

# Selective Liquid Phase Epitaxy of GaAs; Kinetics and Morphology

(비소화갈륨의 선택적 액상 에피층 성장; 성장기구 및 형태)

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## 要 約

비소화갈륨의 선택적 액상 에피성장 기구로서 보통의 액상 에피층 성장에서의 확산에 의해 결정되는 과정과는 달리 표면에서의 반응에 의해 결정성장이 결정됨을 제시하였고, 그 실험적 증거들을 보였다. 2차원 확산 방정식의 컴퓨터 계산에 의하여 이러한 현상들이 2차원적 확산에 의한 물질전달의 증가에 의하여 나타날 수 있었음을 보였으며 성장형으로서 저지수 결정면들의 형성, 고지수 결정면들이 저지수 결정면으로 분리되는 원리, 이러한 저지수 면들이 광집적회로의 각종소자들에 유용함을 언급하였다. 그리고 이러한 현상들이 III-V족 복합 반도체에서 공통적인 현상임을 예측하였다.

## Abstract

In contrast to conventional liquid phase epitaxy of GaAs, surface kinetics limited growth is predominant in selective liquid phase epitaxy. For the stripe openings in the high-index crystallographic directions, the well-known facet formations and the decompositions into the low index planes or smooth circular surfaces are observed depending on the growth kinetics. For the low index direction stripe, surface kinetics limited growth is evident. By a numerical calculation we show that these phenomena are due to the enhanced mass transport by two dimensional diffusion and growth rate anisotropy which is found to be very strong with cusped minima for some singular planes in the solution growth as well as in vapor phase epitaxy. Morphological stability is briefly treated in terms of diffusion and its implications on device application are stated. These phenomena may be common to III-V compound semiconductors as well as GaAs.

## I. Introduction

Selective epitaxy of III-V compound semiconductors has a very high potential of applications to the optoelectronic integrated circuit (OEIC) technology where two less compatible fabrication processes, one for optical devices

and the other for electronic devices, should be employed. Not only for the OEIC technology, selective epitaxy is also a very useful technique for the pure optical and electronic device applications. Because of these versatilities, it has been studied for a long time since the early 1960's. Virtually all the epitaxial techniques, such as vapor phase epitaxy (VPE) [1], liquid phase epitaxy (LPE) [2], metal-organic chemical vapor deposition (MOCVD) [3], molecular beam epitaxy (MBE) [4], have been applied to the selective epitaxy of GaAs.

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The word 'selective epitaxy' has been simultaneously used for some different techniques. The first is a selective area growth technique which uses an inert amorphous films, which are deposited onto the seed substrate as an epitaxial mask to prevent nucleations. Materials for the epitaxial mask should be thermally, chemically, and mechanically stable. Hence dielectrics such as  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$  and refractory metals as Ni, W were often used. The second is a shadow mask technique which is possible only for MBE and chemical beam epitaxy where the source materials for the epitaxial growth are transported onto the seed substrate in a form of beams. The third technique is an epitaxial growth onto an etched substrate, where thermodynamics and kinetics of the epitaxial growth suppress or enhance the growth rate depending on the surface topography of the seed substrate. This is the very widely used technique for the development of the various 3-dimensional waveguide structures for laser diodes. In this study we will use the word 'selective epitaxy' by the first sense using RF-sputtered  $\text{SiO}_2$  film as an epitaxial mask.

Application area of the selective epitaxy is very wide. Some successful applications include laser diodes [5,6], integrated optical circuits [7,8], waveguides [9], power FETs [2], and permeable base transistors [10]. Some of these owe to the lateral over-growth.

For the selective liquid phase epitaxy (SLPE) of GaAs/GaAlAs, in spite of some successful applications to laser diodes [5,6], integrated optical circuits [7], and power FETs [2], full exploitation has not been achieved. This is partly due to the poor controllabilities and morphologies, the lateral over-growth and the enhanced edge growth. But, proper epitaxial growth enables the naturally grown mirror facet for laser diodes, and reduction of scattering loss in laser diodes and other important optical elements including optical waveguides, which are very useful characteristics for OEIC application. Hence deep understanding on the growth mechanism in SLPE, which is seldom studied, may be emphasized.

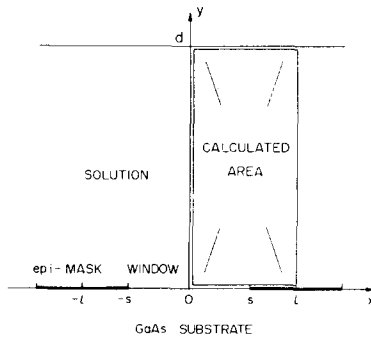
In this study, we would like to discuss about the epitaxial growth mechanism in SLPE of GaAs. It is shown that grown crystals have a tendency to become an equilibrium form in

order to minimize the surface free energy and this form can be understood consistently by considering the growth rate anisotropy. It is also shown that growth on the low Miller index surfaces, such as (111) Ga, (111) As, (100), is a surface kinetics limited process on the contrary to the diffusion limited growth in conventional large area liquid phase epitaxy. In chap. II, numerical results under the assumption of diffusion limited growth are presented. Experimental procedures are described in chap. III. Growth kinetics and its morphological implications are discussed in chap. IV by comparing with the results of chap. II. Finally, some conclusions are drawn in chap. V.

