheless, as the partition coefficients represent key input in the solidification model, it appeared an interesting option to also carry out the fitting on both diffusion and partition coefficients. We shall see that such an approach allows further insights in the validity of the solidification model used.

We shall first review in Section 2 the solidification model applied to the case of Czochralski crystal growth, and outline the main differences with Kodera's approach. We shall then proceed in Section 3 to an analysis of Kodera's data in order to propose new estimates for the diffusion coefficients in molten silicon. We shall finally discuss in Section 4 the accuracy attainable by such an indirect measurement technique.

2. SOLIDIFICATION MODEL

The starting point of our analysis of segregation data is the solute mass conservation equation, that features the density of the liquid phase ρ_L, the solute concentration C_L and the solute mass flux $\mathbf{J}$:

$$\rho_L \partial C_L / \partial t + \nabla \cdot \mathbf{J} = 0 \tag{1}$$

where the symbol ∇ represents the "nabla" derivation operator. For the sake of consistency with the hydrodynamic part of the problem, C_L is expressed in mass fraction. The diffusive contribution to the mass flux is assumed to depend only on the composition gradient (i.e., all cross-coupling effects such as thermodiffusion or barodiffusion are assumed to be negligible), meaning that $\mathbf{J}$ can be written as

$$\mathbf{J} = -\rho_L D_L \nabla C_L + \rho_L C_L \mathbf{V} \tag{2}$$

where D_L and $\mathbf{V}$, respectively, represent the liquid-phase solute diffusion coefficient and the convective velocity in the fluid, the latter being a solution to the Navier–Stokes equation. Combining Eqs. (1) and (2), we find

$$\partial C_{\mathrm{L}}/\partial t + (\mathbf{V}\cdot\nabla)C_{\mathrm{L}} = D_{\mathrm{L}}\nabla^2 C_{\mathrm{L}} \tag{3}$$

The time dependence of Eq. (3) makes it difficult to handle, and the analysis of segregation data is generally (see, e.g., Refs. 10–12) carried out assuming that a quasi-steady state can be reached in a frame moving with the solid–liquid front in which the motion of the fluid toward the interface takes place at a rate $\mathbf{V}_{\mathrm{I}}^{\mathrm{L}}$, which leads to the addition of $(\mathbf{V}_{\mathrm{I}}^{\mathrm{L}}\cdot\nabla)C_{\mathrm{L}}$ term on the right-hand side (RHS) of Eq. (3). It is very important for our present purposes to keep in mind that $\mathbf{V}_{\mathrm{I}}^{\mathrm{L}}$ is not equal to the solidification rate prescribed by the experimenter $\mathbf{V}_{\mathrm{I}}^{\mathrm{S}}$ when, as is the case for silicon, the mass densities of the liquid ρ_{L} and the crystal ρ_{S} are significantly different. More precisely, $\mathbf{V}_{\mathrm{I}}^{\mathrm{L}}$ and $\mathbf{V}_{\mathrm{I}}^{\mathrm{S}}$ can be related from the condition of mass conservation at the interface:

$$\rho_{\mathrm{S}}\mathbf{V}_{\mathrm{I}}^{\mathrm{S}}\cdot\mathbf{n} = \rho_{\mathrm{L}}\mathbf{V}_{\mathrm{I}}^{\mathrm{L}}\cdot\mathbf{n} \tag{4}$$

with **n** standing as the unit vector normal to the interface protruding into the fluid. This fact was not taken into account by Kodera in his analysis of his experimental data, and we shall see that the circa 10% difference between ρ_{L} and ρ_{S} in silicon leads to significant differences in the diffusion coefficient estimates.

The fundamental feature governing segregation in crystal growth from the melt is the fact that all the solute present on the liquid side of the interface cannot generally be incorporated in the solid. Considering the low growth rates generally used, local thermodynamic equilibrium conditions are expected to prevail at the interface, and the partition coefficient k, defined as the ratio $k = C_{\mathrm{S}}^{\mathrm{I}}/C_{\mathrm{L}}^{\mathrm{I}}$, where $C_{\mathrm{S}}^{\mathrm{I}}$ and $C_{\mathrm{L}}^{\mathrm{I}}$, respectively, represent the compositions on the solid and liquid sides of the interface, can be estimated from phase-diagram information.

