



# *Materials for Gallium-Nitride Electronics*

Joff Derluyn

Co-founder and CTO at EpiGaN

# Outline

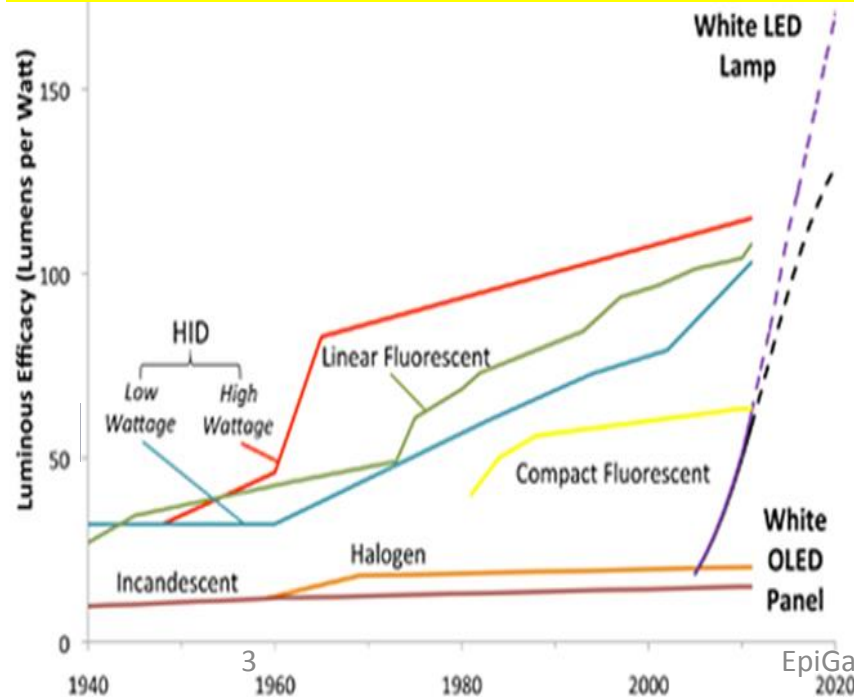
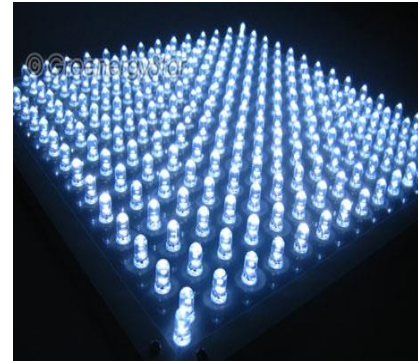
- Material properties of GaN
- Epitaxy of GaN
- GaN on Silicon

Acknowledgement: many thanks to Maarten Leys for course material contributions

# *GaN has already revolutionized Lighting*



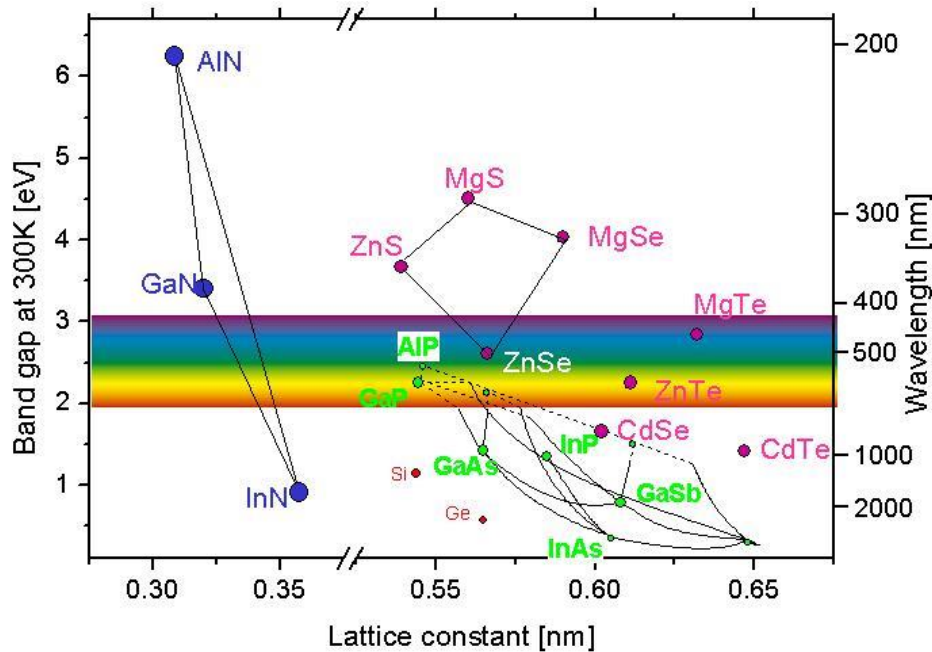
Isamu Akasaki, Hiroshi Amano and Shuji Nakamura,  
**Nobel Prize 2014**



