Crystal Growth: Physics, Technology and Modeling

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Lecture 8. Liquid phase epitaxy and lateral overgrowth

5 April 2022

http://www.unipress.waw.pl/~stach/cg-2021-22



Liquid phase epitaxy and lateral overgrowth

Outline:

- definition + idea of LPE
- history and technical aspects
- solute transport during LPE growth; diffusion, convection
- Liquid Phase Electroepitaxy
- Epitaxial Lateral Overgrowth
- principle and growth control
- filtration of dislocations in ELO
- strain in ELO structures

Liquid Phase Epitaxy - LPE



technique of epitaxial thin films growth *from metallic solution*



• crystal component (e.g. Ga for GaAs)

or low solubility in the crystal (Bi, Sn, In, Pb, etc.)

- low melting point
- high solubility of solute @ T_{epi}
- low vapor pressure @ T_{epi}
- high chemical stability
- high purity
- low price ???

Idea of LPE (example: homoepitaxy of GaAs on GaAs substrate)



the Gibbs phase rule: $f_{(degrees of freedom)} = c_{(components)} - p_{(phases)} + 2(p; T)$ Ga-As \Leftrightarrow GaAs 2 2 p = const. \implies f = 1 (T)



Idea of LPE (example: homoepitaxy of GaAs on GaAs substrate)



growth in T gradient





Crucibles in LPE







rotation

1 cm

Crucibles in LPE cont.







JUJULLI

advantages:

- growth of multilayer structures
- thin layer of the solution
- "skin" of oxides on the solution surface removed disadvantages:
- blurred (not sharp) interfaces

IF PAN

History



H. Nelson: Epitaxial growth from the liquid state and its application to the fabrication to the fabrication of tunnel and laser diodes RCA Rev. <u>24</u> (1963) 603.

Nobel 2000 - H. Kroemer, J. Kilby, Z. Alfierow "for developing semiconductor heterostructures used in high-speed- and opto-electronics"



Why LPE:

- •,,cheap and easy"
- high purity of layers (impurity segregation)
- selective area growth easy
- broad range of compounds can be grown (As, P, ...)
- •,,safe" method (as compared to MOVPE)





Fig. 14. InGaAsP DFB laser structure grown nearly dissolution-free over a first order grating, after [70]. For details, see text

Growth kinetics



<u>usually</u>

the growth temperature in LPE is so high (surface processes so fast), while the bulk solute transport is slow, that solute transport in the bulk of the solution determines the growth rate

LPE: diffusion controlled growth – example: GaAs growth from Ga-As solution





assumptions:

- fast surface kinetics
- no convective mixing
- low growth rate V_{gr}
- fast heat transport
- no diffusion in solid state

transport: mass heat $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial^2 z} + V_{gx} \frac{\partial C}{\partial z} \qquad \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial^2 z} + V_{gr} \frac{\partial}{\partial t}$

mass flux continuity condition

$$V_{gr}\left(C_{s,z=0} - C_{l,z=0}\right) = D_l \frac{\partial C_l}{\partial z} | (z=0) - Ds \frac{\partial C_s}{\partial z} | (z=0)$$

+ initial and boundary conditions (which depend on LPE version, e.g. T(t))

LPE: diffusion controlled growth – example: GaAs growth from Ga-As solution



LPE: constitutional supersaturation



theory:

increase grad T at the interface $(T_B \text{ instead of } T_A)$



Figure 3. Film showing various surface features like ridges, valleys, inclusions, etc.



LPE: constitutional supersaturation





theory:

increase grad T at the interface $(T_B \text{ instead of } T_A)$

practice:

decrease concentration gradient

- thinner solution layer
- lower the growth rate

Udayashankar et al., Bull. Mater. Sci 26 (2003) 685



Figure 3. Film showing various surface features like ridges, valleys, inclusions, etc.

LPE: natural convection





LPE: natural convection cont.





Tiller JCG $\underline{2}$ (1968) 69: no thermal convection if
no solutal convection ifH < 5 mm
H < 2 mm</th>LPE from thin solution
layer !!!

LPE: natural convection cont.





for thin solutions growth on both substrates similar

LPE of multicomponent systems (example: GaAlAs on GaAs)



the Gibbs phase rule: f(degrees of freedom) = c(components) - p(phases) + 2(p; T)

e.g. Ga-Al-As \Leftrightarrow Ga_{1-x}Al_xAs 3 2 p = const. \implies f = 2 (T, x)



Liquid phase electroepitaxy (LPEE)



 $T_0 = const. + DC$ current flow through the solid/liquid interface



S. Dost, Univ. Victoria, BC, Canada

Z.R. Zytkiewicz, IF PAN



LPEE - disadvantages

• LPEE system more complicated (stable electrical contacts needed)

• Joule effect limiting the crystal thickness

no Joule effect

with Joule effect

AlGaAs



growth can be continued if $j_{el} \downarrow$



400 µm

GaAs

LPE – low dimensional structures





4" substrate !!!