## II. Numerical Implementation; A Diffusion Limited Growth

Liquid phase epitaxy can be considered as a serial process consisting of mass-transport of the constituent materials and nucleation on the seed substrate. If the growth rate of the epitaxial layer is determined by the mass-transport of the two serial processes, it may be said that the growth is a mass-transport limited process. Otherwise it is often called a surface kinetics limited process. Two mass-transport mechanisms may be considered in the LPE of GaAs. One is diffusion, and the other is convection. Convection is known as a cause of the instability in growth rate, but it can be neglected. It is a well known fact that conventional large area liquid phase epitaxy of GaAs is a diffusion limited process, that is, the growth rate of the epitaxial layer is mainly determined by the diffusion of the As atoms in the Ga solution. Moreover, usually used graphite boat and Ga solution system has so high a thermal conductivity that isothermal approximation may be valid. This is the isothermal diffusion theory of LPE proposed by D.L. Rode [11].

This chapter deals with the formulation and the numerical results based on the isothermal diffusion theory to give a reference to the subsequent discussions. Hence any attempts to compare with the experimental results are not made. Detailed comparison with experimental results will be published afterwards. As a consequence, problem reduces simply to solving a



**Fig.1.** A schematic cross-sectional diagram showing the numerical field for the two dimensional diffusion equation.

two-dimensional diffusion equation with some proper boundary conditions as [Fig. 1];

$$D(T)\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) - \frac{\partial C}{\partial t} = 0 \quad (1)$$

$$\frac{\partial C}{\partial y} = 0 \quad \text{at } x = [0,1], y = d \\ x = [s,1], y = 0 \quad (2)$$

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } y = [0,d], x = 0 \\ y = [0,d], x = 1 \quad (3)$$

$$C = C_0(T) \text{ at } x = [0,s], y = 0 \quad (4)$$

$$C_0(T) = 2.19 \times 10^{26} \exp(-1.32 \times 10^4/T) \quad (5)$$

$$D(T) = 8.6 \times 10^{-4} \exp(-3240/T) \quad (6)$$

$$T = T_0 - \alpha t \quad (7)$$

where  $C$  = the As concentration in the solution in atoms/cm<sup>3</sup>

$C_0$  = the equilibrium As concentration in the solution in atoms/cm<sup>3</sup>

$d$  = the solution thickness in cm

$l$  = one half of the separation between the nearest windows in cm

$s$  = one half width of the stripe openings where epitaxial layers are to be grown in cm

$t$  = time in sec

$T$  = temperature of the system in °K

$T_0$  = initial temperature of the system in °K

$D$  = Diffusivity of the As atoms in the solution in cm<sup>2</sup>/sec

$\alpha$  = the cooling rate of the substrate temperature in °K/sec

Eq.(1) is a usual 2-dimensional diffusion equation with the diffusivity which is temperature-dependent but not concentration dependent. As is evident, the equation does not consider the moving boundary between the solution and the growing crystal, which can be conveniently neglected. Eq. (2) is a result of neglecting the As-evaporation loss that is known as negligible. Considering the symmetry, Eq.(3) is a natural consequence. Eq.(4) means that the solid-liquid interface is in equilibrium and the growing process is diffusion limited. This is not a valid assumption in a strict sense especially for the low Miller index surfaces, such as (111) Ga, (111) As, and (100) planes.

Let us define the relative supersaturation as;

$$\sigma = \frac{C_s - C_0(T)}{C_0(T)} \quad (8)$$

where  $C_s$  is the As concentration in the solution at the growing solid and solution interface. The values of this relative supersaturation are reported by T. Bryskiewicz [12], who calculated the values from a model equation which relates the growth rate with the  $\sigma$ . He also calculates the values by solving the one dimensional diffusion equation and comparing the calculated growth rate with the experimental one.

The reported values at the low index planes are nearly zero at the initial stage of growth with equilibrium cooling technique and increase with growing time in the case of fairly large cooling rate of 5°C/min for conventional large area LPE. Interesting fact of his results is  $0 \leq \sigma(100) \leq \sigma(\bar{1}\bar{1}\bar{1}) \leq \sigma(111)$ . This result shows that even in the conventional large area LPE surface kinetics plays an important role for the low index planes. And this surface kinetics limited growth becomes evident as the cooling rate becomes high and the time elapses, i.e., as the flux increases. As is discussed in the chap. IV, this is more evident in the case of SLPE by the enhanced mass transport due to the two dimensional diffusion even in the case of small cooling rate. Another factor which should be

taken into consideration is the anisotropy of the surface free energy and the finite curvature of the grown crystals. In comparison to the conventional large area LPE, the grown epitaxial layers necessarily have more surface-to-volume ratio and exhibit various crystal surfaces. Because of these, the equilibrium concentration of the As atoms on these selectively grown epitaxial layers is given as

$$C/C_e = \exp\{ (V_c^0/kT)[(\gamma + \partial^2\gamma/\partial\theta^2)/r_1 + (\gamma + \partial^2\gamma/\partial\theta^2)/r_2]\} \quad (9)$$

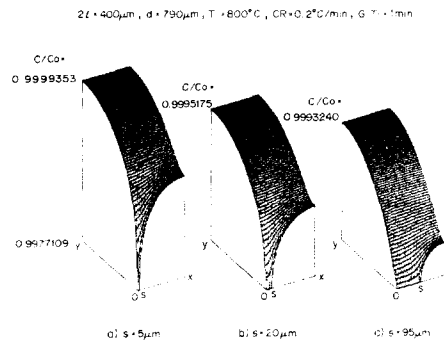
Where C is the equilibrium concentration taking into consideration the anisotropy of the surface free energy and the finite curvature of the grown crystals,  $V_c^0$  is the atomic volume of the condensate,  $C_e$  is the equilibrium concentration for the planar crystal surface, k is the Boltzmann constant, T is the absolute temperature,  $\gamma$  is the surface free energy and  $r_1, r_2$  are the principal radius of curvature of the condensate in the direction of the coordinate axis  $\theta_1, \theta_2$ , respectively. For the isotropic case Eq.(9) shows that the selectively grown epitaxial layers require more-saturated solution compared to the conventional large area LPE in order to maintain equilibrium. For the GaAs, the anisotropy of  $\gamma$  is conspicuous still in the growing high temperature and must be considered.