The mass balance at the growth front can be expressed stating that the excess solute present at the growth front is rejected by diffusion in the fluid. Under the assumption that the effect of solid-state diffusion can be neglected, mass conservation at the interface can be written as

$$\rho_{\mathrm{L}}(\mathbf{V}_{\mathrm{I}}^{\mathrm{L}}\cdot\mathbf{n})C_{\mathrm{L}}^{\mathrm{I}} = -\rho_{\mathrm{L}}D_{\mathrm{L}}(\partial C_{\mathrm{L}}/\partial n)_{\mathrm{I}} + \rho_{\mathrm{S}}(\mathbf{V}_{\mathrm{I}}^{\mathrm{S}}\cdot\mathbf{n})C_{\mathrm{S}}^{\mathrm{I}} \tag{5}$$

The assumption of negligible solid-state diffusion may appear rather drastic, but it is generally made in the crystal growth literature [10–12]. Even though there is no experimental data on the topic, it is believed that the diffusivity in the solid is at least two orders of magnitude smaller than in the liquid. In addition, the concentration gradients are also expected to be smaller in the solid. Unless one focuses on the study of short-range composition variations (the so-called solute striations), Eq. (5) can be safely used.

A further simplification is to suppose that the interface is planar, and that the concentration field only depends on the distance Z to the interface. This is of course a very drastic assumption, but radial segregation can often be neglected to a first approximation in Czochralski growth experiments. Besides, as is the case in Kodera's work, the experimental data are often of a one-dimensional nature, meaning that the information regarding the other dimensions is lost. In any case, the fundamental governing equation and boundary condition to be used for the interpretation of the segregation data can be written as

$$D_\mathrm{L}\mathrm{d}^2C_\mathrm{L}/\mathrm{d}Z^2+(V_\mathrm{I}^\mathrm{L}-W(Z))\mathrm{d}C_\mathrm{L}/\mathrm{d}Z=0 \tag{6}$$

$$-D_\mathrm{L}(\mathrm{d}C_\mathrm{L}/\mathrm{d}Z)_\mathrm{I}=V_\mathrm{I}^\mathrm{L}(1-k)C_\mathrm{L}^\mathrm{I} \tag{7}$$

where W is the Z-component of the fluid velocity. Equation (4) has been used in connection with Eq. (5) to derive the boundary condition, Eq. (7). To fully specify the problem, one may specify a far-field condition of the form,

$$C_\mathrm{L}\rightarrow C_\infty \text{ when } Z\rightarrow\infty \tag{8}$$

The system defined by Eqs. (6)–(8) was first solved by Burton et al. [10] in their pioneering work on solute segregation. However, it should be recalled that the determination of W is in principle a formidable task in Czochralski experiments: indeed, as mentioned earlier, motion in the melt is simultaneously driven by the imposed crystal rotation and the lateral temperature gradients that induce both bulk and surface driven (Marangoni) convection, and possibly by crucible rotation.

To a first order, however, the crystal rotation is the primary driving force: such was the approximation made by Burton et al. [10], who relied on an analytical solution derived by Cochran [13] for the case of an infinite solid rotating over an infinite bath, as input in the transport equation. Briefly speaking, the expression for W is given as

$$W(Z)=-0.51\omega^{3/2}\nu^{-1/2}Z^2 \tag{9}$$

where ω and ν represent, respectively, the crystal rotation rate and the kinematic viscosity of the melt. The minus sign in the above equation comes from the fact that the fluid motion is directed toward the growing interface. According to a number of experimental and modeling studies (see, e.g., the reviews in Refs. 14 and 15), this velocity field is probably correct at the moderate rotation rates (maximum 144 rpm) used in Kodera's experiments. However, it cannot be ruled out that an oscillatory component is superimposed on this steady field. We shall come back to this point in Section 4, since it could well be one of the main factors limiting the accuracy of the diffusion measurements. In any case, Burton et al. showed that the analytical solution to the problem defined by Eqs. (6)–(9) could be written as

$$[(C_{\mathrm{L}}^{\mathrm{I}} - C_{\infty})/(C_{\mathrm{L}}^{\mathrm{I}} - C_{\mathrm{S}}^{\mathrm{I}})] = \int_0^{\infty} \exp(-z - Bz^3)\mathrm{d}z \tag{10}$$

where $z = ZV_{\mathrm{I}}^{\mathrm{L}}/D_{\mathrm{L}}$. The dimensionless parameter B, which essentially represents a measure of the intensity of convective solute transport, is given as

$$B = 0.17(V_{\mathrm{I}}^{\mathrm{L}})^{-3}\omega^{3/2}\nu^{-1/2}D_{\mathrm{L}}^{2} \tag{11}$$

In the limiting case where $B >> 1$, the integral on the right-hand side of Eq. (10) can be expressed as

$$\int_0^{\infty} \exp(-z - Bz^3)\mathrm{d}z = 1.6V_{\mathrm{I}}^{\mathrm{L}}\omega^{-1/2}\nu^{1/6}D_{\mathrm{L}}^{-2/3} \tag{12}$$

In the general case, the integral on the RHS of Eq. (10) can be evaluated via numerical integration as a function of the parameter B. When $B \rightarrow 0$, one recovers the classical result obtained by Tiller et al. [16], namely, that the solute boundary layer thickness scales with $D_{\mathrm{L}}/V_{\mathrm{I}}^{\mathrm{L}}$.