Si 15.6 nm/Si_{0.995}C_{0.005} 5.2 nm



SiGe/Si QDs



LPE - summary

solution growth:

- low concentration of point defects
- high purity of the layers (segregation of impurities)
- selective area epitaxy easy
- wide range of compounds

• technically simple (standard version)

- "cheap and easy"
- "safe" technique
- growth rate $\sim \mu m/min$
- growth of low-dimensional structures very difficult

disadvantages:

limitations due to equilibrium nature of LPE growth

- doping limited by phase diagram (e.g. GaAs:Mn)
- structures requiring a high supersaturation (GaAs/Si) difficult to fabricate
- systems with limited solubility in solid (phase separation) difficult to grow

• no in situ growth monitoring possible (some possibilities in LPEE)

LPE considered as "old fashion" technology – wrong !!! Every technology is important and valuable if properly used

epitaxy:

LPF

• ordered growth of multilayer crystalline structures



for further reading on LPE



Handbook of Crystal Growth, Ed. D.T.J. Hurle vol. 3, Elsevier 1994

- E. Bauser Atomic mechanisms in semiconductor Liquid Phase Epitaxy
- M.B. Small, E.A. Giess and R. Ghez *Liquid Phase Epitaxy*

E. Kuphal Liquid Phase Epitaxy Appl. Phys. A52 (1991) 380.

M.B. Small, I. Crossley *The physical processes occurring during liquid phase epitaxial growth* J. Cryst. Growth <u>27</u> (1974) 35.

M.G. Astles Liquid Phase Epitaxial Growth of III-V Compound Semiconductor Materials and their Device Applications, IOP Publishing 1990.

B. Pamplin (ed.) Crystal growth, Pergamon, 1974

K. Sangwal (ed.) Elementary Crystal Growth, SAAN Publishers, 1994.

Epitaxial Lateral **O**vergrowth (**ELO**)



requirements:

- high growth selectivity (no nucleation on the mask)
- fast lateral (horizontal) growth V_{lat}
- slow normal (vertical) growth V_{ver}

Methods to reduce defect density in lattice mismatched epitaxial structures - summary



There are no universal method to reduce dislocation density in lattice mismatched heterostructures; The best way is to avoid lattice mismatch – find the suitable substrate !!!

ELO = a method to reduce dislocation density in epitaxial structures





wide and thin ELO layers needed

dislocation filtration in ELO – is it a new idea?



Necking in Bridgman growth



Cu crystal – Czochralski growth



recipe: take from the seed info on crystal lattice; do not take defects;

Growth rate of various crystal faces (Krukowki's lecture)





Growth rate of various crystal faces (Krukowki's lecture)



atomically smooth surface w/o dislocations (2D nucleation)



Growth rate of various crystal faces (Krukowki's lecture)



atomically smooth surface with dislocations



Mechanism of ELO growth



to get a high aspect ratio we need:

- smooth top surface (low normal growth rate V_{ver})
- rough side face (high lateral growth rate $V_{\text{lat}})$
- adjust supersaturation to σ_{opt} LPE perfect !!!
 - VPE, MOVPE, HVPE possible
 - MBE ???? problems

Mechanism of ELO growth





8 equivalent window directions on substrate without miscut

1 preferential window orientation on substrate with surface miscut

Zytkiewicz Cryst. Res. Technol. 1999

GaAs layer on (100) GaAs by LPE



Application of ELO structures grown by LPE





- silicon-on-insulator structures



MOS transistor on ELO Si/SiO₂

Bergmann et al. Appl. Phys. A (1992)



ELO Si/SiO₂/Si by LPE



E. Bauser et al. Max-Planck Inst. Stuttgart



origin of strange ELO shape

- the case of dislocation-free Si substrate



FIG. 1. Silicon layers grown from oxide-free seeding areas on $\{111\}$ Si. Substrate partially masked by thermal oxide. Substrate off-orientation 0.3° in the [112] direction (schematic view). The crosshatched area in (b) indicates the seed window.



on dislocated substrate ELO growth possible w/o substrate miscut (miscut used sometimes though; e.g GaAs/Si)

ELO – optimization of supersaturation in LPE

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growth temperature

ELO GaAs - cooling rate



ELO – influence of doping on the aspect ratio (LPE)









