A NUMERICAL ANALYSIS FOR THE SUPERSATURATION DISTRIBUTION AROUND LPE MACROSTEP

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Abstract. Supersaturation distribution around LPE macrostep has been calculated theoretically using parameters determined by photoluminescence image. GaP doped with Zn and O is chosen as an example material since it gives visible photoluminescence. The calculation showed the unsymmetric distribution in both sides of the riser, which reflects the unsymmetric form of the macrostep. The amount of supersaturation imposed on the tread is very small such as ~0.01%. To explain the high rate of impurity incorporation on the tread for such small supersaturation, it is concluded that the diffusion relaxation model is much better to apply than the statistical selection model.

1. Introduction

Macrosteps are very often observed on the crystal surfaces grown by liquid phase epitaxy (LPE).1,2 They also appear, although not frequently, on the surfaces of the melt grown crystals.3,4 Roughly speaking, there are two kinds of macrosteps, macrostep undulation of sinusoidal shape and real macrostep with flat treads and a curved riser. There is a long history explaining the mechanism of the macrostep formation. However, no common understanding exists to explain it. One of the present authors (Nishinaga) et al. applied the morphological stability theory to find the wavelength of the LPE macrostep undulation as a function of various growth parameters.5 Although, they got a qualititative agreement, this theory can not be applied to the real macrostep which is observed most frequently in the experiments. This is because the morphological stability theory assumes atomically rough surface everywhere on the growing surface.

In 1960's, one of the present authors (Chernov) and Budurov developed a theory to give a stable shape for the riser of a real macrostep.6,7 In their
theory, they assumed that the riser is composed of a singular surface and the growth is controlled by growth kinetics. However, the riser of the LPE macrostep of III–V compound semiconductor has a smooth sinusoidal shape and it must be non-singular. Hence, their theory cannot be applied to semiconductor LPE macrosteps. Voronkov made a numerical calculation to obtain a theoretical shape of the macrostep riser with nonsingular surface. He calculated the solute concentration on the riser surface, which coincides with the equilibrium concentration determined by taking into account Gibbs-Thomson effect. The shape of the riser was obtained numerically by iteration technique. In his approximation, he derived for every macrostep one constant angle between the tread and the trace of the riser moved during the growth. On the other hand, it has been shown in experiments that the angle is not unique but changes from macrostep to macrostep. The reason is probably due to the fact that he neglects the effect of growth on the tread to the solute concentration over the riser surface.

In the present paper, numerical calculation has been made taking GaP LPE as an example to obtain solute concentration distribution over a LPE macrostep using parameters determined by photoluminescence images. Growth kinetics is taken into consideration as well as Gibbs-Thomson effect to derive an equation expressing the shape preserving growth of the macrostep. This enables us to determine supersaturation on the macrostep tread and to discuss on the mechanism for different impurity incorporation on the tread and the riser taking zinc and oxygen as examples.

2. Experimental

GaP epitaxial layers are grown on (111)B substrate with no intentional misorientation by conventional LPE technique of equilibrium cooling. Zinc and oxygen are doped to get red luminescence. On the grown surface there often appear well developed macrosteps (real macrostep) sometimes as high as \(\sim 5 \mu m\) for the average growth of 60–100 \(\mu m\) in thickness. The slope of the macrostep riser changes gently and its shape is almost sinusoidal. No crystallographic preferential growth nor faceting are observed on the riser and hence, it is clear that the surface of the riser is non-singular. Photoluminescence image (PLI) has been observed on (110) cleaved cross section of the grown sample using the same technique described in reference. Two examples of PLI are shown in Figs. 1(a) and (b). As shown in the figure, 3 well developed macrosteps are chosen and named as macrostep A, B and C. These grew so big that one can measure the height, the angle between the tread and the riser and so on directly from these photographs.

A schematic picture of the macrostep is given in Fig. 2. The top and the bottom surfaces (the treads) of the macrostep are very flat and are closed to a singular surface, in III–V compound semiconductor LPE, it is (111) or (100)
Fig. 1. Photoluminescence images taken from (110) cross section of LPE GaP doped with zinc and oxygen. Small and Large macrosteps moving in the same direction (a), slowly moving macrostep (b).

