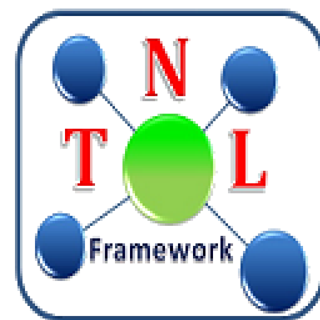
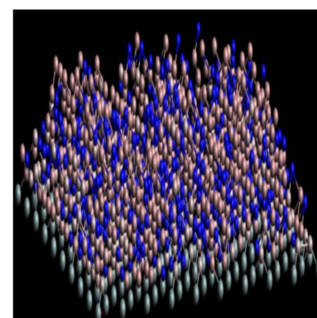
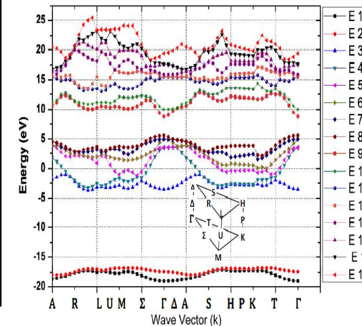
# MOCVD Vertical Flow Reactor

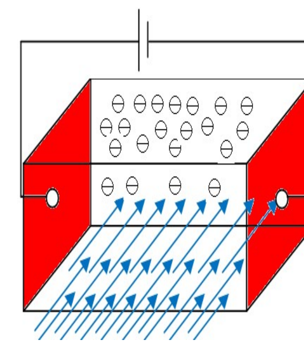
## *TNL-Showerhead Simulator*

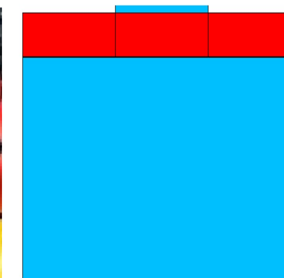
*Technology of Next Level*
*driven through innovation*









# SUBSTRATES AVAILABILITY

### SILICON
- Available in up to >30 cm diameter
- Quite inexpensive and high quality
- Can be obtained *n*-type, *p*-type, or with high resistivity
- Used for Si and SiGe technologies
- Intense reserach to develop Si-based "pseudo-substrates" for GaAs, InP, CdTe...technologies

### GaAs
- Available in up to >12 cm diameter
- High quality, more expensive than Si, but affordable
- Used for GaAs and AlGaAs, and strained InGaAs technologies
- Can be used for electronic and optoelectronic applications

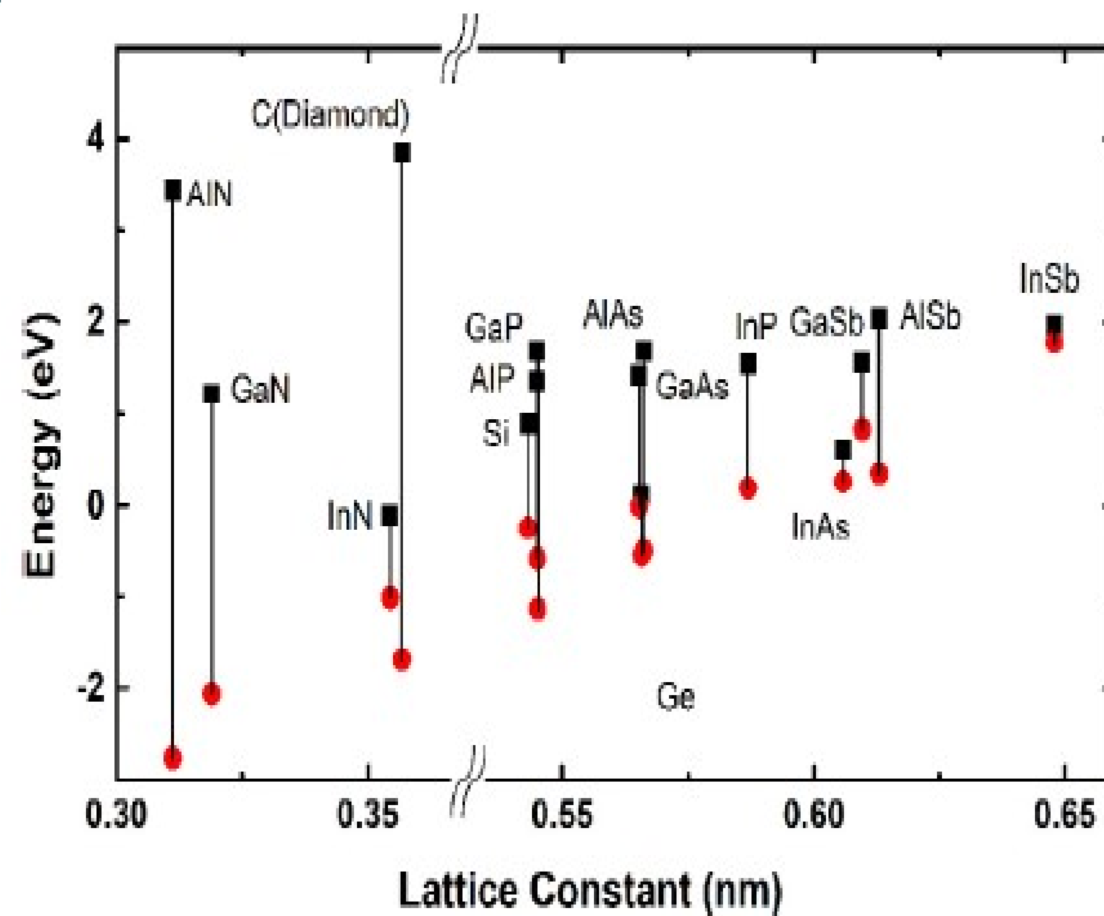
### InP
- 10 cm diameter available, but expensive
- InP and InGaAsP technologies can be grown
- Very important for optoelectronics and high performance electronics

### SiC
- Small, very expensive substrates
- Very important for high power, large gap technologies
- Used for nitride technology

**1**. Bulk Crystal Growth

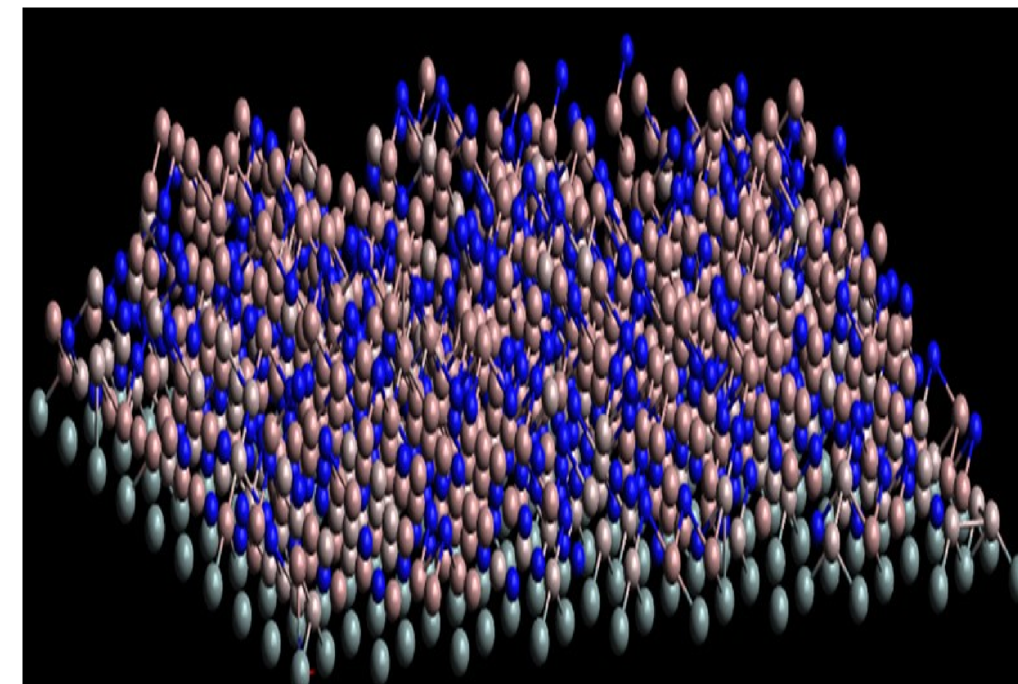
- State of the art device technologies depends on: ***Purity & Perfection of the crystals***
- Limited to ***Si, GaAs*** and upto some extent for ***InP***