But in this numerical implementation these kinetic and thermodynamic effects are not considered because it is not our main concern. Expected difficulties in such a rigorous treatment are not only numerical complexities but also inaccessibilities to the thermodynamic parameters which may be orientation and temperature dependent. Eq. (5) and Eq.(6) are temperature dependences of the equilibrium concentration and the diffusivity of the As atoms in the solution, respectively. Eq. (7) indicates an equilibrium cooling. Extension to step-cooling or supercooling is a very simple problem, and in this study only the equilibrium cooling is considered. Finally there are some possibilities that the isothermal condition may not be applied because of poor thermal conductivity of the SiO<sub>2</sub> epitaxial mask although the film is very thin. This effect, combined with the stress due to a difference in thermal expansion coefficients of SiO<sub>2</sub> and GaAs, may

be suspected to be a cause of local meltback in SLPE.

Prior to discretization all the variables and the parameters are normalized into the dimensionless numbers. Because of the computational simplicity, the Mitchel-Fairweather algorithm [13] of alternating direction implicit method is used with slight modifications to incorporate a non-uniform grid scheme. This method has a local truncation error O [2,4], and has a further advantage of reduction of computer time by eliminating the unnecessary double calculations in each direction implicit.

Fig. 2 shows the As concentration distribution calculated for various conditions. As is evident from the figures, the concentration gradient, hence the flux is larger in the window edge than in the center. This larger flux leads to the enhanced edge growth and the center depressions, and these phenomena are experimentally observed. Further details are discussed in the chapter IV. Another point which should be pointed out for this case of  $1 < d$  is that equi-concentration lines are nearly parallel to the solution-substrate interface except for near to that interface especially when  $1 \ll \sqrt{D \cdot t_{gr}}$ . This means that the concentration field in the SLPE is similar to that in the conventional large area LPE, hence it can be said that the amount of the transported mass in SLPE is nearly the same as that



**Fig.2.** Three dimensional plots showing some numerical results with initial growing temp.; 800°C, step size  $\Delta x$ ; 5  $\mu m$ ,  $\Delta y$ ; 10  $\mu m$ ,  $\Delta t$ ; 0.1 sec, cooling rate; 0.2°C/min, growing time; 1 min, and window half-width of a) 5  $\mu m$ , b) 20  $\mu m$ , c) 95  $\mu m$ .

of the transported mass in conventional large area LPE almost independent of the stripe width if the relation  $1 \ll \sqrt{D \cdot tg}$  is satisfied. But epitaxial growing is confined only to the window region, it is expected that the thickness of the grown epitaxial layer is nearly inversely proportional to the stripe window width  $2s$  unless the ratio  $s/l$  is too small. This fact is clearly shown in Fig.3a). From this argument it may be concluded that the average thickness of the grown epitaxial layer  $h$  is given by

$$h \approx h_0 \frac{1}{s} \quad \text{for } 1 < \sqrt{D \cdot tg} \quad (10)$$

$$h_0 \sqrt{D \cdot tg} \quad \text{for } 1 \geq \sqrt{D \cdot tg}$$

where  $D$  = the average diffusivity of the As atoms in the solution  
 $tg$  = the growing time  
 $h_0$  = the epitaxial layer thickness for  $s = 1$ , i.e., for conventional large area LPE.

For the case of  $1 \geq \sqrt{D \cdot tg}$ ,  $1$  is replaced by the diffusion length  $\sqrt{D \cdot tg}$ , and the reason is evident because only the As atoms inside the area defined by the diffusion length can contribute to the epitaxial growing by diffusion. Thus the layer is about  $\frac{1}{s}$  or  $(D \cdot tg)^{1/2}/s$  times thicker in the selective epitaxy than in the conventional large area LPE.

When the ratio  $s/l$  is small somewhat large deviation from Eq.(10) is observed in Fig. 3a). This is due to the small As sinking capability of the narrow window as is evidenced in Fig. 2 and due to the fact that the validity condition  $1 < \sqrt{D \cdot tg}$  is not satisfied. This regime is particularly important from the kinetic viewpoint, and Fig. 3b) shows the grown layer thickness as a function of the inter-stripe separation for 10  $\mu\text{m}$  wide stripe window with growing time as a parameter. The grown layer thickness increases linearly for small values of  $l$  and saturates to a limiting value. The value of the inter-stripe distance at which the thickness  $h$  starts to saturate is, of course, given by the diffusion length of the As atoms in the solution. Hence the saturation is more evident for the curves of shorter growing times.

