NUMERICAL SIMULATION OF DISSOLUTION AND LIQUID-PHASE-EPITAXIAL GROWTH OF SILICON

H.A. ERBAY†  S. ERBAY†  N. DJILALI†  S. DOST†

Abstract
Numerical simulations of the liquid-phase epitaxial growth and dissolution processes of silicon in a sandwich cell configuration are presented. Time-dependent natural convection and mass transport are analyzed using a finite-volume method with a fully implicit time stepping scheme. The simulations provide a very satisfactory explanation of fundamental aspects of LPE growth and dissolution, and show that natural convection, driven by concentration gradients in a gravitational field, plays a significant role in these processes. Convection greatly enhances growth and dissolution rates in regions of the system where it is predominant. However, convection is also found to cause the formation of wavy irregular substrate shapes. The insight gained from these simulations should prove useful in the development of improved growth techniques for the production of semi-conducting crystals.

1. INTRODUCTION
Liquid Phase Epitaxy (LPE) is a commonly-used method of producing semi-conductor crystals required for the fabrication of electronic devices. In the case of growth of silicon, for example, LPE consists of depositing thin layers of silicon from a dilute solution of indium-silicon onto a substrate. Gradual reduction of the temperature of the solution results in a reduction of the saturation concentration and causes crystallization of the excess solute (i.e. silicon) onto the substrate. The mass transfer between the crystal substrate and the surrounding liquid causes a change in the density of the solution. For sufficiently high density gradients, this is expected to give rise to solutal convection in the solution.

The sources and effects of convection have been identified and reviewed by N erad and Schlichta [1]. Convection has the advantage of increasing growth rate, but may also cause defects such as fluid inclusion or impurity banding. In addition, natural convection reduces the effectiveness of stabilizing techniques, such as forced convection or applied electric currents, used in some growth processes. In order to reduce these adverse effects, experiments have been performed under reduced gravity conditions [1, 2]. Even in such conditions, however, convection may still occur [3], and further understanding of its interaction with solute transport is therefore needed to improve the quality of crystals grown from solutions.

The effect of convection has also been discussed by Long et al. [4] who examined the non-uniform growth problem in steady-state LPE of gallium-arsenide (GaAs). The effect of temperature gradients, growth temperature and substrate location were investigated. When substrates were located on top of the solution, convection, rather than thermal non-uniformity or diffusion,
was identified as the cause of non-uniform epitaxial layers; the driving force for convection was found to be solute gradients rather than thermal gradients.

Recently, Sukegawa, Kimura and Tanaka [5, 6, 7] discussed the effect of convection on both dissolution and epitaxial growth of silicon in an indium-silicon (In-Si) system. A horizontal "sandwich" system consisting of a substrate-solution-substrate arrangement was used. It was found that dissolution of silicon occurs mainly on the lower substrate, whereas growth of the upper substrate is larger than that for the lower substrate. These phenomena were attributed to natural convection driven by solute concentration gradients. To substantiate this conclusion, a numerical simulation using a stream function-vorticity formulation was presented. In this simulation, side wall effects were neglected and the convection cells were assumed to be spatially periodic. Despite these limitations, the simulation confirmed the role of solutal convection.

Most of the available theoretical studies of LPE are based on the assumption that epitaxial growth is controlled by diffusive transport (see, e.g., Wilcox [8] for a summary), in spite of experimental evidence documenting the importance of solutal convection. Although it has been recognized for some time that the gap between many of these theories and experiments is largely due to the neglect of gravity induced convection, very few theoretical or computational studies have addressed this problem. This paper presents the first comprehensive numerical study of solutal convection during LPE growth and dissolution processes. A horizontal In-Si sandwich system (Fig.1) corresponding to the experiments of Sukegawa et al. [5, 6] is considered. The governing equations for momentum and mass transport are solved in their primitive variables form, and are discretized using a finite volume method and implicit time-stepping. A systematic grid refinement study was performed to assess the accuracy of the results and to devise an efficient grid distribution; variable time stepping was also used to resolve the rapid changes in the initial phase of the dissolution process.
2. PHYSICAL PROBLEM

The simulations were performed for the dissolution and LPE growth experiments of Kimura et al. [6] and Sukegawa et al. [5], respectively. A schematic of the of the “sandwich” system used for these experiments is shown in Fig.1.