# Epitaxial Growth Challenges




*E.T. Yu, J.O. McCaldin, T.C. McGill, Band offsets in semiconductor heterojunctions, in: E. Henry, T. David (Eds.), Solid State Physics, Academic Press, 1992, pp. 1–146

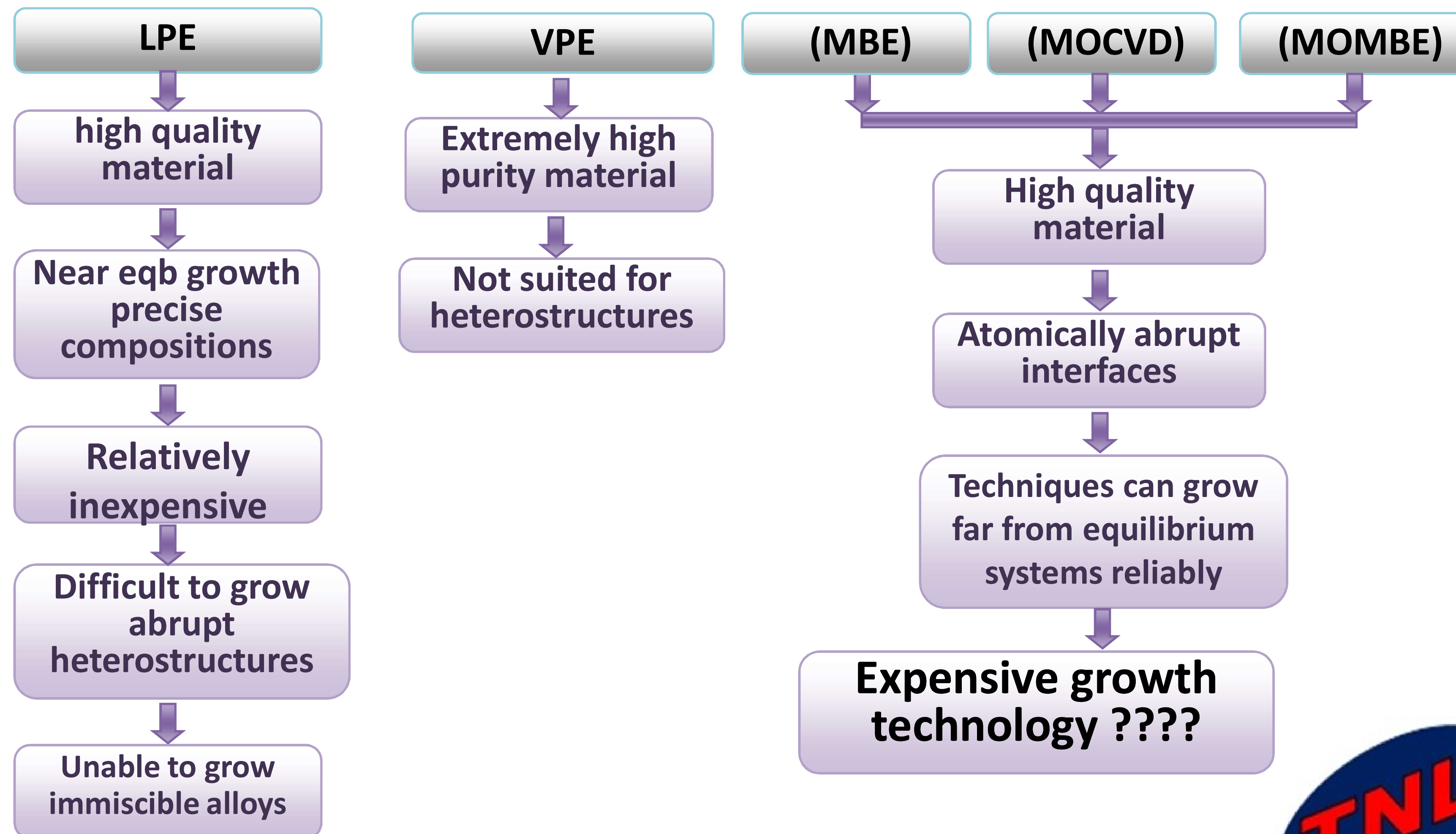
- Development of psuedo- GaAs substrates over Si



# Available Techniques

## Epitaxial Growth Challenges

- ❑ Semiconductor technologies dependent on non ideal substrates
- ❑ Lot of Technological Challenges and issues
- ❑ Need for Pseudo-substrates
- ❑ Low Defect densities
- ❑ Strain Engineering

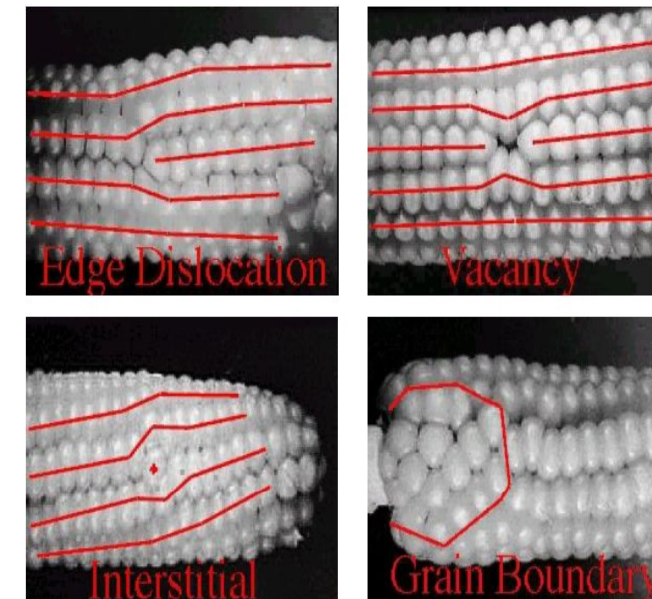


# CHALLENGES

E.g. GaN growth over various substrates:

| Substrate | Si | $Al_2O_3$ | SiC | Bulk GaN | AlN |
|---|---|---|---|---|---|
| Lattice Mismatch (%) | 17 | 16 | 3.4 | - | 2.5 |
| Thermal Conductivity (W/mm-k) | 150 | 35 | 490 | 260 | 319 |
| Resistivity (ohm-cm) | $10^4$ | $10^{14}$ | $\sim10^{12}$ | - | $>10^{14}$ |