In the same seminal work [10], Burton et al. proceeded to show that the segregation data could be analyzed with the help of a stagnant film model, whose thickness δ_{SF} could be defined "so that it yields the same dependence of the composition upon the growth parameters that is given by the exact solution" [10]. However, such a stagnant film model has no solid physical basis, as shown by Wilson [17] when she re-examined the segregation problem in Czochralski growth. In the same article, Wilson gave a proper definition of the solute boundary layer thickness:

$$\delta = -(C_{\mathrm{L}}^{\mathrm{I}} - C_{\infty})/(\mathrm{d}C_{\mathrm{L}}/\mathrm{d}Z)_{\mathrm{I}} \tag{13}$$

and proved that this δ could be fruitfully normalized with respect to its value in purely diffusive conditions, $\delta = D_{\mathrm{L}}/V_{\mathrm{I}}^{\mathrm{L}}$, to define a convecto-diffusive parameter Δ such that

$$\Delta = \delta V_{\mathrm{I}}^{\mathrm{L}}/D_{\mathrm{L}} = \int_0^{\infty} \exp(-z - Bz^3)\mathrm{d}z \tag{14}$$

The convecto-diffusive parameter thus defined scales from values close to zero in the convective regime limit, and reaches one for purely diffusive transport conditions. Wilson [17] also proceeded to show that the effective partition coefficient could be expressed as a function of Δ according to

$$k_{\mathrm{eff}} = k/(1 - (1 - k)\Delta) \tag{15}$$

The fundamental interest of Eq. (14) is that it allows to plot all Czochralski experiments on a master curve relating the process conditions, summed up in the parameter B, to the observed segregation, as measured by Δ, independently of the values of the partition coefficients of each solute. As we shall see later, such a feature will prove very useful when we discuss the statistical adequacy of the model.

The procedure followed by Kodera was to derive the value of the diffusion coefficient from the measurement of the effective partition coefficients pertaining to the various growth conditions. The stagnant film model of Burton et al. and the approximate Eq. (12) were used for the analysis of the data. However, as stated above, the stagnant film model has no sound physical basis. As for the assumption of convective mass transport (or equivalently $B >> 1$), it is often realistic in Czochralski growth, but it is not always the case: we will see that it is not correct at the highest growth velocities and/or lowest rotation rates.

On the other hand, the boundary layer concept introduced by Wilson was later found to be extremely useful for the analysis of segregation phenomena in crystal growth from the melt [12], as it can be used to account for both radial- and time-dependent segregation phenomena [18,19]. As a matter of fact, one of the objectives of this article is to show that it is better suited for the analysis of the data than the model initially used by Kodera.

It may appear that we spent too much time on the presentation of the segregation problem, but it is really at the basis of the diffusion coefficient determination, and we thought it necessary to emphasize all the assumptions made. To sum things up, our approach differs from the one used by Kodera in two main respects:

(i) Effective partition coefficient data will be analyzed in the frame of the physically sound boundary layer model of Eq. (15), taking into account the full dependence of the solute boundary layer thickness on interface velocity (Eq. (14)), as opposed to assuming as in Eq. (12) that solute transport proceeds only by convection.

(ii) We will account for the effect of density change upon freezing, as opposed to assuming that the V_I^L appearing in Eqs. (6) and (7) is merely equal to the pulling rate prescribed by the experimenter.

In addition, the use of the (B, Δ) representation makes it possible to gather all of Kodera's data on a single graph, and thus to implement a χ^2 test to judge the validity of the model used.

3. ANALYSIS OF EXPERIMENTAL DATA

To carry out the best fit procedures along the lines detailed in Section 2, we first have to extract the B and Δ parameters from Kodera's data, plotted as the ratio k_{eff}/k vs. pulling velocity $\mathbf{V}_I^S$ at a given rotation rate ω for each solute. The number of experiments carried out by Kodera ranges from eight in the case of Al and In to 15 for As, Ga, and P. We first derive V_I^L from V_I^S using Eq. (4), and B from Eq. (11) using a trial value for D_L. When the fitting is done solely on D_L, we get Δ from Eq. (15) using literature values for k. When the fitting is done on both D_L and k, an additional step is necessary: we first recalculate the absolute value of k_{eff} from the k values used by Kodera, and then get Δ from Eq. (15) using a trial value for k. The (B, Δ) couples once derived, the determination of the diffusion coefficient is based on the minimization of χ^2 defined as

$$\chi^2 = \sum_1^n (\Delta_i^{\text{exp}} - \Delta_i^{\text{th}})^2/\sigma_i^2 \qquad (16)$$

where Δ_i^{exp} and Δ_i^{th} represent, respectively, the experimentally measured and theoretically derived convecto-diffusive parameters and σ_i stands for an estimate of the variance of Δ_i^{exp}. As for n, it represents the number of data points (growth runs) for the solute considered. The assessment of σ_i is not an easy task, the values used as input to Eq. (16) were taken as

$$\sigma_i = 0.04 \qquad \text{when } \Delta_i^{\text{exp}} \leqslant 0.1 \qquad (17a)$$

$$\sigma_i = (0.4 - 0.3\Delta_i^{\text{exp}})\Delta_i^{\text{exp}} \qquad \text{when } \Delta_i^{\text{exp}} \geqslant 0.1 \qquad (17b)$$

