Growth kinetic model for liquid phase electro epitaxial growth of GaSb

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A two-dimensional growth kinetic model has been proposed to calculate the growth velocity and thickness of GaSb epitaxial layers grown by liquid phase electro epitaxy (LPEE) with a polycrystalline GaSb source material, which can be used to supply the solute species to the depleted growth solution during growth. The solute species (Sb) are continuously supplied from the source material to the growth solution by diffusion and electromigration. In the proposed theoretical model, numerical simulation has been followed to calculate the growth rate and thickness of the GaSb epitaxial layer from a Ga-rich solution. The theoretical findings indicate that the growth rate depends on the growth parameters such as growth temperature, growth time, diffusion of solute species, mobility of solute species, thickness of the substrate and source, thermoelectric effects and applied current density in the solution. The proposed model is based on the assumption that there is no nucleation in the solution. The growth rate, thickness of GaSb epitaxial layer and amount of dissolution of source material for different experimental growth conditions have been determined.

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III-V compound semiconductors are of great interest for microelectronic, optoelectronic and thermophotovoltaic applications. These devices demand a high degree of crystalline and chemical perfection materials. The epitaxial growth techniques like liquid phase epitaxy (LPE), liquid phase electro epitaxy (LPEE), molecular beam epitaxy (MBE), vapor phase epitaxy (VPE), metal organic vapor phase epitaxy (MOVPE) etc, satisfy the requirement for device fabrication at comparatively low growth temperature. The epitaxial layers grown by these techniques have a good stoichiometric and defect-free structure.

Among the epitaxial growth techniques, LPEE is a very promising technique for producing a quality epitaxial layer of III–V compound semiconductors with controlled thickness, low dislocation density, uniform composition and better surface morphology. In LPEE, the growth is initiated and sustained by passing an electric current across the substrate–solution–source interface under isothermal condition. The two mechanisms that are responsible for the growth of epitaxial films, are (i) Peltier cooling at the substrate–solution interface and (ii) electro-migration of solute particles towards the substrate–solution interface. The possibility of achieving precise control of the epitaxial growth process by controlling the electric current passed through the interface. In conventional liquid phase epitaxy (LPE), the precise control of the microscopic growth velocity is still a problem.

Initially, the LPEE technique has been successfully employed for the growth of an epitaxial layer of InSb on InSb from indium and antimony solution. Experimental details of LPEE have been described in detail and it has been used to grow bulk crystals of GaAs with low point defect concentrations, good electronic and structural properties. The dislocation density is significantly reduced after 100 μm of epitaxial growth; it proves the potential to grow defect-free bulk crystals. This technique has been successfully employed for selective epitaxial growth of silicon films for solar cell applications and fabrication of cube-textured Ag-buffered Ni substrates for the growth of biaxially textured high temperature superconducting tapes. The availability of such quality epitaxial layers will open new horizons in the fabrication technology of optoelectronic, thermophotovoltaic and high-power devices. The several advantages of this technique kindled interest among the researchers to understand the growth kinetics of LPEE and number of modeling studies have been carried out in recent years.

In the present study, we have chosen a growth bin setup for theoretical investigations is a conventional sliding LPE growth bin setup with electrical contact
arrangements as shown in Fig. 1. The graphite parts in the growth cell are the electrodes. The growth solution of Ga-rich GaSb solution makes contact with top of the substrate and bottom of the source. The boron nitride is used as electrical insulator. The contact zone provides a uniform current distribution to the substrate. We have attempted the growth kinetic studies of GaSb electroepitaxial growth by making two assumptions (i) the growth kinetic study from the limited solution, i.e., the depletion of the solute atom occurs after a certain time in the growth solution and (ii) the growth kinetic study with the source material, i.e., the solute atoms are continuously supplied from the source material. A two-dimensional (2D) mass transport, thermal and electric field equation has been solved in the growth solution with appropriate boundary conditions for liquid phase electro epitaxial (LPEE) growth of GaSb with source based on diffusion and electromigration of solute species. A numerical simulation technique has been followed to solve the corresponding equations and to construct the concentration profiles of the solute species Sb, temperature and electric field distribution in the growth solution under isothermal condition. The concentration gradients along the substrate–solution interface and source–solution interface can be used to calculate the growth/dissolution velocity as a function of growth time. The effects due to Peltier effect and electromigration during the growth and dissolution have been determined under different experimental growth conditions. The theoretical findings are compared with available experimental results.