In the dissolution experiment, the substrates and the indium solvent were heated uniformly to 974 °C. The indium solvent was then inserted between the upper and lower substrates, and a uniform temperature was maintained (within 0.25 °C) for one hour.

The growth experiment was performed with a constant cooling rate, and initiated at 994 °C using a silicon saturated indium solution. After injecting the solution into the growth cell, the temperature was lowered to the final temperature of 974 °C, with a constant cooling rate of 0.33 °C/min while maintaining a uniform temperature distribution throughout the solution. In both dissolution and growth experiments, substrate thicknesses were measured as a function of time.

3. MATHEMATICAL FORMULATION

Dissolution and LPE growth processes are affected by mass and heat transfer as well as fluid flow. In the physical experiments simulated in this study the temperature was kept constant during dissolution, and was lowered slowly during growth. The processes are therefore assumed to be isothermal.

The system of equations governing the processes are the unsteady, two-dimensional, incompressible Navier-Stokes and mass transport equations. In Cartesian coordinates, these equations are

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0
\]

(1)

**Momentum**

\[
\begin{align*}
\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} &= -\frac{1}{\rho_0} \frac{\partial p}{\partial x} + \nu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \\
\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} &= -\frac{1}{\rho_0} \frac{\partial p}{\partial y} + \nu \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) - \beta (C - C_0) g
\end{align*}
\]

(2)

(3)

**Mass Transport**

\[
\begin{align*}
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} &= D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right)
\end{align*}
\]

where \(u\) and \(v\) are the velocity components, \(t\) time, \(p\) the pressure, \(C\) the silicon concentration in the solution, \(\rho_0\) the initial density of the solution, \(\nu\) the kinematic viscosity, \(\beta\) the solutal expansion coefficient, \(C_0\) the initial concentration of silicon, \(D\) the diffusion coefficient and \(g\) the gravitational constant. We note that in writing these equations the Boussinesq approximation is invoked, i.e. the density is assumed constant except in the body force term of the \(y\)-momentum equation.

A growing or dissolving crystal gives rise to a moving boundary problem. However, the changes in the substrate thicknesses during the growth or dissolution process are very small
Table 1: Parameter values used in simulations

<table>
<thead>
<tr>
<th></th>
<th>Dissolution Process</th>
<th>Growth Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho_0$</td>
<td>$6.434 \times 10^3$ kg/m$^3$</td>
<td>$6.416 \times 10^3$ kg/m$^3$</td>
</tr>
<tr>
<td>Diffusion coefficient, $D$</td>
<td>$1.084 \times 10^{-8}$ m$^2$/sec</td>
<td>$1.101 \times 10^{-8}$ m$^2$/sec</td>
</tr>
<tr>
<td>Viscosity, $\mu$</td>
<td>$5.76 \times 10^{-4}$ kg/(m.sec)</td>
<td>$5.75 \times 10^{-4}$ kg/(m.sec)</td>
</tr>
<tr>
<td>Solutal expansion coefficient, $\beta$</td>
<td>-0.5907</td>
<td>-2.4267</td>
</tr>
</tbody>
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compared to the distance between upper and lower substrates. It is therefore assumed, as a first approximation, that the interfaces are fixed.

The initial and boundary conditions for the dissolution and LPE growth are given by:

*Initial conditions*  
\[ u = v = 0, \quad p = p_0, \quad C = C_0 \quad \text{at} \quad t = 0. \quad (5) \]

*Boundary conditions on vertical walls*  
\[ u = v = 0, \quad \frac{\partial C}{\partial z} = 0 \quad (6) \]

*Interface conditions on horizontal boundaries*  
\[ u = v = 0, \quad C = C_i \quad (7) \]

The values of the concentrations $C_0$, and $C_i$ depend on the case being simulated:

- *Dissolution process*: $C_0 = 0$ and $C_i$ is equal to the solute concentration calculated from the solubility relation at a dissolution temperature of 974 °C.

- *Growth process*: $C_0$ is equal to the initial solute concentration calculated at an initial temperature of 994 °C, and $C_i$ is the solute concentration calculated at a growth temperature of $(994 - (0.33/60) \cdot t)$ °C, where $t$ is time in seconds.