As the segregation profiles are only weakly dependent on the value of Δ in the strongly convective transport regime relevant to Eq. (17a), an absolute uncertainty was selected in the low Δ_i^{exp} range. The increased sensitivity of the segregation profiles at higher values of Δ_i^{exp} is translated in Eq. (17b) assuming a decreasing relative uncertainty, which remains however always higher than 10%. We will come back to the discussion on the factors that

Table I. Thermophysical Parameters at Silicon Melting Temperature Used in the Present Fitting Procedures

ν (kinematic viscosity of molten silicon)	$3.5 \times 10^{-7}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$
ρ_{L} (mass density, liquid phase)	$2.55 \times 10^3\,\mathrm{kg} \cdot \mathrm{m}^{-3}$
ρ_{S} (mass density, solid phase)	$2.3 \times 10^3\,\mathrm{kg} \cdot \mathrm{m}^{-3}$
$\rho_{\mathrm{S}}/\rho_{\mathrm{L}}$ (mass density ratio)	0.9
k (equilibrium partition coefficient)	
Aluminum	0.002
Antimony	0.023
Arsenic	0.3
Boron	0.8
Gallium	0.008
Indium	0.0004
Phosphorus	0.35

intrinsically limit the accuracy of the estimation of Δ_i^{exp} from segregation curves.

At this point, it can indeed be argued that the choices made for σ_i are somewhat arbitrary, but, as will be shown in Section 4, they have fortunately a limited impact on the determination of the diffusion coefficients. The Δ_i^{th}'s were derived through numerical integration of Eq. (14), using the parameters listed in Table I for calculation of the B parameter. We will also come back in Section 4 to the sensitivity of the diffusion coefficient determinations on the values of the thermophysical parameters.

The raw results of the fitting procedure are summarized in Table II. The first thing to note is that the χ^2 values are fairly large, as compared to the number of independent variables. Let us recall that for a given solute with a number n of growth runs, the number of independent variables z should be taken as either $n-1$ or $n-2$, depending on whether the fitting is done solely on D or on both D and k. The requirements for a "moderately good fit," as defined by stating that χ^2 should be of the order of the number of independent variables [20], are not fulfilled in all cases.

However, it may be argued that the number of growth runs per solute is not statistically relevant. Besides, it should be acknowledged that the raw data is often quite scattered: for instance, in the case of phosphorus, Δ values of 0.04, 0.05, 0.10, 0.13, and 0.15 can be obtained from five experiments with identical growth conditions ($V_{\mathrm{I}}^{\mathrm{S}} = 20\,\mu\mathrm{m} \cdot \mathrm{s}^{-1}$, $\omega = 55\,\mathrm{rpm}$). With such scatter, no single curve can thus be expected to provide a nice fit through the data, but we will come back on the assessment of the validity of the physical model in the next section.

Table II. Raw Results of Fitting Procedure

Solute	n	Fit on D D ($\mathrm{m^2 \cdot s^{-1}}$)	χ^2	Fit on D and k D ($\mathrm{m^2 \cdot s^{-1}}$), k	χ^2
Aluminum	8	5.8×10^{-8}	1.2	6.8×10^{-8}, 2.03×10^{-3}	1
Antimony	13	1.4×10^{-8}	21.5	6.4×10^{-9}, 0.02	14
Arsenic	15	2.6×10^{-8}	10.6	1.9×10^{-8}, 0.29	8.1
Boron	11	1.5×10^{-8}	3.8	1.2×10^{-8},0.795	3.1
Gallium	15	4.4×10^{-8}	15.6	3.6×10^{-8}, 7.85×10^{-3}	15
Indium	8	6.1×10^{-8}	5.9	8.2×10^{-8}, 4.1×10^{-4}	5.2
Phosphorus	15	4.2×10^{-8}	17.1	2.3×10^{-8}, 0.332	13
Overall	85		75.7		59.4

The results of both fitting procedures are shown in Fig. 1 for the case of arsenic. As can be seen in Table II, arsenic should be taken as representative of an intermediate situation, when compared to solutes with much lower (Al, B) or much higher (Ga, P, Sb) χ^2's. Looking at Fig. 1, the difference in fit quality between both procedures may not be visually obvious, but we will see in the next section that the two-parameter fit should be given the preference. In any case, we now have to discuss whether meaningful diffusion coefficients, and associated error bars, can be deduced from the solidification experiments.