**Model**

LPEE is a promising technique for growing high-quality epitaxial films and bulk semiconductors from non-stoichiometric solutions. Several mechanisms are believed to play a role in the LPEE growth process such as complex interactions of thermo-mechanical and electromechanical fields, heat and mass transport, surface kinetics and various thermoelectric effects such as Peltier cooling/Peltier heating, Joule effect, Thomson effect, Soret effect and Dufour effect. In LPEE, Soret, Dufour and Thomson effects are neglected since their contributions are very small due to low temperature gradients. In LPEE, the growth mainly depends on the Peltier effect and electromigration of the solute atoms in the solution and it is directly proportional to the direction of the applied current density. The Peltier effect is a thermoelectric effect occurring when an electric current passes through a junction of two materials having different thermoelectric coefficients; heat is absorbed or evolved depending on the direction of the applied electric current. In the case of Peltier cooling, heat is absorbed at the interface and supersaturation in the vicinity of the substrate occurs, resulting in epitaxial growth. In the case of Peltier heating, heat is evolved at the interface and dissolution of the substrate occurs. In III–V solutions and other metallic solutions, electromigration takes place due to electrostatic field forces and electron-momentum exchange. Some of the neglected secondary effects may become significant depending on the LPEE growth set-up. The proposed model considers steady-state heat conduction with Peltier effect, steady-state electric current flow and incorporation of electromigration to the transient mass transport equation.

**Governing Equations**

The growth cell is described using the Cartesian coordinates (X, Y) with the Y-axis being perpendicular to the substrate-solution and source-solution interface. We have proposed a growth kinetics model for LPEE growth based on 2D diffusion equation, incorporating the electromigration effect and to study the electro-epitaxial growth kinetics of GaSb. Efforts have been made to understand the growth kinetics by electromigration only and by diffusion and electromigration.

**Steady-state heat conduction equation**

The mass and thermal analysis covers only the growth solution zone of $0.6 \times 0.6$ cm$^2$. In liquid phase electro epitaxial growth, the temperature of the growth system is kept constant throughout the growth.
process. When we apply an electric current to the solution through the substrate or source induce temperature gradients at the substrate-solution or source-solution interface due to the difference in the thermoelectric coefficients of substrate and solution, which are independent of time. The substrate or source is a semiconductor and solution is metallic in nature. Using the steady-state thermal analysis, the temperature distribution for a given substrate or source is governed by

$$k_X \left( \frac{\partial^2 T}{\partial X^2} \right) + k_Y \left( \frac{\partial^2 T}{\partial Y^2} \right) = 0 \quad \text{(1)}$$

where $k_X$ and $k_Y$ are the thermal conductivities of the substrate or source in the $X$ and $Y$ directions. In LPEE growth, the Joulean heat is neglected, since the growth time is long compared to the onset of the equilibrium. The boundary conditions applied to the steady-state heat conduction are

(i) $\partial T/\partial X = 0$ at distance along the substrate and source (ii) $T = T_0$ at outside walls.

The condition at the substrate-solution interface is

$$k_Y \left( \frac{\partial T}{\partial Y} \right) = Q_{pc} \quad \text{(2)}$$

and condition at source-solution interface is

$$k_Y \left( \frac{\partial T}{\partial Y} \right) = Q_{pb} \quad \text{(3)}$$

where $k_Y$ and $k_Y$ are the thermal conductivities of the substrate and solution perpendicular to the plane of interface. $Q_{pc}$ and $Q_{pb}$ are Peltier cooling and Peltier heating at the corresponding interfaces. The electric current passes directly through the substrate–solution and source–solution interface and electric current density remains uniform throughout the solution.

**Mass transport equation**

When the electric current is applied to the solution, the liquid phase electro epitaxial growth proceeds by both Peltier cooling and electromigration of the solute species towards the substrate, simultaneously dissolution occurs at the source and will replenish the solute concentration in the solution. The Peltier cooling/Peltier heating induces a concentration gradient in the solution resulting in supersaturation at the substrate-solution interface and dissolution at the source-solution interface. In addition, the solute species in the metallic solution gain energy from the applied electric current, which causes electromigration towards the substrate. This process induces supersaturation at the interface. Incorporating these effects in the two-dimensional transient mass transport equation for an electroepitaxial system as

$$D_i \left( \frac{\partial^2 C_i}{\partial X^2} + \frac{\partial^2 C_i}{\partial Y^2} \right) + \mu_i E \left( \frac{\partial C_i}{\partial X} + v \frac{\partial C_i}{\partial Y} \right) \pm \mu_i E \left( \frac{\partial^2 C_i}{\partial Y^2} \right) = \frac{\partial C_i}{\partial t} \quad \text{(4)}$$

where $D_i$ is the diffusion coefficient, $\mu_i$ is the mobility, $C_i$ is the concentration of the solute species $(i = \text{Sb})$, $u$ and $v$ are the velocity components in $X$ and $Y$ directions in the solution and $E$ is the applied electric field. $X$ is the direction parallel to the plane of interface towards the solution and $Y$ is the direction perpendicular to the plane of interface. The sign of the electromigration term is determined by the direction of the current flow. The mass transport equation is subjected to the following boundary conditions