The interface concentration is obtained from the solubility relation given by [9]. The values of the physical parameters used in the simulations of the dissolution and growth processes are given in Table 1. The densities, viscosities, diffusion coefficients and solutal expansion coefficients are obtained on the basis of relations given by Smithells [10]. Further details for the calculation of these parameters are given in [11].

The dissolution depths and growth thicknesses $H(t)$, the most important quantities from a practical standpoint, are computed at the end of each time step using the following relation:

\[ H(t) = \frac{\rho D}{\rho_{Si}} \int_0^t \frac{1}{1 - C} \frac{\partial C}{\partial y} \, dt \quad (8) \]

where $\rho$ is the density of the solution, and $\rho_{Si}$ is the density of silicon. Equation (8) was derived by Wilcox [12] as an interface jump condition representing solute conservation.
4. COMPUTATIONAL PROCEDURE

4.1 Solution Method

The governing time-dependent equations are discretized using a finite volume method. A hybrid central/upwind differencing discretization scheme is used in conjunction with the SIMPLE algorithm [13] and a fully implicit scheme is employed for time stepping. A staggered nonuniform grid arrangement, with velocity nodes offset from scalar nodes is used to avoid spurious oscillations in the pressure field. The discretized difference equations are solved iteratively using a block-iterative technique and a tridiagonal matrix solver. At each time step, the iteration cycle is terminated and the time step is advanced when the normalized sum of the absolute difference between two successive iterations is smaller than $5 \times 10^{-5}$. In natural convection problems, reference values such as inlet mass flow are not available. In this study, the reference value for each variable $\phi$ was taken as the sum of the absolute values over the computational field and the following convergence criterion was used

$$\frac{\sum_{i=1}^{n_{i}} \sum_{j=1}^{n_{j}} |\phi_n(i,j) - \phi_{n-1}(i,j)|}{\sum_{i=1}^{n_{i}} \sum_{j=1}^{n_{j}} |\phi_n(i,j)|} \leq 5 \times 10^{-5} \quad (9)$$

4.2 Grid Layout

Preliminary computations were first performed using a domain covering the entire system shown in Fig.1. Symmetrical solutions were obtained at all time steps, and therefore all subsequent computations were performed for a domain covering half of the system only, and the appropriate symmetry boundary condition was applied. A typical grid distribution is shown in Fig.2. High density clustering was used close to the vertical wall where the velocity gradients are highest.

Grid distributions from $71 \times 29$ to $135 \times 55$ were used to investigate grid dependency. The major advantage of a non-uniform grid is that it allows denser clusterings only in regions where a high resolution is required, thereby reducing the number of computational nodes. However, a non-uniform grid introduces an extra truncation error in the discretized equation [14]. This may result in a deterioration of both accuracy and convergence rate if the grid expansion/contraction...
ratio, \( \epsilon_x = (\delta z)_1/(\delta z)_1 \), is too high. Tests with various values of \( \epsilon_x \) were performed, and the predicted values of \( H \) were examined for both dissolution and growth at \( t = 60 \text{ min} \). As shown in Fig.3, an abrupt deterioration of the predicted lower substrate dissolution depth occurs for \( \epsilon_x \geq 1.17 \). A similar behaviour is observed for the upper substrate in the growth case. The reasons for the localized effect are discussed in the next Section.

A general observation made during these tests is that the convergence rate improves for the flowfield equations with highly stretched grids, and deteriorates for the mass conservation equation. This highlights the difficulty in devising a grid appropriate for both fluid flow and mass transport. First, the Schmidt number for the solution is much larger than unity, implying that solute concentration boundary layers at the interface would be thinner than momentum boundary layers. Secondly, because of the transient nature of the process, regions of high gradients appear in different parts of the domain as time evolves. Final grid expansion ratios are chosen to ensure optimum convergence characteristics for both flowfield and mass transport. These values are \( \epsilon_x, \epsilon_y = 1.14 \) for dissolution and \( \epsilon_x, \epsilon_y = 1.11 \) for growth.