Fig. 2. A schematic picture of the macrostep and definitions of parameters to characterize the macrostep behavior.
plane. Although the riser is weak sinusoidal, we assume it planar in solving the diffusion equation. This is reasonable since the detailed structure of the growing interface is not so important to determine a whole diffusion field.

As shown in the figure, parameters related to the macrostep growth are defined as,

\[ h: \text{macrostep height}, \]
\[ \alpha \pi: \text{angle between tread and riser}, \]
\[ \theta: \text{angle between tread and the trace of macrostep moved during the growth}, \]
\[ v_1: \text{normal growth rate of riser}, \]
\[ v_2: \text{normal growth rate of tread}. \]

These values are measured for the macrostep A, B and C and listed in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha \pi ) (in deg.)</th>
<th>( \theta ) (in deg.)</th>
<th>( \alpha )</th>
<th>( \gamma )</th>
<th>( h ) (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>12.1</td>
<td>36.1</td>
<td>0.067</td>
<td>1.264</td>
<td>2.7</td>
</tr>
<tr>
<td>B</td>
<td>19.4</td>
<td>60.0</td>
<td>0.108</td>
<td>1.135</td>
<td>5.2</td>
</tr>
<tr>
<td>C</td>
<td>16.6</td>
<td>70.1</td>
<td>0.092</td>
<td>1.062</td>
<td>2.4</td>
</tr>
</tbody>
</table>

3. \textit{Theoretical Consideration}

Solute concentration around the macrostep can be given by solving 2-dimensional diffusion equation. Quite similar problem have been already solved by one of the present authors (Chernov) and Dudurov, who calculated the solute concentration distribution along the riser plane.\(^6\)\(^7\) In their treatment, they assumed that the growth occurs only on the riser surface. But, in the present case, it is clear the growth occurs also on the tread. So, we extend their treatment to cover the case where growth occurs all over the macrostep surface.

Let us consider Schwarz-Christoffel transformation,

\[ w = \mu_0 \int_0^x (t + 1)^a (t - 1)^a \, dt + w_0 \]  

which defines a relation between two vectors in \( w \) and \( z \)-plane. In Eq. (1), \( w_0 \) is the vector to the middle point of the riser from an origin (arbitrary) in \( w \)-plane. By this transformation, the part above \( A'-A-B-B' \) in \( w \)-plane is mapped into upper half of \( z \)-plane and the points A and B are translated into \( x = -1 \) and...
\[ r = \mu_0 \int_{-1}^{x} \left( \frac{1 + t}{1 - t} \right)^a \, dt \]
\[ = 2 \mu_0 \, S \, \frac{1}{\alpha + 1} \, _2F_1 \left( 2, \alpha + 1, \alpha + 2; -S \right) \]  \hspace{1cm} (2)

where
\[ \mu_0 = \frac{a \sin \alpha \pi}{2 \alpha \pi}, \]
\[ S = \frac{1 + x}{1 - x} \]  \hspace{1cm} (3)

and \(_2F_1 (\alpha, \beta, \gamma; z)\) is hypergeometric function. As will be shown in the later section, non-linearity of the translation is not large for usual LPE macrostep.

The solute concentration expressed in \(z\)-plane is given by
\[
C(z) = \text{Re} \left\{ \frac{q_2 \mu_0}{\pi} \int_{-\infty}^{1} \ln|z - \xi| \left( \frac{\xi + 1}{\xi - 1} \right)^a \, d\xi \right\}
\]
\[ + \text{Re} \left\{ \frac{q_1 \mu_0}{\pi} \int_{-1}^{1} \ln|z - \xi| \left( \frac{1 + \xi}{1 - \xi} \right)^a \, d\xi \right\}
\]
\[ + \text{Re} \left\{ \frac{q_2 \mu_0}{\pi} \int_{1}^{\infty} \ln|z - \xi| \left( \frac{\xi + 1}{\xi - 1} \right)^a \, d\xi \right\} \]  \hspace{1cm} (4)

where \(q_1\) and \(q_2\) are defined respectively as
\[ q_1 = \frac{v_1 \, C_s}{D} \]

and
\[ q_2 = \frac{v_2 \, C_s}{D} \]