**Defects**

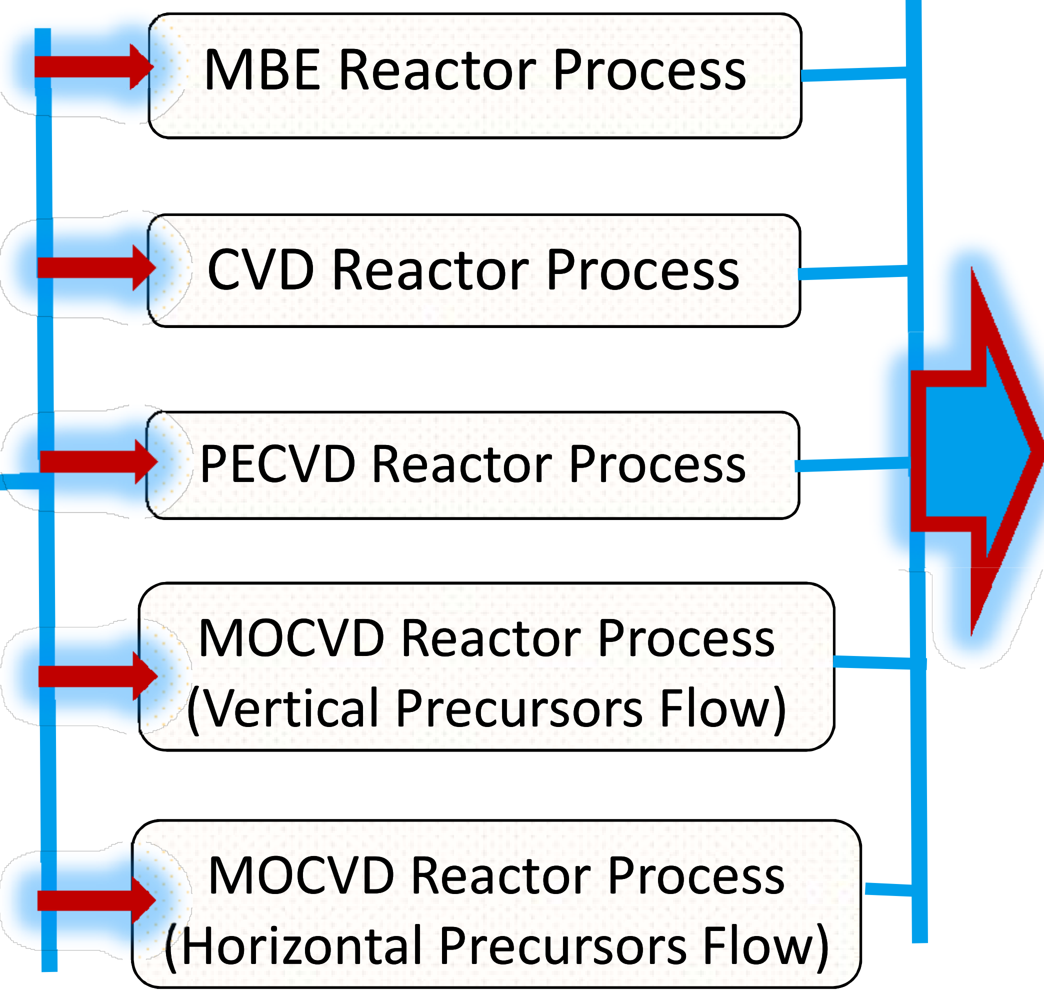



- Group IV, III-V, II-VI epi-growth with multi components
- Point defects, e.g. vacancies, interstitial atoms
- Extended defects within the film, generally dislocations and stacking faults
- Dislocations: reduce or relax strain through lattice mismatch or thermal expansion differences.

# Epitaxy Process Solution

Innovative Atomistic Scale Reactor Simulation without use of Continuum models

**TNL Framework**




User's Input Growth Conditions

Surface Profile (Roughness)

Strain Mapping (layer by Layer

Lattice parameter

Defects
(Vacancies, Interstitials, Dislocations, Stacking Faults)

# INPUTS : MOCVD PROCESS

**Chamber Condition**

☑ Showerhead Based

☐ Injector Based

Viscosity (poise): 100

Mass Diffusivity (cm2/s): 800

Chamber Radius (cm): 15

**ShowerHead Parameters**

| Parameter | Value | Unit |
|---|---|---|
| Shower hole's diameter | 1.0 | |
| Chamber Volume (ltrs.) | 1.4 | |
| Chamber Pressure | 10 | torr |
| Ceiling Height (cm) | 2.0 | |
| Chamber Temperature (C) | 100 | |
| Sticking Coeff. | 1 | |

**Precurssor Condition**

Number of Port: 0

Precursor 1: Select Prec...

Flow Rate: [ ] atm cc/s

Load Reaction — Step 1 — Load 1

**Precurssor Condition**

Number of Port: 4

Precursor 1: Select Prec...

- Select Precurso
- Ga(CH3)3
- (CH3)3CAsH2
- H2
- Al(CH3)3
- NH3
- CH3
- O2

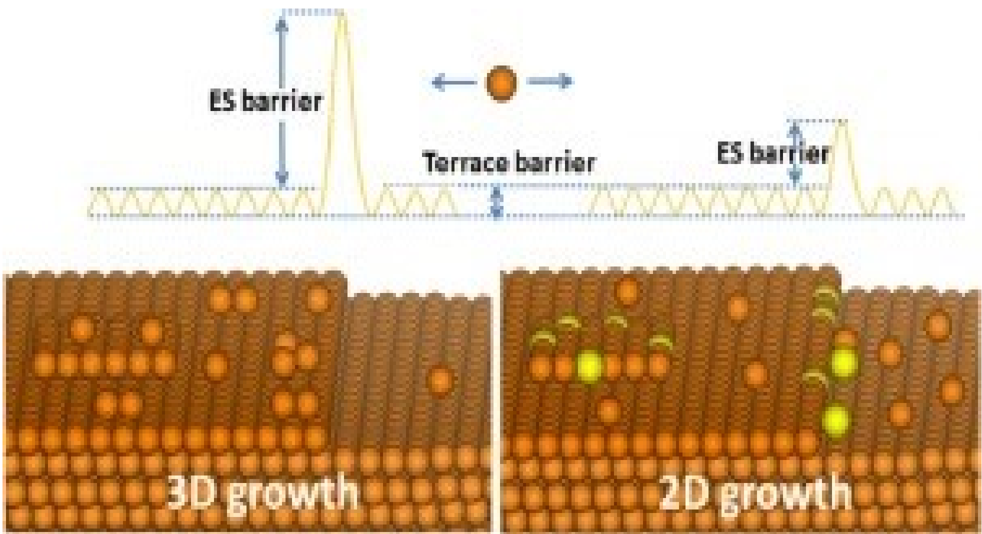
Flow Rate: m cc/s

Load Reaction — Load 1

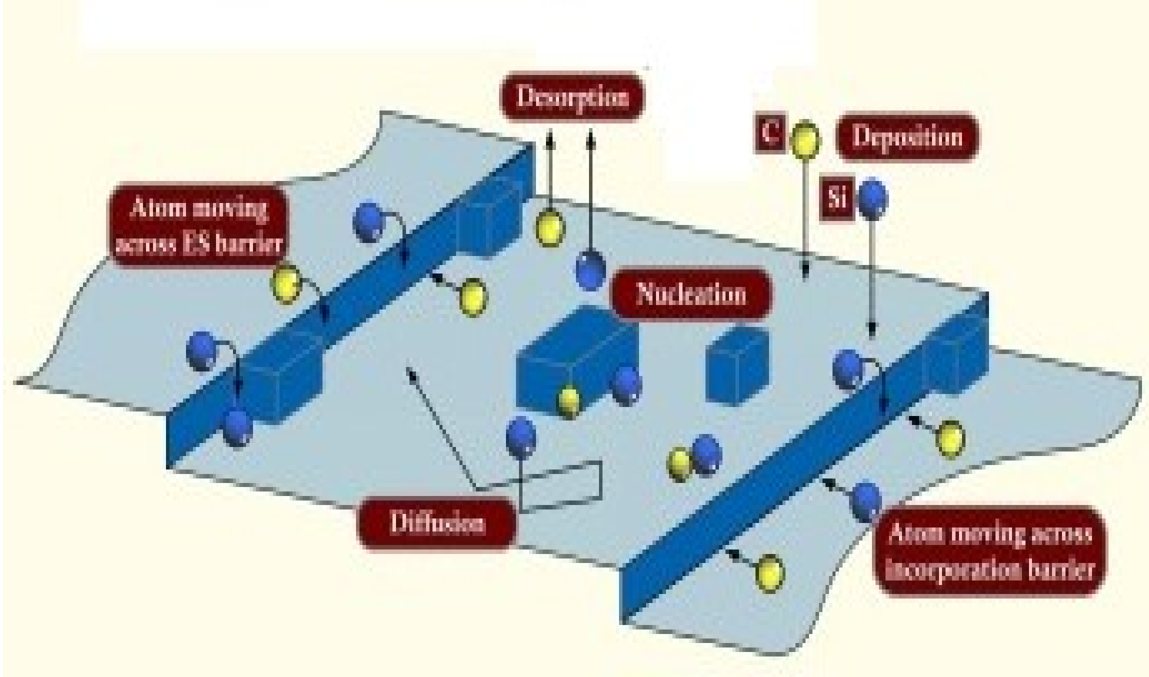
Many More parameters details Require ..........