During dissolution, fluid flow motion and time rates of change are relatively large at the beginning of the process, but decrease significantly as time increases and as the process approaches an equilibrium state due to the decreasing concentration gradients. Consequently, a
variable time step is used in the computations, increasing gradually from a value of 0.1 second at the beginning of the computations, to about 25 seconds after 800 time steps. The effect of time step on the solutions was investigated, and it was found that predicted dissolution depths change by less than 1% when the number of time steps is increased from 800 to 1300. In the growth process, we recall that a constant, low cooling rate is used. The simulations are therefore performed with 1600 constant time-steps of 2.25 seconds.

5. RESULTS AND DISCUSSION

5.1 Dissolution Process

The time evolution of average dissolution depths for the upper and lower substrates are shown for two grid distributions in Fig.4. The predictions obtained with the two grids are essentially identical, and the fine grid solution can be considered to be "grid independent" for all practical purposes. All results presented in this Section were obtained using the finer grid. The overall agreement between measured and predicted dissolution depths is quite satisfactory; in particular the simulations correctly predict the difference between upper and lower substrate dissolution depths, and the much higher dissolution rates during the initial phase of the process up to \( t \approx 500 \) sec. The dissolution of the lower density silicon reduces the density of the solution in the vicinity of the substrates. Stable stratification is therefore established in the upper region, whereas unstable stratification develops in the lower region. This results, very soon after the onset of the process, in buoyancy-induced upward motion as shown in the isoconcentration and streamline patterns in Fig.5.

Initially, the isoconcentration patterns are almost flat, indicating that mass transport is essentially controlled by diffusion, except in the lower corners where isolated convective cells first appear with upward velocities near the vertical wall. As time proceeds, the initial corner cells move towards the upper substrate, and weak secondary cells appear in the central region. A complex evolution of the flowfield, with a pseudo-cyclic formation and amalgamation of secondary cells, takes place during the first 200 seconds of the process. Throughout this phase convection dominates the lower region, whereas little fluid motion takes place near the upper substrate. The concentration gradients vary significantly along the lower substrate, and, as a result of enhanced convective transport, are much higher than along the upper substrate. After about 200 seconds, due to the reduction of the concentration gradients driving the motion, convection gradually dies out, becoming insignificant after about 700 seconds.

The solutal convection which dominates the initial phase of the process is responsible for the enhanced mass transfer, which in turn results in the higher dissolution rates shown in Fig.4. This effect is much more pronounced for the lower substrate, where, as shown earlier in Fig.5, convection and concentration gradients are much higher. The agreement between computations and experiments is not as good for the lower substrate as it is for the upper. The small discrepancies could be caused, in part, by numerical diffusion which can be present in convection dominated regions of the field where the upwind discretization scheme is used. This numerical diffusion, or false diffusion would tend to smear flow when the local flow velocity is not aligned with the grid lines and when gradients are large [15]. The predominance of convection in the lower region is also responsible for the higher sensitivity to grid stretching observed in the previous section for the lower substrate dissolution depths.

Another very interesting consequence of natural convection is the evolution of the shape
Fig. 4: Time dependence of upper and lower substrate dissolution depths obtained with coarse (71 x 29) and fine (101 x 41) grid systems.

of the substrates, shown in Fig. 6. The upper substrate remains smooth and almost flat. The lower substrate, on the other hand, develops a ragged wavy shape due to solutal transport associated with the complex convection patterns shown earlier. The waviness increases during the first 300 seconds or so, and stabilizes thereafter with a more uniform dissolution rate across the substrate. No smoothing was used in these plots, and the spikes in the central portion correspond to grid points; the spikes are attenuated near the walls where grid spacings are much smaller.

5.2 Growth Process

The effect of grid refinement on average growth thickness is shown in Fig. 7; the predictions with the coarse and fine grid are essentially identical. We recall that for this process, temperature is lowered at a constant rate (0.33 °C/min) causing supercooling of the solution. This initiates growth by diffusion. As the process continues, the growth induces unstable stratification near the upper substrate. The build-up of destabilizing concentration gradients triggers convection. These two phases of the growth process are clearly seen in the figure, where growth rate increases steadily during the initial phase, and becomes approximately constant about 90 seconds after the beginning of the process; hence the choice of a constant time step for the growth simulation. In agreement with the experimental observations of Ref.[5], the upper substrate grows at a much faster rate than the lower substrate, and is about twice as thick. As in the case of dissolution, solutal convection enhances the upward motion of silicon particles. Whereas during dissolution this results in a depletion near the lower substrate, thereby enhancing dissolution depth, in the growth process, the upward migration of Si results in an enrichment of Si in the upper region.
Fig. 5: Flow patterns during initial phase of the dissolution process

(a) streamlines
(b) isoconcentrations
Fig. 6: Evolution of substrate surfaces during dissolution process

and an enhanced growth rate.