At $t = 0$, $C_i^{eq} = C_0$ for all $X$ and $Y$ \quad \text{(5a)}

At $t > 0$, $C_i^{eq} = C_0$ for $X = 0$ and $30 \epsilon$ \quad \text{(5b)}

or

At $t > 0$, $C_i^{eq} = C_1$ for $Y = 0$; (growth follows the liquidus line) \quad \text{(5c)}

$C_i^{eq} = C_2$ for $Y = 30 \epsilon$; (dissolution at the source-solution interface) \quad \text{(5d)}

$C_0$ is taken as the equilibrium concentration of Sb in the GaSb solution at a given growth temperature and $\epsilon$ is the width of the segment. $C_1$ is the interface concentration at substrate-solution interface and $C_2$ is the interface concentration at source-solution interface which can be determined from the Ga-Sb phase diagram. The initial concentration of Sb at the growth temperature in the Ga-rich solution has been calculated from

$$C_0 = 6.38 \times 10^{22} \exp \left[ 8.1207 - (9.157 \times 10^3) / T \right] \text{ atoms/cc} \quad \text{(6)}$$
Growth rate

The growth rate \((R)\) depending on the number of solute atoms flowing towards the growth interface is given by\(^{23}\),

\[
R = \frac{\Delta T_P}{C_S - C_i(0,t)} \frac{dC_i}{dT} \left( \frac{D_l}{\pi t} \right)_L^{1/2} \\
\pm \mu_i E \left( \frac{C_i(0,t)}{C_S - C_i(0,t)} \right) 
\]

\[(7)\]

In LPEE, the growth mainly depends on the Peltier effect and electromigration effect. The first term on the right-hand side of Eq. (7) represents the contribution of the Peltier effect and the second term represents the electromigration of the solute atoms to the growth velocity. \(\Delta T_P\) is the change in interface temperature due to Peltier effect, \(\pi\) is the Peltier coefficient, \(C_S\) is the concentration in the solid and \(C_i(0,t)\) is the concentration of solute species at the interface. The thickness of the epitaxial layer at any given time can be obtained by integrating the growth rate.

Computational method

The transient mass transport and thermal analysis problem defined in the preceding section has been solved by the numerical simulation technique. For computational convenience, the thermal analysis and mass transport covers only the solution zone. The growth solution has been segmented into 30 × 30 finite number of computational cells with equal width \(\varepsilon\) in the X and Y directions of an area of 0.6 × 0.6 cm\(^2\). The governing partial differential equations are integrated over the cells and are solved by the central difference scheme. By maintaining the numerical stability and its accuracy, we have taken the successive time increment as one second. A computer package was developed using the visual C++ program to solve the thermal and mass transport analysis. The overall computational procedure is shown in the flowchart (Fig. 2). The growth and physical parameters used for the present calculation are given in Table 1.

Results and Discussion

Numerical analysis is a right tool, to study the growth kinetics of LPEE growth of III–V compound semiconductors from the concentration of solute species in the solution, which reduces the experimental cost. From the phase diagram of the Ga-Sb system, the concentration of Sb in the Ga-rich solution has been calculated as a function of temperature. The growth temperature has been taken as 580°C. The concentration profiles of Sb in the solution have been computed at successive increments of time for various experimental growth conditions. Knowing the solute concentration in the solution, the growth rate and thickness of the epitaxial layer at every time increment can be determined.