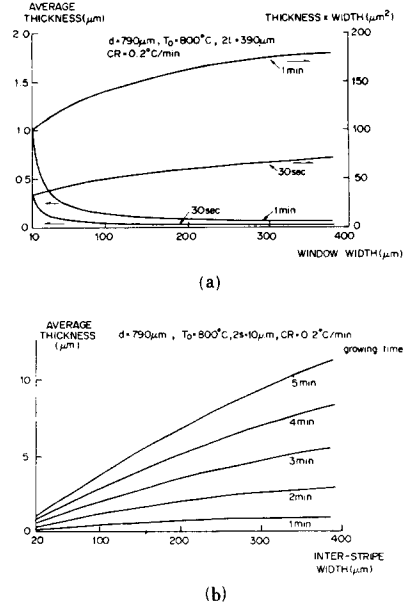
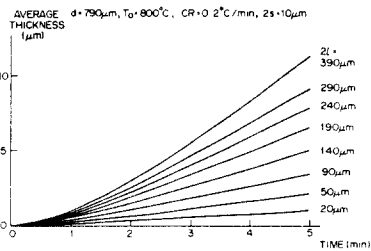


Fig.3. a) Numerical results which show a relationship between the grown layer thickness and the stripe window width. It is shown that amount of the crystallized mass is nearly constant.  
 b) Grown layer thickness for a constant window width of 10  $\mu\text{m}$  as a function of inter-stripe distance with growing time as a parameter.

Fig. 4 shows the time dependence of the grown layer thickness for some values of the inter-stripe separation. In addition to the higher growth rate for the windows of larger inter-stripe separations, there are noticeable changes in the slope of each curve.

When the growing time is sufficiently long so that the corresponding diffusion length is comparable to or larger than the solution depth, reduction of the growth rate due to the source limitation occurs. In this regime the time dependence of the layer thickness changes from  $t^{3/2}$  to linear dependence for the equilibrium cooling case in conventional LPE. This is also the case for SLPE. Thus for longer growing times the curves become linear irrespective of the inter-stripe separations. Note that the transition time at which the time dependence changes is shorter for larger  $s/l$  ratio windows.



**Fig.4.** Grown layer thickness with time. This shows an approximately  $t^{3/2}$  dependence same as for equilibrium cooling in the conventional LPE. Linear dependence for growing time longer than about 3 minutes is due to source limitation, i.e., because the solution depth is not much larger than the corresponding diffusion length.

At the initial stage of growing, the window have a two-dimensional exposure to the saturated solution in SLPE contrary to the one-dimensional exposure in conventional LPE, and the exponent to the time is larger than  $3/2$ . Thus for the curve of  $2l=390\text{ }\mu\text{m}$  in Fig. 4, the exponent decreases monotonically with growing time from 1.623 at the first 1-minute to 1.375 at the fifth 1-minute interval, and eventually converges to 1.0. The transition time at which the value becomes less than  $3/2$  is 3 minute with the corresponding diffusion length of  $869\text{ }\mu\text{m}$  which is comparable in magnitude to the solution depth of  $790\text{ }\mu\text{m}$ . Similar curves as Fig. 4 can be obtained for a fixed value of the interstripe separation with the window width as a parameter.

Additionally considering two major assumptions in deriving the  $t^{3/2}$  dependence, which are constant diffusivity and linear liquidus relation, it becomes evident that deviations from those assumptions may result in the slight deviations from the  $t^{3/2}$  dependence because the approximations are sufficiently accurate for this small cooling. Therefore above discussions on growth rate are to be more accurate for step cooling technique with sufficiently thick solution, where constant growing temperature justifies the above assumption on constant diffusivity and linear liquidus approximation is not needed any more. Of course, in this case of step cooling, the grown layer

thickness has a  $t^{1/2}$  dependence instead of the  $t^{3/2}$  dependence in equilibrium cooling.

From the above discussions we can draw following conclusions.

- 1) When the inter-stripe distance  $2l$  is less than the diffusion length of the As atoms in the solution, the total amount of the transported As atoms by diffusion in selective liquid phase epitaxy is nearly constant independent of the window width  $s$  and nearly equals to that in conventional large area LPE. Therefore the averaged grown layer thickness is  $1/s$  times as large as that in conventional large area LPE as given by the Eq.10.
- 2) The concentration gradient hence the flux of the As atoms is larger in the stripe-window edge than in the center. Therefore enhanced edge growth and center depression are expected.
- 3) Because the diffusion of the As atoms in the solution is an isotropic process, any orientation dependence cannot be expected.
- 4) For the stripe-windows with small ratio of  $s/l$  deviations to the Eq.10 are observed due to the small sinking capability.
- 5) The grown layer thickness has an approximately same time dependence as in conventional LPE. The value of the exponent decreases to a value  $3/2$  with the increment of growing time if the solution depth  $d$  is much larger than the corresponding diffusion length.

### III. Experimental Procedures

n-type (100) GaAs wafer doped with Si by  $10^{18}\text{ cm}^{-3}$  is used as a seed substrate. Cutted  $1\text{cm}\times 1\text{cm}$  wafer is cleaned in the boiling TCE, acetone, and methanol for 5 min, respectively. After rinsing with deionized water, photolithography for lift-off is performed. About  $750\text{ \AA}$  thick  $\text{SiO}_2$  film is rf sputter-deposited as an epitaxial mask under forward power of 100 W and rf peak voltage of 800 V. Relatively low peak voltage and thin  $\text{SiO}_2$  film are used for the minimization of sputtering damage and stress resulting from the large difference in thermal expansion coefficients between the  $\text{SiO}_2$  film and GaAs substrate, respectively.