# Methodology: MOCVD Process

**Schwoebel barrier:** The atom diffuses from the site exactly above the edge atom to the site immediately next to the edge atom as;




**Incorporation barrier:** The atom incorporates into the edge on the same surface level.




TNL

# Chemical Kinetics Solution

- TNL Chemical Kinetics database includes gas- and surface phase chemical reactions
- Users may chose any desired equation or set of equations for the precursors they input based on requirements
- Users have flexibilities to write their own chemical reactions

**TNL_Chemical Kinetics**

**Precursors**

H2,SiH4 Load

| No. | Name | A | n | E(Cal) |
|---|---|---|---|---|
| 1 | G 1 SiH4 --> SiH2 + H2 | 9.49 | 1.7 | 54710 |
| 2 | G 2 SiH4 + SiH2 --> Si2H6 | 10.26 | 1.7 | 50200 |
| 3 | G 3 Si2H6 + SiH2 --> HSiSiH3 +... | 14.24 | 0.4 | 8900 |
| 4 | G 4 Si2H6 --> H2 + HSiSiH3 | 9.96 | 1.8 | 54200 |
| 5 | G 5 HSiSiH3 --> H2SiSiH2 | 13.40 | 0.2 | 5380 |
| 6 | G 6 HSiSiH3+H2 --> SiH2 + SiH4 | 13.97 | 0 | 4092 |

Add_Gas

**Output_Window**

| No. | Gas_Reaction | A | n | E(Cal) |
|---|---|---|---|---|
| 1 | G 1 SiH4 --> SiH2 + H2 | 9.49 | 1.7 | 54710 |
| 2 | G 2 SiH4 + SiH2 --> Si2H6 | 10.26 | 1.7 | 50200 |
| 3 | G 3 Si2H6 + SiH2 --> HSiSiH3 + SiH4 | 14.24 | 0.4 | 8900 |
| 4 | G 4 Si2H6 --> H2 + HSiSiH3 | 9.96 | 1.8 | 54200 |
| 5 | G 5 HSiSiH3 --> H2SiSiH2 | 13.40 | 0.2 | 5380 |

| No. | Name | A | n | E(Cal) |
|---|---|---|---|---|
| 2 | S 2 SiH2 + sigma --> Si+H2 | 11.76 | 0.5 | 0 |
| 3 | S 3 H2 + 2sigma --> 2H* | 11.36 | 0.5 | 17250 |

Add_Surface

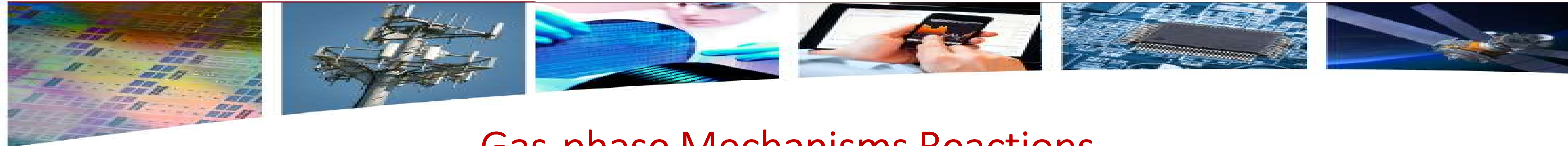
| No. | Surface_Reaction | A | n | E(Cal) |
|---|---|---|---|---|
| 2 | S 2 SiH2 + sigma --> Si+H2 | 11.76 | 0.5 | 0 |
| 3 | S 3 H2 + 2sigma --> 2H* | 11.36 | 0.5 | 17250 |

**Editor**

Add_Gas save Add_Surface

Remove Save Apply

# TMG, $NH_3$ & $N_2/H_2$/ARGON



## Gas-phase Mechanisms Reactions

| $k = AT^n e^{-E_a/RT}$ | | | | | | | | | | $A$ | $n$ | $E_a$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| G1 | TMG | = | DMG | + | $CH_3$ | | | | | $1.00 \times 10^{47}$ | −9.18 | 76,996 |
| G2 | DMG | = | MMG | + | $CH_3$ | | | | | $7.67 \times 10^{43}$ | −9.8 | 34,017 |
| G3 | MMG | = | Ga | + | $CH_3$ | | | | | $1.68 \times 10^{30}$ | −5.07 | 84,030 |
| G4 | TMG | + | $NH_3$ | → | $TMG{:}NH_3$ | | | | | $2.28 \times 10^{34}$ | −8.31 | 3115 |
| G5 | TMG | + | $NH_3$ | → | $DMG{:}NH_2$ | + | $CH_4$ | | | $1.70 \times 10^{4}$ | 2 | 19,969 |
| G6 | DMG | + | $NH_3$ | → | $DMG{:}NH_3$ | | | | | $4.08 \times 10^{31}$ | −7.03 | 3234 |
| G7 | DMG | + | $NH_3$ | → | $MMG{:}NH_2$ | + | $CH_4$ | | | $5.30 \times 10^{5}$ | 1.56 | 20,744 |
| G8 | MMG | + | $NH_3$ | → | $MMG{:}NH_3$ | | | | | $7.95 \times 10^{24}$ | −5.21 | 2094 |
| G9 | MMG | + | $NH_3$ | → | $GaNH_2$ | + | $CH_4$ | | | $8.10 \times 10^{5}$ | 1.3 | 17,722 |
| G10 | $NH_3$ | + | $CH_3$ | → | $NH_2$ | + | $CH_4$ | | | $3.31 \times 10^{3}$ | 2.51 | 9859 |
| G11 | $CH_3$ | + | $H_2$ | → | $CH_4$ | + | H | | | $1.20 \times 10^{12}$ | 0 | 12,518 |
| G12 | TMG | + | H | → | DMG | + | $CH_4$ | | | $5.00 \times 10^{13}$ | 0 | 10,036 |
| G13 | DMG | + | H | → | MMG | + | $CH_4$ | | | $5.00 \times 10^{13}$ | 0 | 10,036 |
| G14 | $TMG{:}NH_3$ | → | MMG | + | $2CH_3$ | + | $NH_3$ | | | $1.33 \times 10^{44}$ | −8.24 | 77,791 |
| G15 | $CH_3$ | + | H | + | M | → | $CH_4$ | + | $NH_3$ | $2.40 \times 10^{22}$ | −1 | 0 |
| G16 | $2CH_3$ | = | $C_2H_6$ | | | | | | | $2.00 \times 10^{13}$ | 0 | 0 |
| G17 | 2H | + | M | = | $H_2$ | + | M | | | $2.00 \times 10^{16}$ | 0 | 0 |