4. DISCUSSION AND ERROR ANALYSIS

4.1. Assessment of the Validity of the Physical Model and the Fitting Procedure

The first issue that needs to be addressed is that of the validity of the solidification model itself. As can be seen in Table II, the χ^2 for the cases of Ga, Sb, and P is rather large compared to the number of independent variables z, which indicates that the model may not be suitable for the analysis of the data [20]. As a result of the universal (B, Δ) representation used in the present article, this χ^2 vs. number of independent variables criterion can also be tested on a global scale. The data coming from the experiments on all solutes are gathered in Fig. 2, along with the $\Delta = f(B)$ master curve from the numerical integration of Eq. (14), and it can be seen that the trends are in agreement.

More specifically, when the fitting is done solely on D, the global χ^2, derived by summation of all the solute specific χ^2, is 75.7. The total number of independent variables Z being 78 ($N = 85$ individual experiments,

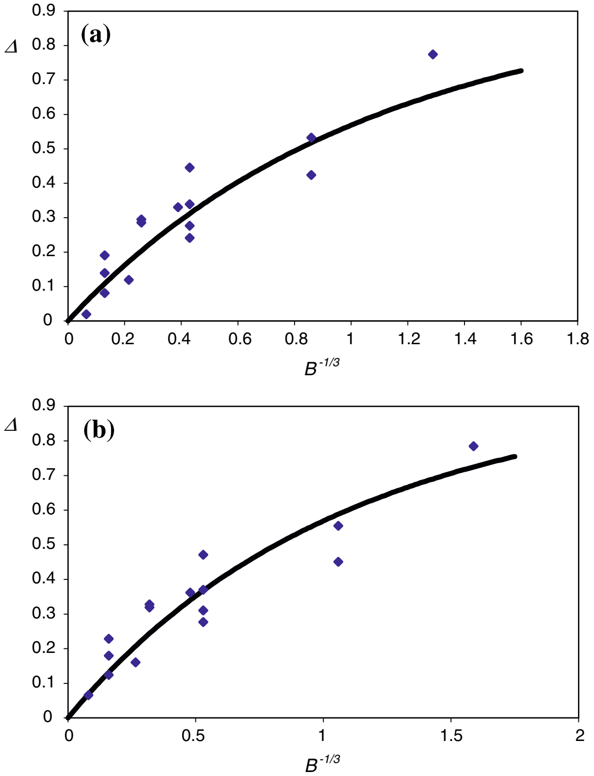

Fig. 1. Raw data and fits for arsenic; (a) fitting done only on D and (b) fitting done on both D and k.

bound by the seven best fit diffusion coefficient determinations for each solute), we find that χ^2 is slightly less than the number of independent variables, which fulfills the requirement for a "moderately good fit" [20]. In other words, and even though the scatter is large, the segregation model we used cannot be invalidated.

The odds for the validity of the model are even better when the fitting is done on both D and k: the global χ^2 is 59.4, whereas the total number of independent variables is now 71 (the $N = 85$ individual experiments, bound by the seven best fit diffusion coefficients and seven best fit partition coefficient determinations for each solute). An important point is that the values of the partition coefficients coming from the fit are in close agreement with values from the literature. In all cases (except for the case of antimony where it reaches 13%), the data are well within the 10%

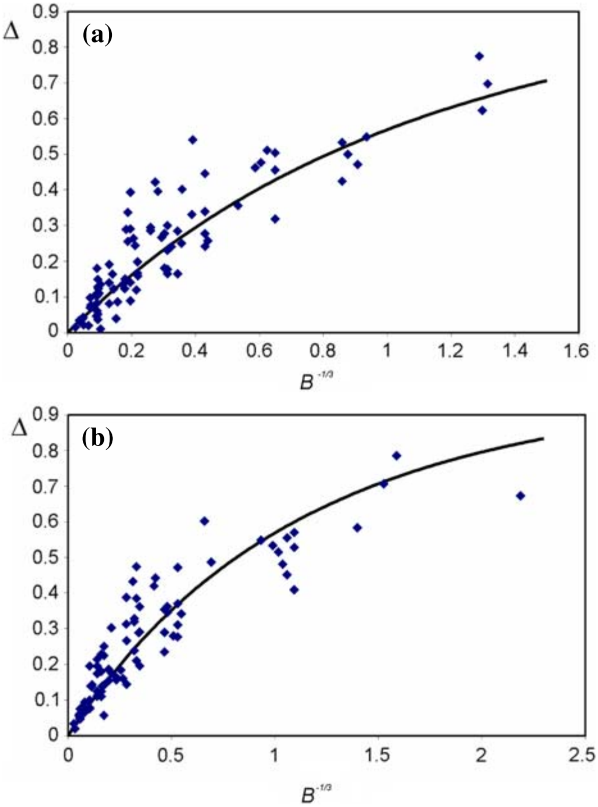

Fig. 2. Overall fits for both fitting procedures; (a) fitting done only on D and (b) fitting done on both D and k.