Prebaking of 6N Ga is done at  $880^{\circ}\text{C}$  for 5 hours in the flowing purified  $\text{H}_2$  ambient. After prebaking of Ga, cleaned substrate and source GaAs are loaded. Native oxide on GaAs substrate is removed by dilute HCl. Homogenization of the solution and dummy contact is done at  $800^{\circ}\text{C}$  for 90 minutes and 30 minutes, respectively. And epitaxial layers are grown under a cooling rate of  $0.2^{\circ}\text{C}/\text{min}$ . No intentional dopant is added. Further details were described elsewhere.[14]

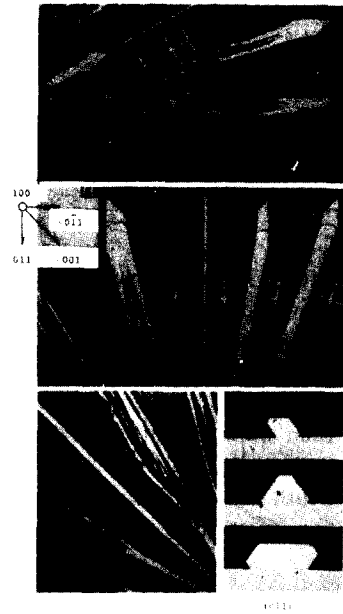
Two types of mask patterns are used in this study. One is composed of long-narrow stripe openings ( $25\ \mu\text{m}$  width  $\times$   $2000\sim 3000\ \mu\text{m}$  length) in various orientations for studying the orientation dependences. And the other is with concentric ring windows for the study of morphology.

#### IV. Results and Discussions

##### 1. Growth Kinetics

Fig. 5 shows typical experimental results which has been selectively grown on a n-type (100) GaAs substrate with the patterned  $\text{SiO}_2$  epitaxial mask for 30 minutes. The windows on which the epitaxial layers are to be grown are  $25\ \mu\text{m}$  wide long-narrow stripes in the directions of every  $10^{\circ}$  or  $15^{\circ}$  with respect to the [011] direction. This figure clearly shows the growth rate anisotropy. Epitaxial layers grown on the stripe windows in the directions of  $0^{\circ}$ ,  $45^{\circ}$  and  $90^{\circ}$  with respect to the [011] direction are very narrow and faithfully reflect the original window shape with small lateral overgrowth. Note that these directions are  $\langle 011 \rangle$  and  $\langle 001 \rangle$  low Miller-index directions. Also note that these epitaxial layers are defined by clear facets which are  $\{111\}$  or  $\{100\}$  planes as is evident in the cross-sectional microphotographs in Fig.5. Morphological stability of these facets is discussed in the next subsection.

The crystals grown on the stripes on the other directions show significant lateral overgrowth about 10 times larger than those of the low-index stripes. And it is also noticeable that the width of the grown crystals decreases as the inter-stripe separation is reduced contrary to the constant width of the epitaxial layers on the low index direction

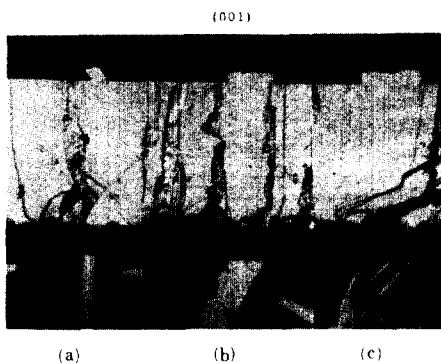


**Fig.5.** Photomicrographs which show strong growth rate anisotropy, surface kinetics, and lateral over growth. Decompositions into the low-index singular facets and reconstructions are also shown. Cross-sectional shapes of the low index direction stripes show clear faceted forms which is enclosed by  $\{111\}$  and  $\{100\}$  planes on which surface kinetics limited process is predominant.

stripes. At the tips of the stripes where the crystals have larger exposure to the solution, decompositions into the low-index singular facets, such as (111) Ga, (111) As, and  $\{100\}$  are clearly observed in Fig.5.

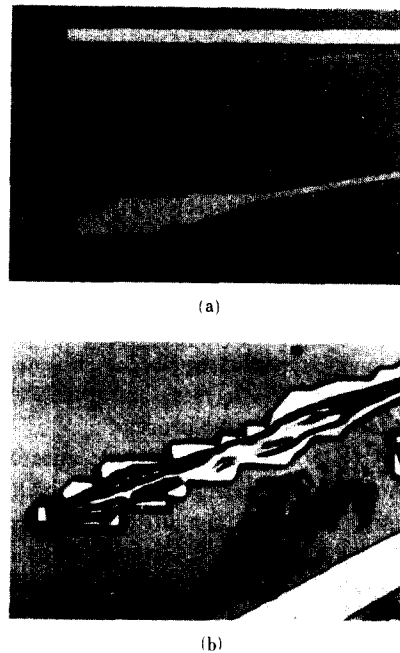
Also shown in Fig.5 is rounded macro-steps which are formed near the tips of the crystals. Remembering the difficulties in the direct nucleation on these singular facets and that the crystal growing on these facets is progressed by the movement of these macrosteps from the tips according to the Kossel mechanism, it may be understood that these macrosteps are formed by the step bunching. As a step moves the inter-stripe distance decreases, and the amount of available mass also decreases as shown in Fig.3b). Because the moving speed of a step decreases, another subsequent step catches up the previous one, thus macrostep will be

formed by a step bunching. Note that the moving speed is slower at the center than at the edge region because of smaller flux in the center region as explained in the chapter II. In addition center depression is evident for wide epitaxial layers. This also can be understood by the smaller flux in the center region. It should be noted that the low index direction stripes where the lateral overgrowth is not so significant have not such center depressions and the stripes retain (100) facets as in Fig. 6. This morphological stability is discussed further in the next subsection.