# TMG, $NH_3$ & $N_2/H_2$/ARGON

## Surface phase Reactions: PATH 1

| Path 1, $k = AT^{n}e^{-Ea/RT}$ | | | | | | | | $A$ | $n$ | $E_a$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MMG | + | N(S) | → | MMG(S) | | | $1.16 \times 10^{5}$ | 2.98 | 0 |
| 2 | MMG(S) | → | MMG | + | N(S) | | | $1.12 \times 10^{14}$ | 0.55 | 107,673 |
| 3 | $NH_3$ | + | MMG(S) | → | COMPM1(S) | | | $3.35 \times 10^{7}$ | 3.33 | 0 |
| 4 | COMPM1(S) | → | $NH_3$ | + | MMG(S) | | | $5.70 \times 10^{13}$ | −0.16 | 8146 |
| 5 | MMG | + | COMPM1(S) | → | CH4 | + | COMPM2(S) | $1.23 \times 10^{10}$ | 3.22 | 23,446 |
| 6 | $NH_3$ | + | COMPM2(S) | → | COMPM3(S) | | | $3.35 \times 10^{7}$ | 3.33 | 0 |
| 7 | COMPM3(S) | → | $NH_3$ | + | COMPM2(S) | | | $5.70 \times 10^{13}$ | −0.161 | 8146 |
| 8 | MMG | + | COMPM3(S) | → | $CH_4$ | + | COMPM4(S) | $1.23 \times 10^{10}$ | 3.22 | 23,446 |
| 9 | $NH_3$ | + | COMPM4(S) | → | COMPM5(S) | | | $3.35 \times 10^{7}$ | 3.33 | 0 |
| 10 | COMPM5(S) | → | $NH_3$ | + | COMPM4(S) | | | $5.70 \times 10^{13}$ | −0.161 | 8146 |
| 11 | COMPM5(S) | → | CH4 | + | RINGM1(S) | | | $1.23 \times 10^{7}$ | 3.22 | 23,446 |
| 12 | Ga(S) | + | RINGM1(S) | → | RINGM2(S) | + | N(S) | $3.35 \times 10^{7}$ | 3.33 | 0 |
| 13 | RINGM2(S) | → | $3H_2$ | + | 3GaN(B) | + | Ga(S) | $3.68 \times 10^{9}$ | 2.05 | 59,610 |

# TMG, $NH_3$ & $N_2/H_2$/ARGON

## Surface phase Reactions: PATH 2

| | Path 2, $k = AT^n e^{-Ea/RT}$ | | | | | $A$ | $n$ | $E_a$ |
|---|---|---|---|---|---|---|---|---|
| 14 | $CH_3$ | + | Ga(S) | → | MMG(S) | $1.76 \times 10^{9}$ | 1.39 | 0 |
| 15 | MMG(S) | → | $CH_3$ | + | Ga(S) | $4.54 \times 10^{13}$ | 0.0346 | 79,480 |
| 16 | $NH_2$ | + | Ga(S) | → | $NH_2$(S) | $3.17 \times 10^{8}$ | 1.83 | 0 |
| 17 | $GaNH_2$ | + | N(S) | → | $GaNH_2$(s) | $2.27 \times 10^{6}$ | 2.247 | 0 |
| 18 | $GaNH_2$(S) | → | $GaNH_2$ | + | N(S) | $4.83 \times 10^{13}$ | 0.614 | 83,881 |
| 19 | COMPMM1(S) | → | $CH_4$ | + | $GaNH_2$(S) | $1.49 \times 10^{11}$ | 0.609 | 25,950 |
| 20 | MMG | + | $GaNH_2$(S) | → | COMPMM1(S) | $1.16 \times 10^{5}$ | 2.98 | 0 |
| 21 | $NH_3$ | + | COMPMM1(S) | → | COMPMM2(S) | $3.35 \times 10^{7}$ | 3.33 | 0 |
| 22 | COMPMM2(S) | → | $CH_4$ | + | COMPMM3(S) | $1.49 \times 10^{11}$ | 0.609 | 25,950 |
| 23 | MMG | + | COMPMM3(S) | → | COMPMM4(S) | $1.16 \times 10^{5}$ | 2.98 | 0 |
| 24 | $NH_3$ | + | COMPMM4(S) | → | COMPMM5(S) | $3.35 \times 10^{7}$ | 3.33 | 0 |
| 25 | COMPMM5(S) | → | $CH_4$ | + | RINGM1(S) | $1.49 \times 10^{11}$ | 0.609 | 25,950 |
| 26 | $NH_2$(S) | → | $NH_2$ | + | Ga(S) | $1.45 \times 10^{14}$ | 0.09 | 59,786 |
| 27 | COMPMM1(S) | → | MMG | + | $GaNH_2$(S) | $1.00 \times 10^{14}$ | 0.55 | 42,819 |
| 28 | COMPMM2(S) | → | $NH_3$ | + | COMPMM1(S) | $5.70 \times 10^{13}$ | −0.1 | 8146 |
| 29 | COMPMM4(S) | → | MMG | + | COMPMM3(S) | $1.00 \times 10^{14}$ | 0.55 | 42,819 |
| 30 | COMPMM5(S) | → | $NH_3$ | + | COMPMM4(S) | $5.70 \times 10^{13}$ | −0.1 | 8146 |
| 31 | Ga | + | N(S) | → | Ga(S) | $1.00 \times 10^{11}$ | 1.5 | 0 |
| 32 | Ga(S) | + | $NH_2$(S) | → | $GaNH_2$ +Ga(S) | $1.00 \times 10^{25}$ | 0 | 0 |
| 33 | Ga(S) | → | Ga | + | N(S) | $1.00 \times 10^{13}$ | 0 | 45,168 |
| 34 | $6CH_3$ | + | RINGM2(S) | → | COM1(S) | $7.55 \times 10^{7}$ | 2.31 | 0 |
| 35 | COM1(S) | → | $6CH_3$ | + | RINGM2(S) | $1.00 \times 10^{13}$ | 0.71 | 45,506 |
| 36 | COM1(S) | → | $6CH_4$ | + | 3GaN(B) +Ga(S) | $4.00 \times 10^{12}$ | 0 | 49,675 |

# TMG, $NH_3$ & $N_2/H_2$/ARGON

## Surface phase Reactions: PATH 3

| | Path 3, $k = AT^n e^{-Ea/RT}$ | | | | | | | A | n | $E_a$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 37 | TMG | + | N(S) | → | TMG(S) | | | $1.16 \times 10^5$ | 2.98 | 0 |
| 38 | $NH_3$ | + | TMG(S) | → | TCOM1(S) | | | $3.35 \times 10^7$ | 3.33 | 0 |
| 39 | TCOM1(S) | → | $CH_4$ | + | TCOM2(S) | | | $1.49 \times 10^{11}$ | 0.609 | 32,785 |
| 40 | Ga(S) | + | TCOM2(S) | → | TCOM3(S) | + | N(S) | $3.35 \times 10^7$ | 3.33 | 0 |
| 41 | TCOM3(S) | → | $2CH_4$ | + | GaN(B) | + | Ga(S) | $1.49 \times 10^{11}$ | 0.609 | 49,675 |
| 42 | TMG(S) | → | TMG | + | N(S) | | | $1.12 \times 10^{14}$ | 0.55 | 49,675 |
| 43 | TCOM1(S) | → | $NH_3$ | + | TMG(S) | | | $5.70 \times 10^{13}$ | −0.161 | 11,922 |
| 44 | $TMG{:}NH_3$ | + | N(S) | → | TCOM1(S) | | | $1.16 \times 10^5$ | 2.98 | 0 |
| 45 | TCOM1(S) | → | $TMG{:}NH_3$ | + | N(S) | | | $1.12 \times 10^{14}$ | 0.55 | 49,675 |
| 46 | TCOM1(S) | → | $2CH_3$ | + | MMG(S) | + | $NH_3$ +N(S) | $1.12 \times 10^{14}$ | 0.55 | 10,7673 |
| 47 | $MMGNH_3$ | + | N(S) | → | COMPM1(S) | | | $1.16 \times 10^5$ | 2.98 | 0 |
| 48 | COMPM1(S) | → | $MMG{:}NH_3$ | + | N(S) | | | $1.12 \times 10^{14}$ | 0.55 | 107,673 |
| 49 | $MMG{:}NH_3$ | + | COMPM1(S) | → | $CH_4$ | + | COMPM3(S) | $1.23 \times 10^{10}$ | 3.22 | 23,446 |
| 50 | $MMG{:}NH_3$ | + | COMPM3(S) | → | $CH_4$ | + | COMPM5(S) | $1.23 \times 10^{10}$ | 3.22 | 23,446 |
| 51 | $MMG{:}NH_3$ | + | $GaNH_2$(S) | → | COMPMM2(S) | | | $1.16 \times 10^5$ | 2.98 | 0 |
| 52 | $MMG{:}NH_3$ | + | COMPMM3(S) | → | COMPMM5(S) | | | $1.16 \times 10^5$ | 2.98 | 0 |