limit estimated by Trumbore [9] as the best possible uncertainty on partition coefficients. There is therefore no reason to believe that the partition coefficients should be taken exactly as they are given in the literature. However, since minute differences in k translate to significant variations on D, our opinion is that the results from the procedure that uses both D and k as fit variables are to be preferred.

Another issue is that the odds for a model attempting to fit a straight line to the data shown in Fig. 2 to be correct are significantly less, as can be inferred from the curvature of the data in the high $B^{-1/3}$ range. Any attempt to try to fit a straight line must necessarily lead to a much higher χ^2. For instance, when the fitting is done solely on D, we obtained a value of χ^2 above 92. We also analyzed the data using the stagnant film model of Burton et al. [10] in connection with Eq. (12), i.e., the procedure followed by Kodera, and found a χ^2 of 128. Keeping in mind that there are only $Z=78$ independent experiments in that case, such a χ^2 value makes it very unlikely for the model used by Kodera to be correct, which justifies the re-examination of the segregation data carried out in the present work.

Regarding the assessment of the validity of the fitting procedure, we also checked the impact of the rather arbitrary choice for σ_i made in Eqs. (17). We tried, for instance, to use fully absolute uncertainties (i.e., σ_i independent of $\Delta_i^{\exp}$) and proportional uncertainties (i.e., a constant ratio between σ_i and $\Delta_i^{\exp}$). With a mixed absolute-relative scheme as in Eq. (17), we also checked the effect of a modification of the numerical factors. The overall conclusion is that the diffusivity results are fairly sensitive to the choice of σ_i, discrepancies in excess of 20% with respect to the results obtained using Eqs. (17) being fairly common. While this may appear as a weakness likely to undermine the validity of the results, we shall see that the error bars on the diffusion coefficients always significantly exceed 20%, so that the fitting procedure may nevertheless be considered as sufficiently robust.

4.2. Thermophysical Parameters

Since the expression for the B parameter from Eq. (11) features the solid and liquid mass densities, as well as the kinematic viscosity, it can be expected that the values selected for these parameters will impact the determination of the diffusion coefficient. To start with, we checked that when these parameters are changed, the best fit value of the diffusion coefficient adjusts so as to keep B constant. Since B from Eq. (11) can be written as $B=0.17\ (\rho_S/\rho_L)^{-3}(V_I^S)^{-3}\,\omega^{3/2}\,\nu^{-1/2}\,D_L^2$, assuming a prescribed solidification velocity V_I^S (at least its average value) and the crystal rotation rate ω to be accurately known, it is possible to derive from the above relation the sensitivity of the diffusion coefficient to the other thermophysical parameters with the relation using the condition, $\Delta B/B=0$,

$$\Delta D/D=(3/2)[\Delta(\rho_S/\rho_L)/(\rho_S/\rho_L)]+(1/4)[\Delta\nu/\nu] \tag{18}$$

The “historical” reference sources for the values of the thermophysical parameters of silicon are the works of Glazov et al. [21] and Yaws et al. [22], a more recent synthesis being proposed by Kimura and Terashima [23]. If we turn to mass density, experiments have been attempted for liquid-phase measurements using Archimedian [24], as well as electrostatic [25] or electromagnetic [26] levitation techniques. The values listed in Ref. 26 range from $\rho_L=2.52\times10^3$ to $2.6\times10^3\,\mathrm{kg\cdot m^{-3}}$. As for ρ_S, the proposed values range between 2.29×10^3 and $2.33 \times 10^3\,\mathrm{kg \cdot m^{-3}}$. We decided to take $\rho_{\mathrm{L}} = 2.55 \times 10^3\,\mathrm{kg \cdot m^{-3}}$ and $\rho_{\mathrm{S}} = 2.3 \times 10^3\,\mathrm{kg \cdot m^{-3}}$, a choice consistent with $\rho_{\mathrm{S}}/\rho_{\mathrm{L}} = 0.9$. For both the solid and liquid cases, we estimated the error bar to be 1%, translating to a 2% uncertainty on $\rho_{\mathrm{S}}/\rho_{\mathrm{L}}$, and thus 3% on D from Eq. (21). For purposes of comparison, using the same equation, the neglect by Kodera of the effect of the density change upon solidification amounts to a shift of 10% in $\rho_{\mathrm{S}}/\rho_{\mathrm{L}}$, and thus to a bias of 15% in the diffusivity values.