**Fig. 6.** A comparison of plan views and cross-sectional views for the stripes of a) [011] direction, b)  $30^\circ$ , c)  $40^\circ$  with respect to [011]. Note the coexistence of (100) facet and rounded sidewall in b), and the center depression in c).

Strong tendency to reconstruct the nearest singular facet can be also noticed in the Fig.5. Similar results are shown in Fig.7. This tendency is attributed as a cause of the terrace formation [15] in the conventional large area LPE of GaAs on the slightly misoriented (100) wafer. It is also found that this phenomenon is more pronounced for (111) As planes and destroyed for the critically oriented substrate and diminished at high temperature. At high temperature anisotropy of the surface free energy is weakened and the diminishment of the terrace at high temperature can be understood. But in the selective epitaxy such a terrace structure is not observed for a slightly misoriented stripe by up to several degrees



**Fig. 7.** Epitaxial layers grown on the stripes in the direction of [011] and of  $10^\circ$ ,  $20^\circ$  with respect to [011]. Strong tendency to reconstruct the singular facets is clearly shown.

because a full reconstruction of the singular facet is possible due to the enhanced mass transport. For the stripes with misorientations of few tens of degrees corrugations whose spatial frequency is dependent on mass transport and higher for a more misoriented stripe are observed. These corrugations may be enclosed by either singular facets or smooth surfaces depending on the kinetics. Thus mass transport has great effects on the formation of a terrace structure.

Up to now various experimental results are presented. In order to obtain a comprehensive understanding of these experimental results some premises are presented.

1) Crystal growing on the singular facets is progressed by the Kossel mechanism, i.e., two dimensional nucleation [16]. As explained previously epitaxial layer is grown by the step movement because of difficulties in direct nucleation on the singular surface under the low supersaturation. Nucleation may take place on the edges where the



nucleation barrier is small and the solution is more supersaturated. Of course direct nucleation on the singular facet may be also possible under sufficiently high supersaturation of the solution. But in the liquid phase epitaxy where equilibrium prevails such a situation may be seldomly encountered especially for low cooling rate. This nucleation limited process is called as a "surface kinetics limited process". For the high-index planes nucleation centers are so sufficient that mass transport by diffusion determine the crystal growth rate, and this situation is a "diffusion limited process".

- 2) (111) Ga, (111) As, and  $\{100\}$  planes of the GaAs crystal are singular ones which have cusped minima in the surface energy polar plot.[11] Since  $\int \gamma dA$  is minimum in the equilibrium state these singular planes have strong tendency to reconstruct in order to minimize total free energy by enlarging themselves instead of the other high surface energy planes.

It may be mentioned that premise 1) and 2) are closely related. Roughly speaking, the smaller the surface energy of a singular crystallographic plane is, the more atomically smooth the plane becomes. Therefore growth rate on that plane has a local minimum due to the high nucleation barrier in a surface kinetics limited regime and as crystal growing proceeds the plane becomes a major constituent surface determining the crystal shape as schematically shown in Fig. 8. Thus it may be possible that thermodynamic consideration and kinetic effect may give consistent results of the crystal shape not in general but in this case of SLPE.

Considering these two kinetic and thermodynamic effects and the conclusions on the diffusional mass transport in Chapter II, it can be concluded that epitaxial growing on the low-index direction stripes is a surface kinetics limited process contrary to a diffusion limited growing on the high-index direction stripes. This conclusion is supported by the much smaller crystallized mass in the low-index direction stripes, which are enclosed by the singular facets, in spite of the same mass transport conditions. Further, growth on the high-index direction stripes is somewhat complicated. For these epitaxial layers both surface