# Composition of Intermediates

Chemical Composition of compound on the surface

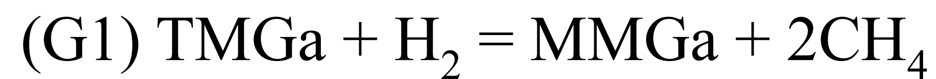
| Compounds Names | Chemical Formula |
|---|---|
| COMPM1(S) | $NH_3 \cdot MMG(S)$ |
| COMPM2(S) | $Ga \cdot NH_2 \cdot MMG(S)$ |
| COMPM3(S) | $NH_3 \cdot Ga \cdot NH_2 \cdot MMG(S)$ |
| COMPM4(S) | $Ga \cdot NH_2 \cdot Ga \cdot NH_2 \cdot MMG(S)$ |
| COMPM5(S) | $NH_3 \cdot Ga \cdot NH_2 \cdot Ga \cdot NH_2 \cdot MMG(S)$ |
| RINGM1(S) | $NH_2 \cdot Ga \cdot NH_2 \cdot Ga \cdot NH_2 \cdot Ga(S)$ |
| RINGM2(S) | $(S)NH_2 \cdot Ga \cdot NH_2 \cdot Ga \cdot NH_2 \cdot Ga(S)$ |
| COMPMM1(S) | $MMG \cdot GaNH_2(S)$ |
| COMPMM2(S) | $NH_3 \cdot MMG \cdot GaNH_2 \cdot Ga(S)$ |
| COMPMM3(S) | $NH_2 \cdot Ga \cdot NH_2 \cdot Ga(S)$ |
| COMPMM4(S) | $MMG \cdot NH_2 \cdot Ga \cdot NH_2 \cdot Ga(S)$ |
| COMPMM5(S) | $NH_3 \cdot MMG \cdot NH_2 \cdot Ga \cdot NH_2 \cdot Ga(S)$ |
| TCOM1(S) | $NH_3 \cdot TMG(S)$ |
| TCOM2(S) | $NH_2 \cdot DMG(S)$ |
| TCOM3(3) | $(S)NH_2 \cdot DMG(S)$ |
| COM1(S) | $RINGM2(S) \cdot CH_3$ complex |

# CASE STUDY: **GaAs** OVER **GaAs** *

*P. K. Saxena, P. Srivastava, R. Trigunayat, An innovative approach for controlled epitaxial growth of GaAs in real MOCVD reactor environment, *Journal of Alloys and Compounds* 809 (2019) 151752.

# CHEMICAL KINETICS

**Gas-phase reactions:**



(G1) $TMGa + H_2 = MMGa + 2CH_4$

(G2) $TBAs = AsH + C_4H_8 + H_2$

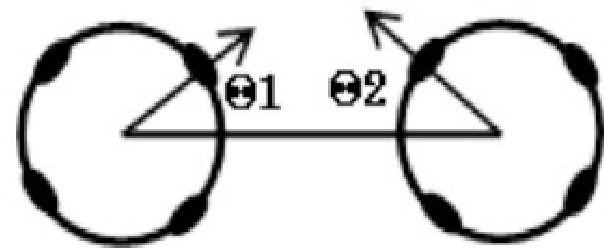
**Surface reaction:**

(S1) $MMGa + AsH = GaAs(s) + CH_4$

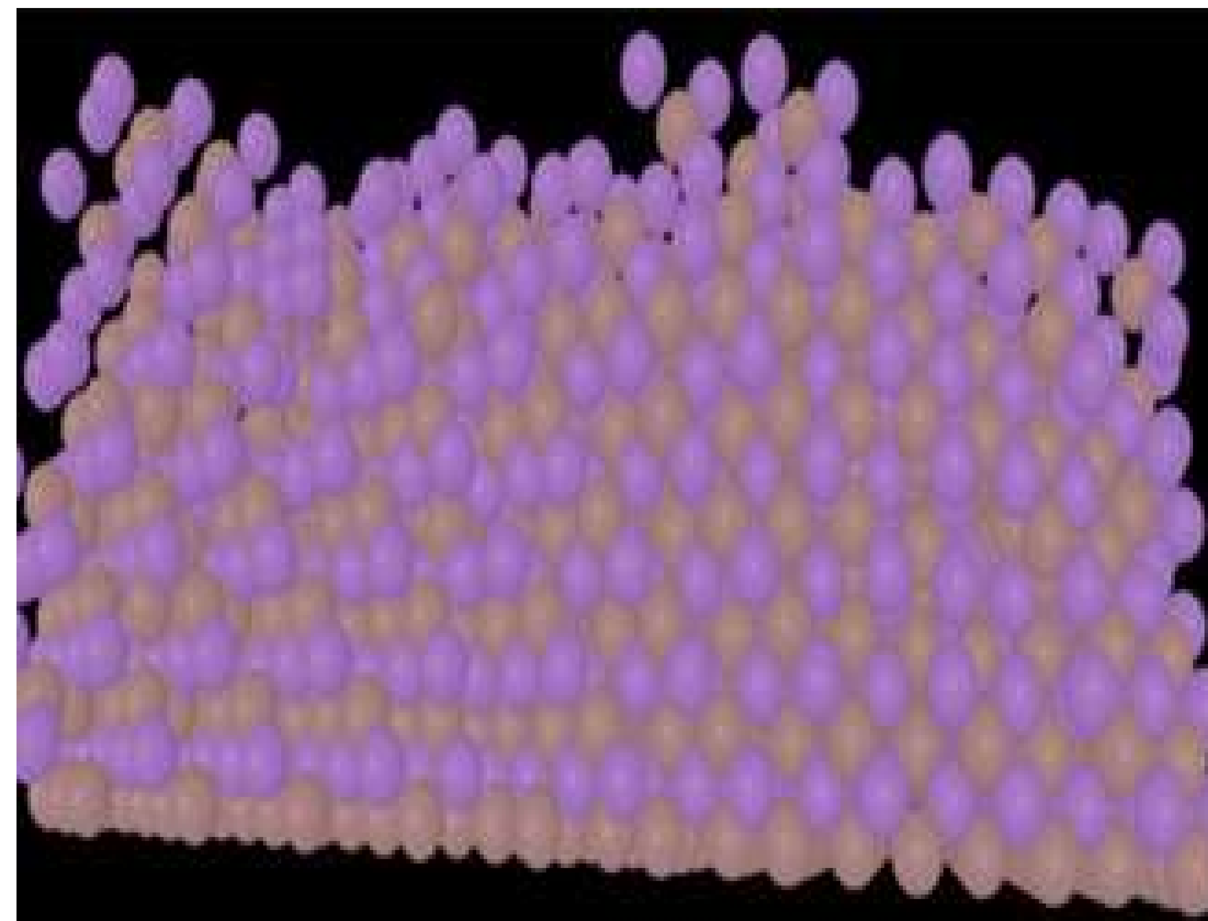
Reactions included in the gas-phase and surface-phase model

| Kinetic Parameter | Value | Unit |
|---|---|---|
| $A_{G1}$ | $1.2 \times 10^{15}$ | $S^{-1}$ |
| $A_{G2}$ | $5.32 \times 10^{15}$ | $S^{-1}$ |
| $A_{S1}$ | $1.23 \times 10^{9}$ | m/s |
| $E_{G1}$ | 196 | kJ/mol |
| $E_{G2}$ | 203 | kJ/mol |
| $E_{S1}$ | 130 | kJ/mol |