Regarding the kinematic viscosity, Refs. 21 and 22 both propose a value $\nu = 3.5 \times 10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$. Using $\rho_{\mathrm{L}} = 2.55 \times 10^3\,\mathrm{kg \cdot m^{-3}}$, we get for the dynamic viscosity at the melting point $\eta = 8.9 \times 10^{-4}\,\mathrm{Pa \cdot s}$, in good agreement with the recent measurement carried out by Sasaki et al. [27] using the oscillating cup method. However, the data of Sasaki et al. exhibit a strong dependence of η on temperature, and we thus decided to associate a rather large error bar of 20% to the determination of ν. Fortunately, due to the 1/4 coefficient in Eq. (21), such a choice results only in a 5% uncertainty on D. It should be noted that Kodera used a very different value for the kinematic viscosity, namely, $\nu = 1.06 \times 10^{-6}\mathrm{m^2 \cdot s^{-1}}$, which was deduced from theoretical considerations in the absence of available experimental data. For purposes of comparison, even with the damping effect of the 1/4 coefficient in Eq. (21), Kodera's choice translates into a bias on the diffusivity values in excess of 30%.

4.3. Estimation of Error Bars

Our objective in this subsection is to finalize the estimation of the error bars that can be ascribed to the data from Kodera's experiments. In the following, no attempt will be made at a quantitative definition of the uncertainties: the indicated error bars should only be taken as an assessment of our opinion that the exact value is very likely to be found within the given interval. As the technique proposed in the present work is essentially a fit using a $\Delta = f(B)$ master curve, the error sources can be split into (i) those coming from the determination of Δ from the segregation curves and (ii) those related to the uncertainties in the values of mass density and kinematic viscosity that combine in the B parameter. In the general case, the implicit dependence of Δ on B does not allow for an analytic expression of the error bar as a function of the sources discussed above. For purposes of simplicity, we decided to use an additivity rule based on asymptotic Eq. (12) for estimation of the overall uncertainty:

$$\Delta D/D = (3/2)\sigma_{\Delta} + (3/2)[\Delta(\rho_{\mathrm{L}}/\rho_{\mathrm{S}})/(\rho_{\mathrm{L}}/\rho_{\mathrm{S}})] + (1/4)[\Delta\nu/\nu] \qquad (19)$$

Table III. Recommended Diffusivity Values, with Associated Error Bars, along with Initial Values from Kodera

Solute	D ($\mathrm{m^2 \cdot s^{-1}}$)	Error bar (%)	Kodera's data ($\mathrm{m^2 \cdot s^{-1}}$)
Aluminum	6.8×10^{-8}	44	7.0×10^{-8}
Antimony	6.4×10^{-9}	53	1.5×10^{-8}
Arsenic	1.9×10^{-8}	44	3.3×10^{-8}
Boron	1.2×10^{-8}	37	2.4×10^{-8}
Gallium	3.6×10^{-8}	83	4.8×10^{-8}
Indium	8.2×10^{-8}	62	6.9×10^{-8}
Phosphorus	2.3×10^{-8}	55	5.1×10^{-8}

The last issue to be discussed is the assignment of an uncertainty to the determination in Δ, denoted σ_Δ in the following, from the spread of the data around the $\Delta = f(B)$ master curve. To do so, we shall define σ_Δ for each solute as the standard deviation that yields a value $\chi^2 = z = n - 2$. This may look like a trick, but the validity of the model once checked from *a priori* physically sound choices for the standard deviations (see Eqs. (17)), what we are doing is simply setting the χ^2 to its mean value. The values obtained for σ_Δ are, respectively, 0.24 for Al, 0.3 for Sb, 0.24 for As, 0.19 for B, 0.51 for Ga, 0.35 for In, and 0.31 for P.

After stating in Section 3 that a relative uncertainty is not expected to be physically relevant in the low Δ range, it may appear surprising to re-introduce it at this point. Our opinion is that too much meaning should not be given to the values of σ_Δ listed above, and that σ_Δ should only be taken as an auxiliary variable allowing a measurement of the experimental spread of the effective partition coefficients and associated Δ values, and thus of the diffusivities for each solute.

To sum things up, the values for the diffusion coefficients and the associated uncertainties from Eq. (19) are listed in Table III along with the initial data of Kodera. Due to the large uncertainties, the data are found to overlap in all cases, except for the case of Sb. A similar conclusion can be drawn regarding the data of Table II. An interesting result is that the contribution of the uncertainty associated with the thermophysical parameters is rather limited (8% with the choices made in the present work), meaning that the spread of the Δ values around the master curve is by far the dominant error source.