The averaged solute concentration profiles are shown in Fig. 8. In contrast with the dissolution case where the interface concentration remains constant, the constant cooling rate used in the growth process produces decreasing interface concentrations as shown in the figure. Although the absolute values of the concentrations decrease steadily throughout the process, due to crystallization, the profiles and the gradients at the substrates remain similar. This is consistent with the predicted constant growth rate.

Figure 9 shows the streamline patterns throughout the 3600 seconds of the growth process. At the initial stages, convection is confined to the upper corners, and the fluid rises forming a boundary layer on the vertical walls. Gradually, fluid motion propagates to the entire domain, the original corner cells move towards the middle, and new counter-rotating cells, in which the direction of the flow along the vertical walls is reversed, form at the corners. Because concentration gradients are maintained, convection is sustained during the entire process, except in the lower region where convection is insignificant. The changes in flow patterns are most noticeable in the middle of the domain where secondary cells form, merge and vanish in a cyclic fashion.

Figure 10 shows the corresponding isoconcentration patterns. The contours are initially horizontal lines typical of a pure diffusion. The onset of convection in the upper corners distorts these contours, and higher gradients arise first close to the extremities, and later along
the entire surface of the upper substrate. Following the formation and merging of cells in the middle of the domain, the concentration gradients vary substantially during the process. The isoconcentrations in the lower part of the domain remain almost horizontal and evenly spaced throughout the growth process.

As would be expected from earlier observations in the dissolution case, the convective patterns and the substantial variations in concentration gradients which now occur in the upper region have a significant effect on the shape of the substrate. Figure 11 shows that the upper substrate exhibits a similar kind of waviness to that previously observed at the lower substrate during dissolution. The lower substrate in this case is essentially flat except at the edges near the walls where it is thicker. This feature has also been observed in recent experiments [16]. The reduced growth rates near the walls at the upper substrate are due to the downward motion along the walls, illustrated in Fig.9. This motion, which persists throughout the process, transports silicon away from the upper corners resulting in local depletion. No experimental observations are available to confirm the predicted behaviour of the upper substrate near the walls.

6. CONCLUSIONS
The LPE growth and dissolution experiments of Sukegawa, Kimura and Tanaka [5, 6] were simulated using a model which accounts for both diffusive and convective mass transport. The
Fig. 8: Variation of solute concentration distribution with vertical distance at various times. Time in seconds: (a) 90, (b) 450, (c) 900, (d) 1350, (e) 1800, (f) 2250, (g) 2700, (h) 3150, (i) 3600.

Results of the simulations are found to be in good agreement with these experiments. The present solutal convection model is very satisfactory in explaining the fundamental aspects of both dissolution and growth, and shows that convection, driven by concentration gradients in a gravitational field, plays a significant role in these processes. The simulations clearly demonstrate that a model based only on diffusion would fail to reproduce basic features such as differences between substrate thicknesses and more vivid consequences of convection such as wavy substrate shapes.

The predicted flow and concentration patterns illustrated the unsteady nature of the processes showing that regions of high gradients move continuously around the domain during the process. The proper tracking of these gradients, the modelling of the moving boundaries at the interfaces, the incorporation of non-isothermal boundary conditions, and the reduction of possible numerical diffusion errors would contribute to a more accurate model capable of simulating most of the physical processes of interest. These further developments will be considered in future work.

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From top to bottom on left; $T = 45, 67, 78, 90, 450, 900$
From top to bottom on right; $T = 1350, 1800, 2250, 2700, 3150, 3600$

Fig. 9: Evolution of streamline patterns with time with growth process
From top to bottom on left; $T = 45, 67, 78, 90, 450, 900$
From top to bottom on right; $T = 1350, 1800, 2250, 2700, 3150, 3600$

Fig. 10: Evolution of isoconcentrations with time during growth process
Fig. 11: Evolution of substrate surfaces during growth process

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