# MOCVD GaAs over GaAs



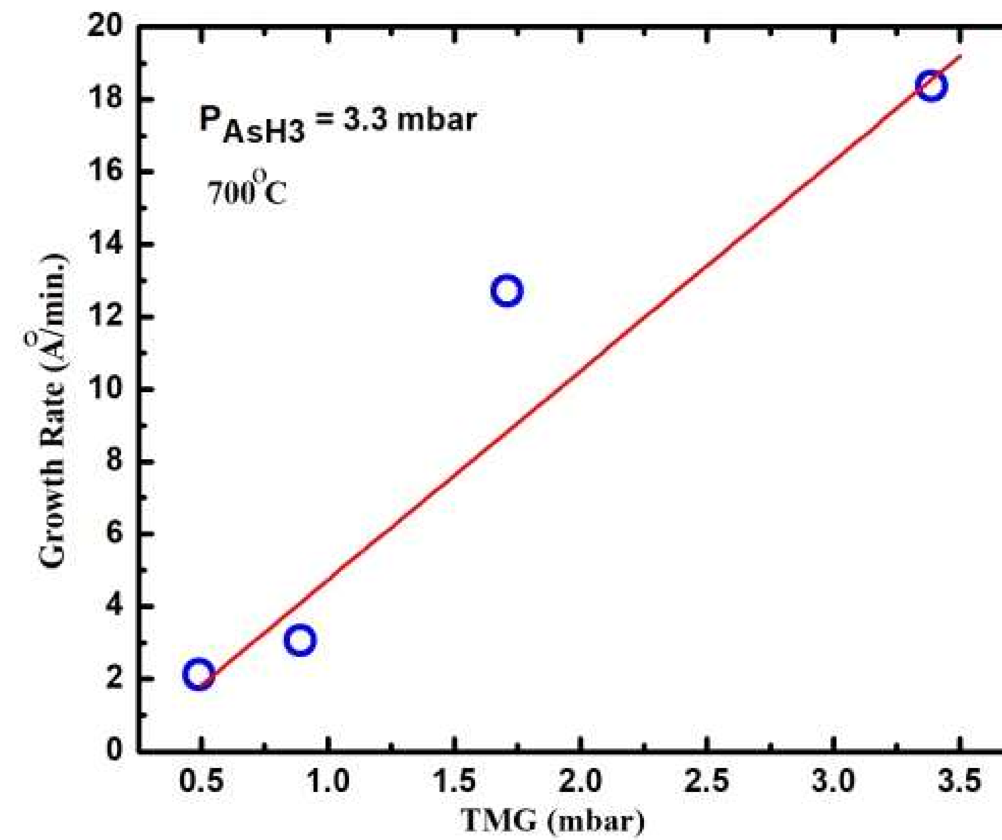

An atom makes bond with another atom when its patches lie in a line. The interaction between two atoms depends upon the angle its patches make with each other.



* Journal of Alloys and Compounds 809 (2019) 151752.

# MOCVD Growth Rate

| Parameters | Values | Units |
|---|---|---|
| Substrate surface energy ($E_s$) | 1.75 | eV |
| Schwoebel barrier energy ($E_{shw}$) | 0.02 | eV |
| Incorporation barrier energy ($E_i$) | 0.05 | eV |