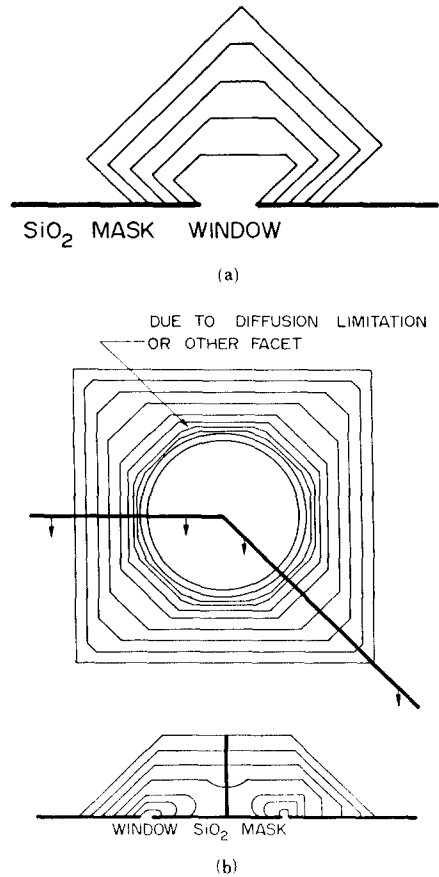


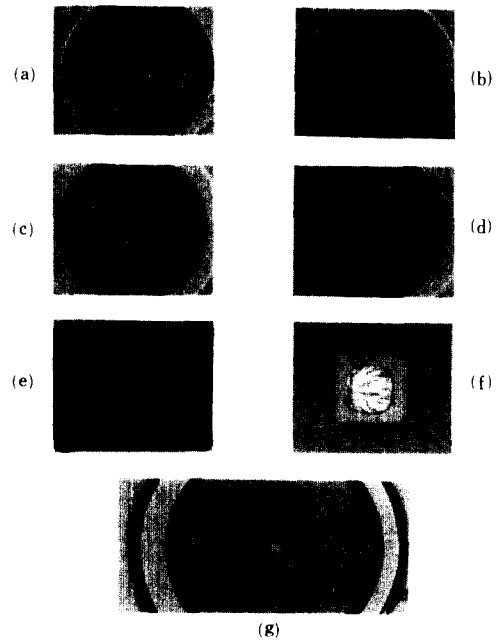
Fig. 8. Schematic diagrams showing a relationship between growth rate anisotropy and growth shape, a) cross-sectional view in surface kinetics limited regime, b) plan view and corresponding cross-sectional view. Failure to facet formation due to the limitation by diffusion is also shown. Compare this with Fig. 9. Shaded ring is a window on which the crystal starts to grow.

kinetics limited process on the singular facet and diffusion limited process on the side walls are coexisting. This is supported by the narrowing of the width of the epilayers, which is a clear evidence of the diffusion limited process, as the interstripe distance decreases, while macro-steps on the singular facets are evidences for the surface kinetics limited process. Thus both kinetics and morphology of a high-index direction stripe are strongly

dependent on the mass transport condition such as inter-stripe distance, stripe width etc., and surface kinetics limited processes are observed only for the singular facets. Close examination reveals that the values of relative supersaturation  $\sigma$  on these facets are larger than 0, i.e., the interfaces are supersaturated.

Another aspect which should be considered is a growth rate anisotropy which determines the shape of the grown crystals in the surface-kinetics limited regime. Fig.8 shows the relationship between the growth rate anisotropy and the shape of the grown crystal schematically. As is evident from the figure only the surfaces with slowest growth rate can be exhibited in a final form for this case of outward growing without a protrusion. For inward growing, only the fastest surfaces can remain. As the crystal growing proceeds outwards crystal planes with relatively fast growth rate disappear sequentially, and finally only some of the slowest crystal planes can remain. Also shown is the way by which mass transport affects the crystal shape through the limitation due to diffusion. In the crystal growing this growth rate anisotropy determines the shape of a grown crystal, which is often called "growth form". On the other hand the anisotropy of the surface free energy determines the crystal shape in equilibrium state satisfying the minimization condition of the total surface free-energy  $\int \gamma dA$ . This shape which satisfies the minimization condition is an "equilibrium form" [17] distinguished from the "growth form". It is not clear for us whether the equilibrium form is identical to the growth form in SLPE of GaAs. But considering the near equilibrium nature of LPE and above discussions on the premise 2) the growth form tends to become the equilibrium form although further study is necessary to the decision. Circular sidewalls in the high index direction stripes, where  $\gamma$  is considered to be isotropic, are believed to exhibit such an equilibrium form. Grown crystals with faceted surfaces also show such a tendency.

Epitaxial layers selectively grown on ring-shaped windows in circular diffusion field for eliminating an orientation dependence of the As flux are shown in Fig.9 in a facet developing sequence which is schematically



**Fig. 9.** Epitaxial layers grown on the ring shape windows with a circular diffusion field. Only the inside and outside area of these ring windows are covered with the  $\text{SiO}_2$  epitaxial mask of concentric circular patterns, which ensures a circular diffusion field. Compare these experimental results with Fig. 8b.

shown in Fig.8b). For the outer edge initial ring shape in (a) which duplicates the mask pattern becomes to exhibit facets where growth rate is slow due to the surface kinetics. Once these facets are revealed, they become more conspicuous due to the slow growth rate and the epitaxial layer is wholly enclosed by the singular facets such as  $\{111\}$  Ga,  $\{111\}$  As and  $\{100\}$  planes in (e). In this stage the outer edge shows clear octagonal shape, while the circular inner edge remains intact. The surfaces of the inner edge are non-singular fastest growth-rate surfaces where diffusion limited process is predominant hence reflecting the circular diffusion field. Finally the octagonal outer edge becomes to a rectangular form which is entirely surrounded by  $\{111\}$  Ga and  $\{111\}$  As planes in (g) since vertical  $\{100\}$  planes which have formed the octagonal edge with  $\{111\}$  planes have higher growth rate than  $\{111\}$  planes. Although

not shown here, pyramidal shape enclosed by the four  $\{111\}$  planes is expected to be a final form. Realizing that the  $\{111\}$  planes are of minimum surface free energy the pyramid may be said to be the equilibrium form. Note the square edge in Fig.9 (g). The four sloped  $\{111\}$  surfaces are composed of two corresponding (111) Ga and (111) As planes, and this square form means that growth rates of these two surfaces are nearly equal. Therefore we can say that growth rate  $r$  in the surface kinetics limited regime has the following relationship;  $r(100) < r(111) \text{ As} \sim r(111) \text{ Ga}$ . Thus crystalline GaAs shows a strong anisotropy both in surface free energy and in growth rate, and this is revealed clearly in SLPE by the confined growth and the surface kinetics limited process due to the enhanced mass transport which is a characteristic feature inherent in SLPE. This strong anisotropy has not been observed in conventional large area LPE due to the limitations by diffusion.