Gibbs-Thomson effect \Rightarrow S. Krukowski's lecture

Gibbs – Thomson effect a – phase equilibrium on curved surface depends on radius of phase boundary

 Γ - capillarity constant (~ 10⁻⁷ cm = 1 nm)

$$\mathbf{R} = \mathbf{p}(\infty) \cdot \left(1 + \frac{\Gamma}{R}\right) \qquad \mathbf{C}(\mathbf{R}) = \mathbf{C}(\infty) \cdot \left(1 + \frac{\Gamma}{R}\right)$$



equilibrium pressure (solute concentration) on curved surface is larger than on the planar one



Gibbs-Thomson effect \Rightarrow S. Krukowski's lecture

simulations: ELO of GaAs byLPE



GaAs ELO layers on GaAs substrates by LPE



 $L = 172 \ \mu m; t = 2.8 \ \mu m$



Why the layer is thinner at the edge? nonuniform growth ... bowing ...

Filtration of dislocations in ELO - examples



LPE - GaAs/Si

LPE - GaSb/GaAs



MBE grown GaAs/Si (GaSb/GaAs) templates; ELO by LPE

Filtration of dislocations in ELO: TEM of GaAs/Si





Filtration of dislocations in ELO: TEM of HVPE GaN/sapphire



Sakai et al. APL 1998

TEM



width of the ELO wing

	MOVPE	LPE	LPE
	GaN^*	GaAs/Si ^{**}	GaAs/GaAs
wing width L	$\leq 5 \ \mu m$	≤ 90 µm	≤ 200 µm
*	<u></u>		

Fini et al. JCG (2000) ** Chang et al. JCG (1998)

Filtration of dislocations in ELO: cathodoluminescence



Zytkiewicz Thin Solid Films 412 (2002) 64

Yu et al. MRS Internet Nitride Semicond. Res. 1998

LPE GaAs/Si

integrated CL



MOVPE GaN on sapphire

band edge emission 365 nm



ELO structures for devices





large leakage current due to TD

Semicond. Res. 4S1, G1.1 (1999)

CW RT blue LD - Nichia



Strain in ELO layers XRD – lecture by M. Leszczyński

XRD geometry







Strain in ELO layers – local XRD



X-ray beam $5 - 10 \ \mu\text{m} \times 0.5 - 10 \ \text{mm}$ sample movement step $5 - 20 \ \mu\text{m}$ RC, RSM, ... measured *locally* \rightarrow Rocking Curve mapping





Strain in ELO layers – local XRD



Bending of ELO layers





Bending of ELO layers - common in ELO (GaN, Si, GaAs, etc.)





ELO GaN on sapphire

Kim et al. JCG 2002





- tilt angle and tilt direction from electron diffraction in TEM
- synchrotron XRD

FIG. 2. TEM cross-section images and electron diffraction patterns taken from (a) and (b) window and (c) and (d) mask region.

Coalescence of ELO stripes



....

no dislocations above the mask edge

Similar effect in:

ELO Si on Si - Banhart et al. Appl. Phys. 1993 ELO GaN on sapphire - Sakai et al. APL 1998 PE GaN on sapphire - Chen et al. APL 1999

Thermal strain in ELO structures (GaAs/SiO₂/GaAs/Si)











Thermal strain in ELO structures (GaAs/SiO₂/GaAs/Si)





Another ELO concepts (e.g. Pendeo-epitaxy)

Epitaxial Lateral Overgrowth









Pendeo-epitaxy



pendeo - "hanging on" "suspending from" ™ Nitronex Corp., Raileigh, North Caroline University



NCSU

5KU

16

PE vs. ELO: reduction of TD density over the whole wafer within one PE process

Pendeo-epitaxy



Chen et al. APL 1999



TEM



Advantage: maskless versions of PE possible for GaN on SiC or SiC-coated Si Strittmatter et al. APL 2001; Davis et al. JCG 2001





 Frajtag et al. APL 2011 98 023115

 10⁹ cm⁻²
 3.9x10⁷ cm⁻²

 GaN film grown
 b) GaN film overgrown

PAN





S. Tanaka et al., Jpn. J. Appl. Phys. 39, L831 (2000)

ELO summary





a tool for fabrication of low-dislocation density epilayers on heavily dislocated substrates

take from the seed info on crystal lattice; do not take defects!!!

ELO – all lattice mismatch-induced problems solved?

Achievements:

- 1. significant reduction of dislocation density in lattice-mismatched heterostructures
- 2. easier elastic relaxation of thermal strain

Problems:

- 1. interaction of ELO layers with the mask; bending
- 2. generation of defects at the front of coalescence