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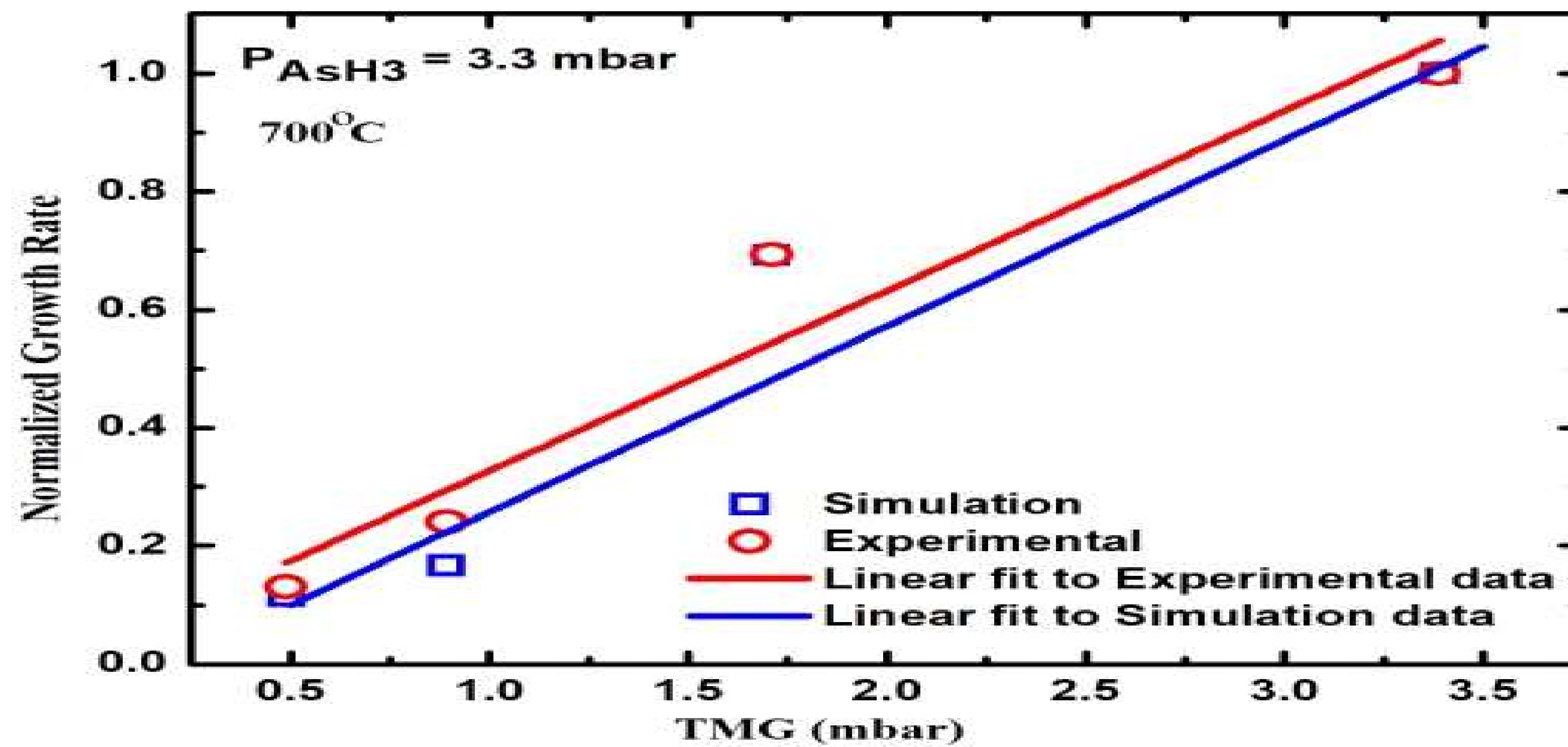
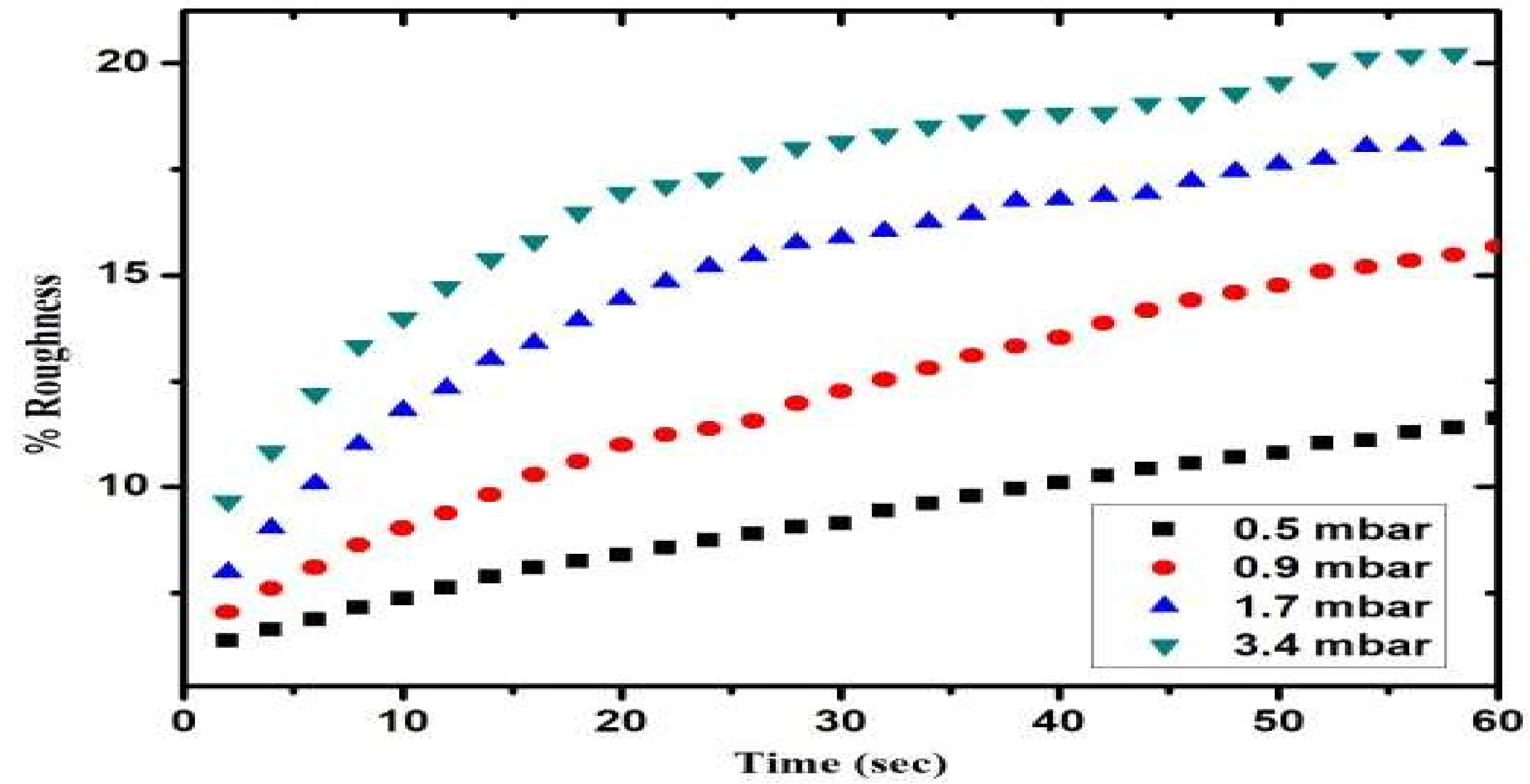
# MOCVD Growth Rate

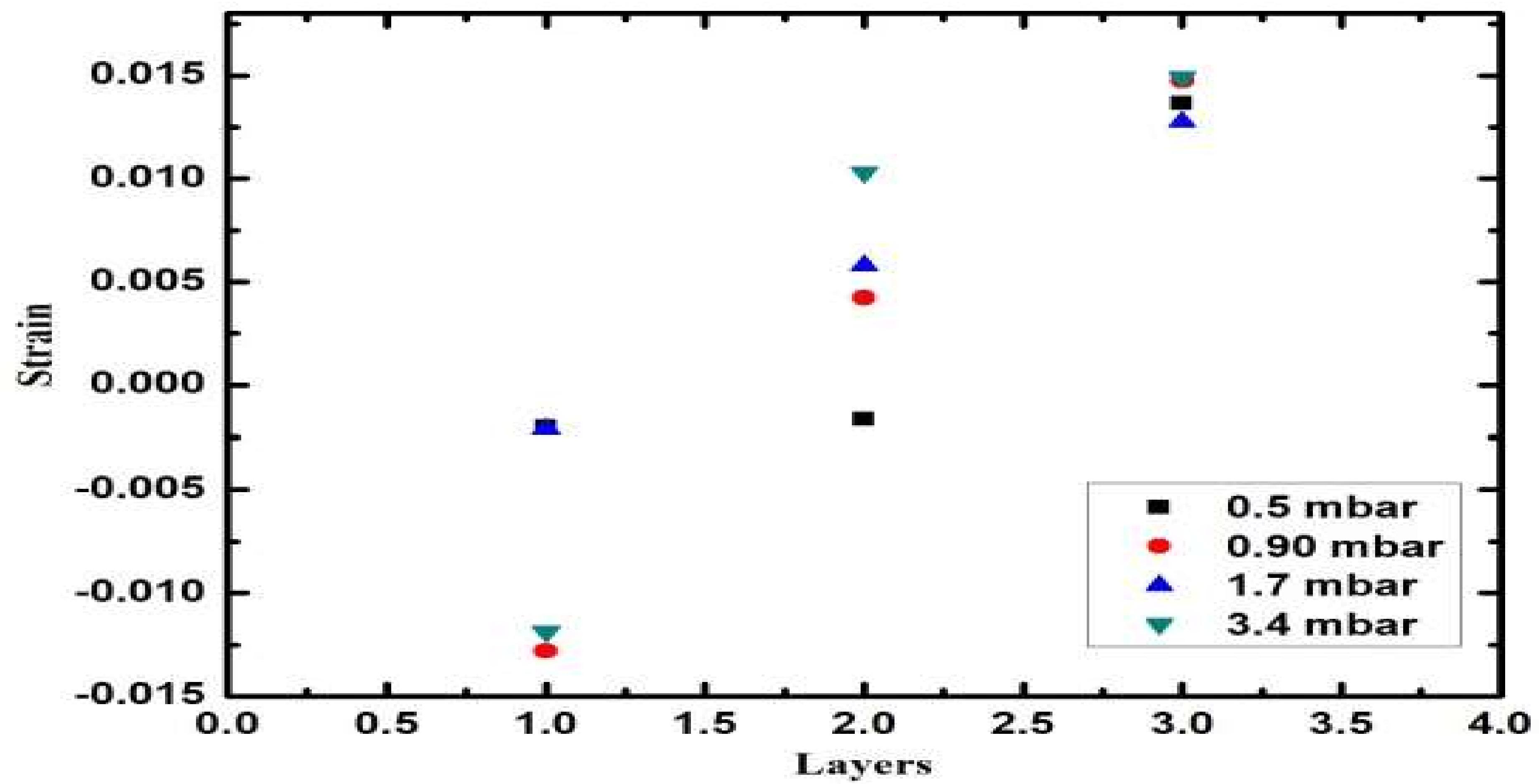



* Journal of Alloys and Compounds 809 (2019) 151752.

# ROUGHNESS



# STRAIN



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