Table 1—Physical Parameters of the LPEE GaSb System

<table>
<thead>
<tr>
<th>Geometry (cm)</th>
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<tbody>
<tr>
<td>Substrate Length</td>
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</tr>
<tr>
<td>Substrate Breadth</td>
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</tr>
<tr>
<td>Solution height</td>
<td>0.6</td>
</tr>
<tr>
<td>Substrate thickness</td>
<td>0.04</td>
</tr>
<tr>
<td>Source thickness</td>
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<tr>
<td>Thermal Conductivity W/m K</td>
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<table>
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<tr>
<th>Solution</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>6.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth temperature (T_g)</td>
<td>580 °C</td>
</tr>
<tr>
<td>Current density (J)</td>
<td>10 Acm(^{-2})</td>
</tr>
<tr>
<td>Peltier coefficient (\pi)</td>
<td>0.15 V</td>
</tr>
<tr>
<td>Thermal diffusivity (\alpha)</td>
<td>0.23 cm(^2) s(^{-1})</td>
</tr>
<tr>
<td>Solutal diffusivity (D)</td>
<td>2×10(^5) cm(^2) s(^{-1})</td>
</tr>
<tr>
<td>Solutal mobility (\mu)</td>
<td>1.05×10(^2) cmV(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Solution density (\rho)</td>
<td>5.738 gcm(^{-3})</td>
</tr>
<tr>
<td>Electric conductivity of the solution (\sigma)</td>
<td>2.5×10(^5) Ω(^{-1}) cm(^{-1})</td>
</tr>
</tbody>
</table>
Concentration profile surfaces of Sb in the Ga-rich solution during LPEE growth of GaSb at various current densities are shown in Figs 3a–d. The liquid phase electroepitaxial growth mainly depends on Peltier cooling at the substrate-solution interface and electromigration of the solute species towards the growth interface. With the growth of the epitaxial layer due to Peltier cooling, there is a decrease in concentration of the solute species near the substrate-solution interface. Peltier heating at the source-solution interface increases the concentration of the solute species at the interface due to dissolution of the source, which replenish the solute to the growth solution. In addition to Peltier cooling, the epitaxial growth depends on the electromigration of the solute species towards the substrate by the applied electric current. Along the substrate-solution interface, the concentration increases from the cell center to outer wall of the growth cell, whereas in source-solution interface concentration increases from cell wall to cell center and results in a non-uniform temperature distribution along the interfaces.

Fig. 4 shows the growth/dissolution rate for various current densities along the interfaces. The first curve shows the growth rate for a current density of 5 A cm$^{-2}$ and other curves are for increment of 5 A cm$^{-2}$ on each side. The non-uniform concentration along the interfaces causes a non-uniform growth/dissolution rate along the interface. At higher current densities the induced Peltier effect increases the non-uniformity along the interfaces. The growth/dissolution rate at the cell center is uniform when compared to the cell

Fig. 3—Concentration profile surfaces of Sb in the Ga-rich solution for various applied current densities: (a) 5 Acm$^{-2}$, (b) 10 Acm$^{-2}$, (c) 15 Acm$^{-2}$, (d) 20 Acm$^{-2}$.
This shows the growth/dissolution rate is electromigration-dominant. Fig. 5 shows the growth rate at cell center and cell wall against the growth time. The growth rate at the cell wall is lower than in the cell center and both decrease with growth time. The inserted figures clearly show the difference in growth rate at cell wall and cell center. The growth rate attains saturation after a certain time, which indicates that the growth is electromigration-dominant.

Fig. 6 shows the independent contribution of Peltier cooling and electromigration to the growth rate with the growth time. Initially, the Peltier effect contribution to the growth is dominant after certain time it attains saturation due to onset of thermal equilibrium and it is very low compared to electromigration, which shows clearly in the inserted figure. The electromigration contribution to the growth is uniform throughout the growth time, which indicates that the growth is electromigration-dominant.

Fig. 4—Growth/dissolution rate for various applied current densities.

Fig. 5—Growth rate at cell center and cell wall versus growth time.

Fig. 6—Growth rate due to Peltier cooling and electromigration effect against growth time.
dominant. Fig. 7 shows the thickness of the epitaxial layer at a current density of 10 A cm\(^{-2}\) as a function of growth time. The bottom curve corresponds to a growth time of 10 h; the other curves are for successive increments of 10 h. At the cell center, the thickness of the grown epitaxial layer is uniform; it shows the electromigration-dominant growth. Increasing the growth cell dimensions has increased the uniformity along the substrate. Fig. 8 shows the average growth rate as a function of current density. Increase in current density increases the electromigration of the solute species in the solution, which makes a linear variation in the growth rate of the epitaxial layer. The resulting growth velocity is proportional to the applied current density. The growth rate determined is compared with the experimentally reported values.

Fig. 7—Calculated thickness of the epitaxial layer as a function of growth time.

Fig. 8—Average growth rate as a function of current density.

Conclusions

A 2D growth kinetic model for the liquid phase electroepitaxial growth of GaSb was presented. Computations were carried out using the specially developed software package using the visual C++ program. The effect of Peltier effect and electromigration in the growth solution was investigated. Numerical results show that the concentration profile in the central region of the growth cell becomes uniform and at the interfaces non-uniform concentration profiles have been observed due to a non-uniform temperature distribution in the solution. Mass transfer by electromigration plays a dominant role for the growth of the electro-epitaxial layer. The resulting growth velocity is proportional to the applied current density. The growth rate determined is compared with the experimentally reported values.

References
1 Bryskiewicz T, J Cryst Growth, 43 (1978) 567.