In summary, singular low-index facets are developed in SLPE due to the surface kinetics which could be exhibited by the enhanced mass transport by two dimensional diffusion contrary to the one dimensional diffusion in conventional LPE. Crystal shape is determined by the growth rate anisotropy and the shape is believed to tend to become an equilibrium form which is determined by the anisotropy of the surface free energy because these singular facets have a large nucleation barrier and hence low growth rate. Sometimes these singular facets may become unstable as shown in the center depressions. In the following subsection the morphological stability will be treated.

## 2. Morphological Implications

When an arbitrary perturbation on the morphology decays in time and the interface returns to the original morphology it is said to be morphologically stable. Only a thermodynamic equilibrium form is stable at equilibrium state because it is a shape of minimum surface free-energy. During growth mass transport may be a cause of instability which is known as growth instability compared to thermodynamic instability. In this section we concentrate only

on the growth instability of the singular facets caused by diffusion [18].

In the chapter II it is pointed out that the edges which have larger exposure to the solution receive larger flux of As atoms than the center region. These edges have lower nucleation barrier and higher supersaturation and act as nucleation centers for step generation, thereby epitaxial growing proceeds by the movement of this step. When the mass-transport is sufficient for this step to move full reconstruction of a singular facet, in this case (100) plane, is possible and this facet is stable because the reconstruction of the facet is possible by this step movement when a perturbation on these facet is applied. However, if the width of the grown epitaxial layer is so large that the diffusion of As atoms is insufficient for the step to move in the center region of the stripe, the facet becomes unstable, thus macro steps [Fig. 5] or more seriously center depressions [Fig. 6c] are generated. Fig. 10(a) shows clearly the

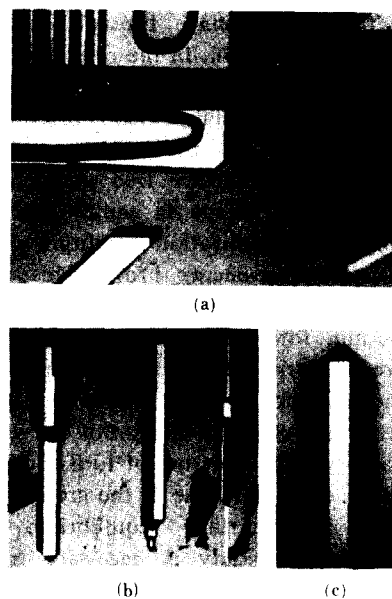


Fig. 10. a) Influences of diffusion and stripe width on the morphological stability of [100] facets.  
 b) Macro-step generations due to exotic barriers which may be caused by some contaminations.  
 c) Typical example of a morphologically stable facet growth on a narrow, low index direction stripe.

effects of diffusion and the width of the epitaxial layer on the morphology. Several factors are related to this phenomenon. One of them is the diffusivity of As atoms in the solution, and a given facet tends to be more stable as the diffusivity increases. The second factor is the nucleation rate at the edge. The higher the rate of nucleation is, the more frequently the step is generated. This requires a larger mass transport to preserve the facet hence the morphology becomes unstable. The third factor is the width of the epitaxial layer. Those epitaxial layers grown on the high index direction stripes exhibit the center depressions more often because lateral overgrowth widens the width of the grown layer significantly. Thus the critical size of the crystals beyond which they become unstable is roughly proportional to the diffusivity and inversely proportional to the nucleation rate at the edges. Because the nucleation rate is a function of supersaturation, the critical size is determined by the distribution of supersaturation over the crystals. Consequently, for a facet to be morphologically stable in SLPE the kinetic coefficient, which relates the growth rate to the supersaturation at the interface, must compensate the supersaturation inhomogeneity inherent in SLPE.

Another factor which affects the morphology is an exotic barrier which inhibits the step movement as in Fig.10 (b). This is also a cause of macrostep generation. Exact nature of the barrier is not identified in this stage.

In conclusion, for the uniform epilayer growing it is preferable for the epitaxial layers to be grown in the surface kinetics limited regime with the morphological stability condition satisfied in view of the inherent inhomogeneity of the interface supersturation in SLPE.

## V. Conclusion

In this study, we present some experimental evidences for surface kinetics limited growth in SLPE of GaAs on the contrary to the diffusion limited growth in conventional large area LPE, and show that mass transport has great influences on the morphologies of the grown epilayers. Decompositions into singular facets and

reconstruction of the facets are observed and understood comprehensively from the kinetic viewpoints. It is also shown that GaAs has strong growth rate anisotropy with cusped minima for low index planes in solution growth as in vapor phase epitaxy.

Wetting properties between the solution and the epitaxial mask material and stress induced by the difference in thermal expansion coefficients as well as some deviations from the isothermal assumption resulting from the poor thermal conductivity of the mask material may have some influences on the kinetics and morphology in SLPE although not considered.

Grown epitaxial layers on two-index direction windows smaller than the critical size show very clear faceted surfaces [Fig. 10c)] and will be very useful for applications to integrated optical devices such as lasers, waveguides, modulators, prisms, etc, because these devices require faceted clean surfaces in order to reduce the scattering loss.

Above observations may be common to the III-V compound semiconductors and experimentally verified also for the InP/ InGaAsP system [19].

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