Here, \(D\) and \(C_s\) are respectively diffusion coefficient and concentration in the grown crystal of the solute, in this case phosphorus in gallium solution. To calculate the concentration on the growing surface, \(C^*\), it is easier first to
calculate gradient along the surface and then to integrate it. The gradient of \( C* \) can be given in analytical formula as,

\[
G (x) = \frac{aq^2}{2 \alpha \pi} \{ -S^\alpha - 1 \} \left( \gamma - \cos \alpha \pi \right) \quad x > 1, \ x < -1 \\
= \frac{aq^2}{2 \alpha \pi} \{ \cos \alpha \pi - \gamma - S^\alpha \left( 1 - \gamma \cos \alpha \pi \right) \}, \quad 1 > x > -1
\]

(5)

where \( \gamma = q_1 / q_2 \). Although \( C* \) can be also expressed analytically using hypergeometric function, the numerical calculation is not easy to carry out. Instead of using this expression, it is much easier to calculate \( C* \) by integrating Eq. (5) numerically. Since the calculated \( C* \) diverges to infinity as the distance from the riser increases, one can not use the boundary condition at infinite point. To determine one integral constant involved in \( C* \), we use another differential equation which is derived from the requirement of the steady state growth of the macrosteps. As mentioned before, the riser is largely misoriented from a singular tread. This means the riser has large kinetics coefficient \( \beta_1 \) which is defined as

\[
\beta_1 = \frac{\nu_1}{C* - C_e}
\]

(6)

where \( C_e \) is the equilibrium concentration of the solute on the growing surface. We assume here that \( \beta_1 \) is large and constant all over the riser surface. This assumption allows us to write

\[
C_s \nu_1 = \beta_1 \left[ C* - C_{eo} \left( 1 - \frac{\Gamma_D}{(1 + p^2)^{3/2}} \frac{dp}{dx} \right) \right]
\]

(7)

where \( C_{eo} \), \( \Gamma_D \) and \( p \) are respectively the equilibrium concentration of the solute for a planar interface, the capillary constant and the slope of the surface. In the following calculation, \( \Gamma_D = 0.7 \times 10^{-7} \) cm is used tentatively.\(^5\) \( p \) is give by

\[
p = \frac{dy}{dx}
\]

(8)

where \( y \) denotes the position of the surface. Since \( C* \) is given as a function of \( x \) except one integral constant, Eq. (7) can be solved numerically using Runge-Kutta method to give a correct shape of the macrostep as originally employed for \( C* \) calculation. Since the actual shape of the riser is sinusoidal, the points of \( p = 0 \) are not necessarily \( x = \pm 1 \). To avoid discontinuity in supersaturation
\[ \sigma = \frac{C^*}{C_e} - 1 \]  

(9)

on the bottom tread \((x>0)\), one can determine one of the positions for \(p=0\). The other point is determined to give the correct height of the macrostep.

4. **Numerical Calculation**

Firstly, the calculation have been carried out for macrostep A in Fig. 1(a). Figure 3 shows the relation between \(r\) and \(x\) given by Eq. (2). The maximum distortion occurs at the middle of the riser. Namely, the mid point of the riser in real space is translated into the point at \(x=0.1\) which means maximum 10% in error when one uses \(x\) instead of \(r\) coordinate to express the riser. Since this value is not large, we shall give the concentration as a function of \(x\).

![Graph](image)

**Fig. 3.** \(r\)-\(x\) relationship calculated by Eq. (2) for the macrostep A.

To find \(C^*\), in the first step, we assume \(\beta_1=\infty\) in Eq. (7). Then, an integral constant involved in \(C^*\) can be uniquely determined by the process described in the last part of the previous section. Thus determined positions of riser-tread boundary are given as \(x=-1.2\) and \(x=1.7\). Once the integral constant is determined, \(C^*\) is readily calculated for finite \(\beta_1\) and is shown in Fig. 4. The amount of super saturation, \(C^*-C_e\), changes as a function of position and is shown in Fig. 5 for \(\beta_1=1.0\) cm/sec. If we use different \(\beta_1\), the curve simply shifts vertically, for instance, the curve shifts downward for the bottom to touch the line of \(C^*-C_e=0\) for \(\beta_1=\infty\). One sees in Fig. 5 that the supersaturation is unsymmetrical, namely the supersaturation on the upper tread is higher than that on the lower tread. This is the result of unsymmetry in
Fig. 4. Surface concentration of the solute $C^*$ for the macrostep A measured from $C_{eo}$. Riser-tread boundary locates at $x= -1.2$ and 1.7 respectively for the upper and the lower treads.