4.4. Toward More Accurate Data

From the above conclusion, it appears that the key to a truly accurate determination of D would be a significant reduction of the uncertainties on Δ, i.e., of σ_Δ. In this respect, the Czochralski technique used by Kodera may not be the most suitable. It is in principle possible to select growth conditions such that the fluid velocity field, as given by Eq. (9), remains steady. However, its interactions with bulk and surface driven natural convection, as well as with the forced flow generated by crucible rotation, have a strong impact on the transition toward oscillatory behavior. In practice, and even in the vicinity of the interface, one should consider that an unsteady fluid velocity component is often superimposed on the steady field of Eq. (9).

In any case, this oscillatory melt convection will impact both directly and indirectly (through fluctuations on the growth rate) on the amount of incorporated solute, translating in turn in significant dispersions on Δ. In addition, from a technological standpoint, the control of the crystal pulling system is a very complex task. This results in unavoidable growth rate variations, which also translate in significant dispersions on Δ. Depending on their frequencies, the induced perturbations can be somewhat filtered by the solute boundary layer [18], but will in general result in a fairly high intrinsic uncertainty on the determination of Δ. Altogether, our opinion is that σ_Δ cannot be expected to be significantly less than 20%.

To fix this problem, the bottom seeded vertical Bridgman method, with its stabilizing thermal gradient is an *a priori* interesting option. However, it is quite difficult to control the horizontal temperature differences that act as a convective driving force. In this respect, the horizontal Bridgman configuration could be an interesting option. Nevertheless, as with all solidification techniques, the control of the convective flow is not an easy task, which may render the interpretation of the experimental data far from obvious. In any case, a complete numerical model of the experimental configuration would be necessary, which is still by itself an issue that is far from obvious.

In view of the above limitations, our opinion is that the best chance to accurately measure the diffusion coefficients would be to set-up a dedicated experiment aiming at a one-dimensional implementation of Fick's law. The microgravity environment of space offers promising possibilities to circumvent the problem of unwanted convective transport, and interesting results have thus been obtained, see e.g., Ref. 8 and references therein. Alternatively, one could think of magnetic fields to either control [28] or strongly damp [29] fluid flow. In all cases however, the problem of the reactivity of liquid silicon with crucible materials would have to be tackled.

5. CONCLUDING REMARKS

Our objective in this work was to re-examine the seminal work of Kodera on the determination of the diffusion coefficients of various dopants in silicon from Czochralski solidification experiments. Since the segregation model used by Kodera was shown to be incorrect, such a re-examination appeared necessary. We also performed a sensitivity check on the thermophysical parameters (namely, kinematic viscosity and mass density) necessary for the data analysis. There again, Kodera's choices appear questionable in view of recently published values, justifying the approach of the present work.

In addition, we extended the work of Kodera by allowing the fit of the experimental data to be carried on both the diffusion and partition coefficients. Our results show that the values of the partition coefficients available in the literature are essentially correct. Nevertheless, the slight variations with respect to published data were found to have a significant impact on the determination of the diffusion coefficients. Our opinion is that the data coming from the fit on both the diffusion and partition coefficients are to be preferred. Since the literature values on the partition coefficients bears a rather large uncertainty, the slight but significant χ^2 test advantage should be given due recognition.

As the analysis procedures and the values of the thermophysical parameters are fairly different, no general trend can be deduced from the comparison of our results with Kodera's initial data recalled in Table III. For instance, the fact that Kodera takes $V_{\mathrm{I}}^{\mathrm{L}}$ to be equal to the solidification rate prescribed by the experimenter $V_{\mathrm{I}}^{\mathrm{S}}$ tends to shift his fitted D to higher values, as does his choice of a larger kinematic viscosity. On the other hand, his use of the stagnant film model has the effect of shifting D to lower values. Altogether, it can be stated that Kodera's values are somewhat higher than ours, but remain in the same range.

As a matter of fact, an important issue is that the error bars may appear deceptively high (often amounting to more than 50% in relative terms), but it should be recalled that solidification experiments are a rather indirect way for the measurement of diffusion coefficients. Another sobering thought is that, even though Kodera used a wrong model and wrong values of the thermophysical parameters, his values and ours overlap in nearly all cases. Nevertheless, as Kodera's data are still quoted as a reference nowadays, it seemed worthwhile to put the analysis on a sound procedural basis.

Finally, we also discussed whether other measurement techniques could improve the accuracy in the diffusion coefficients. Better control of the convective flow in the Bridgman configuration could lead to significant improvements, but the real breakthrough would be to work on a direct approach, e.g., through long capillary or shearing cell techniques. However, it should be stated that whether the extremely reactive nature of liquid silicon will allow such techniques to be implemented remains an open question.

ACKNOWLEDGMENTS

It is a pleasure for the author to thank his colleagues D. Camel, B. Drevet, G. Mathiak, and A. Griesche for their help during the preparation of the manuscript.

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