Fig. 5. Distribution of supersaturation ($C^*-C_o$) over the macrostep A with $\beta_1 = 1.0$ cm/sec.

The macrostep shape. The change of $C^*$ on the riser is compensated by Gibbs-Thomson effect to give uniform supersaturation.

The shape of the macrostep can be reproduced by integrating $p$ which is the solution of Eq. (7) and is shown in Fig. 6. Since $p$ and $dp/dx$ is directly related with $C_o$, the macrostep shape is independent of $\beta_1$ and is uniquely determined. It is almost sinusoidal in good agreement with the actual macrostep. The broken line in the same figure shows the assumed macrostep shape to obtain $C^*$ from Eq. (5).

As another example, the similar calculations have been made for the macrostep B and C in Figs. 1(a) and (b). Figures 7 and 8 shows $C^*-C_{eo}$ as a function of position for macrostep B and C respectively assuming $\beta_1 = 0.5$
Fig. 6. Theoretically reproduced shape of the macrostep A (solid line) and the simplified one originally employed in solving the diffusion equation (broken line).

Fig. 7. Distribution of $C^*$ for the macrostep B given in Fig. 1(a). $\beta_1 = 0.5$ cm/sec is assumed.

Fig. 8. $C^*$ vs $x$ for the macrostep C given in Fig. 1(b). $\beta_1 = 0.5$ cm/sec is also assumed.
cm/sec. In both cases, unsymmetric behavior of $C^*$ is much more enhanced than that of the macrostep A. We shall discuss this point later.

5. Discussion

It has been pointed out that in semiconductor LPE the average growth rate is completely given by diffusion theory. Hsieh obtained LPE growth rate of GaAs experimentally and found the growth obeys diffusion law for very wide range of the growth time, such as from 10 sec to several ten minutes.\textsuperscript{12} Ghez et al. derived an expression for the growth rate when both diffusion and kinetics control the growth.\textsuperscript{13} Numerical calculation using this expression shows, for the kinetics coefficient $\beta$ larger than $0.1$ cm/sec, no significant difference is found in the growth rates of the diffusion and the partly kinetics controls for the growth time longer than 10 sec. This means, for typical semiconductor LPE, we can choose the average kinetics coefficient larger than $0.1$ cm/sec. Hence, the kinetics coefficient on the riser must be much larger than this value. If we tentatively choose $\beta_1 = 0.5$ cm/sec, we get $\beta_2$ on the upper and the lower treads respectively $0.08$ cm/sec and $0.14$ cm/sec. Even if we choose $\beta_1 = \infty$, $\beta_2$ differ not much and are $0.10$ cm/sec and $0.22$ cm/sec respectively. Hence, we can conclude that $\beta_2$ is of the order of $0.1$ cm/sec which is consistent with the experimental results given by Hsieh. The supersaturation on the tread is given in the same way as $\sim 0.01\%$. This value is very small from the view point of usual crystal growth experiment.

As shown in Figs. 1(a) and (b), impurities such as Zn and O are doped inhomogeneously. It is shown that impurity with segregation coefficient less than unity is doped much more on the tread than the riser.\textsuperscript{10,11} This has been understood as the well-known faceting effect. Namely, on the tread such impurities are doped with high concentration due to the non-equilibrium segregation at rapidly moving front of atomical step. In Si melt growth, this faceting phenomenon is believed to occur due to the failure of statistical selection at kink site of the step since the step moves there with the velocity some times as high as $2$ m/sec.\textsuperscript{14} On the other hand, in semiconductor LPE, supersaturation is so low that one can not apply the same mechanism as Si. Actually by substituting $\sigma = \Delta \mu / kT$ of the present case into the equation (26) given in ref.(15), one finds no deviation from the equilibrium distribution coefficient. Another mechanism to explain the faceting phenomena has been given by one of the present author (Chernov). This is called diffusion relaxation model.\textsuperscript{16} A characteristic parameter for this model is give as $D_s / \nu h_s$, where $D_s$ is the diffusion coefficient of the impurity near the growing interface and in the solid, $\nu$ is the vertical growth velocity and $h_s$ is the height of the growth step. If we take $D_s$ the same as bulk value, $D_s / \nu h_s$ is now of the order of $10^{-4}$ which is much less than unity and this means diffusion relaxation time is much less than that required for the growth step to cover the growing
surface. In other words, the segregation is not carried out in equilibrium. However, since no information is available on the actual number of $D_{ax}$, we can not proceed the discussion further except one suggestion that the diffusion relaxation model is much better to explain the faceting phenomena in semiconductor LPE. Finally, we will compare the supersaturation distribution of the macrostep B and C with that of the macrostep A. In the case of the macrostep B, the difference of the supersaturation between the upper and the lower treads is very large in comparison with the macrostep A. This is simply because the macrostep B is twice as high as the macrostep A. To keep the growth rate of both treads equal, the supersaturation of the lower tread decreases to give an equal concentration gradient. It is possible only if the kinetics coefficient of the lower tread increases to keep the growth rate constant. In other words, large density of the atomical step should exists there to keep the steady state growth of large macrostep. If there are not enough atomical step, the macrostep may gain the height continuously.

Macrostep C is interesting because it moved very slowly during the growth although the height is almost the same as the macrostep A. The supersaturation on the treads of the macrostep C is relatively small, namely less than the half of the macrostep A. This is because the growth rate of the treads is very close to that of the riser, in other words, the growth occurs almost uniformly over the macrostep. To realize this situation, again one must assume large density of atomical step, this time, on both of the upper and the lower treads. These facts indicate that the shape and the propagation velocity of the macrostep is determined by the density of atomical step existing on the treads. Namely, the density of screw dislocation is one of the key factors determining the behavior of the macrostep.

6. Conclusions

Solute concentration distribution over the LPE macrostep has been calculated theoretically using the experimentally determined parameters. The calculation shows that the concentration is quite unsymmetric on both sides of the riser reflecting the unsymmetric shape of the macrostep. The shape of the macrostep is reproduced theoretically. It is almost sinusoidal in good agreement with the experiment. This means the concentration change along the riser can be compensated completely by Gibbs-Thomson effect. By assuming the kinetics coefficient on the riser, one gets the value of the supersaturation on the treads. Since the average value of the kinetics coefficient over the macrostep is estimated larger than 0.1 cm/sec, the supersaturation on the tread must be of the order of 0.01%. This value is very small in comparison with the usual solution growth. It is concluded that the statistical selection model can not explain the impurity doping inhomogeneity around the LPE macrostep. On the other hand, it has been suggested that
diffusion relaxation model is much better to explain the inhomogeneity. The calculation of $C^*$ for other macrosteps suggests that the density of atomic step on treads is very important in determining the behavior of the macrostep.

This work was supported in part by the Kurata Research Grant.

REFERENCES


Discussion

Müller-Krumbhaar
You seem to be solving the Laplace-equation. What is the boundary-condition far away from the interface?
A: We don’t use that boundary condition; instead we have used condition for steady state growth.

Van der Eerden
Can you explain what is the role of the Gibbs-Thomson effect in your calculation. Is it in fact a two step-type of calculation.
A: On the riser, concentration change is cancelled by Gibbs-Thomson effect to give a uniform supersaturation and hence uniform growth. I don’t know what you mean “two step-type”. The procedure to find surface concentration $C^*$ is as follows. 1st we assume a shape of macrostep and calculate to find $C^*$. Then, the integral constant involved in $C^*$ is determined by the requirement for steady state growth.

Kuroda
I have a question about experimental value of $\beta$. When $\beta$ was estimated experimentally, what value of surface supersaturation $\sigma_s$ was used? If $\sigma_s$ was assumed to be equal to the supersaturation of bulk solution, the value of $\beta$ was underestimated.
A: The supersaturation has been determined by the calculated surface concentration $C^*$ assuming a certain value for the kinetics coefficient of the riser. We don’t use bulk supersaturation.