EpiGaN proprietary 2017

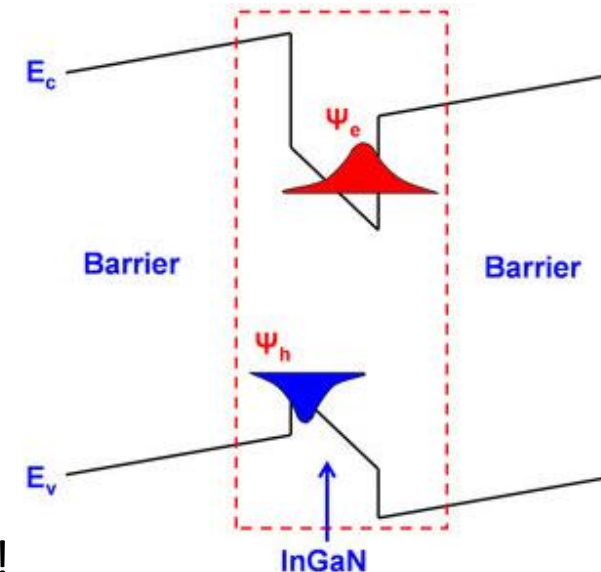
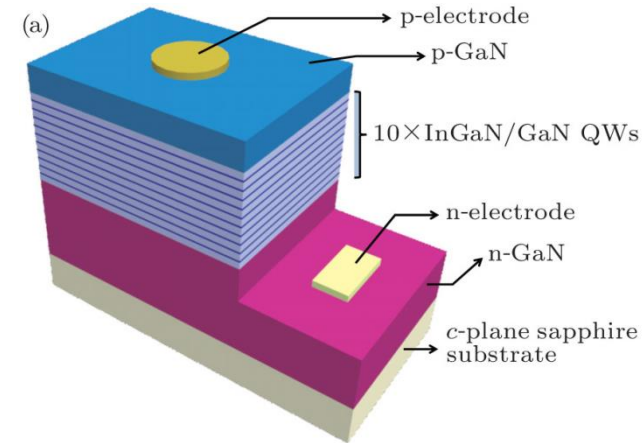


# GaN for opto-electronics



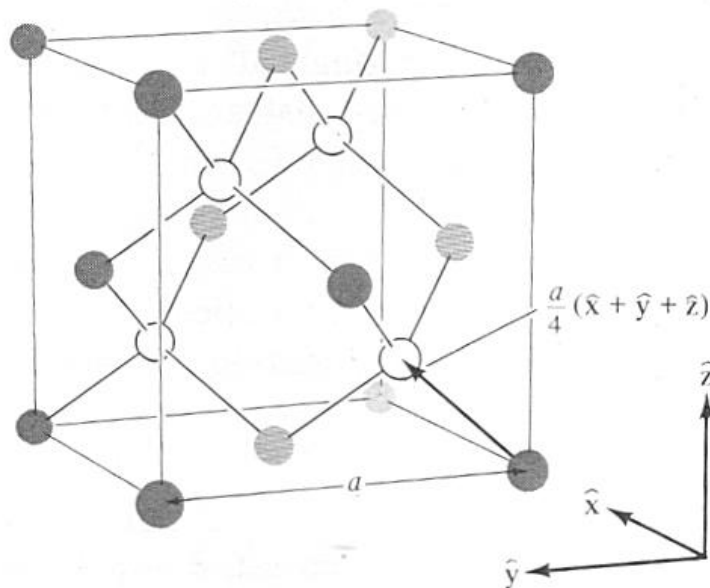
- Direct bandgap
- InGaN alloys cover **Green to UV** photon emission
- Blue/UV/white LED's use InGaN QW's

But: Polarisation effects reduce recombination efficiency!  
(Quantum Confined Stark Effect)



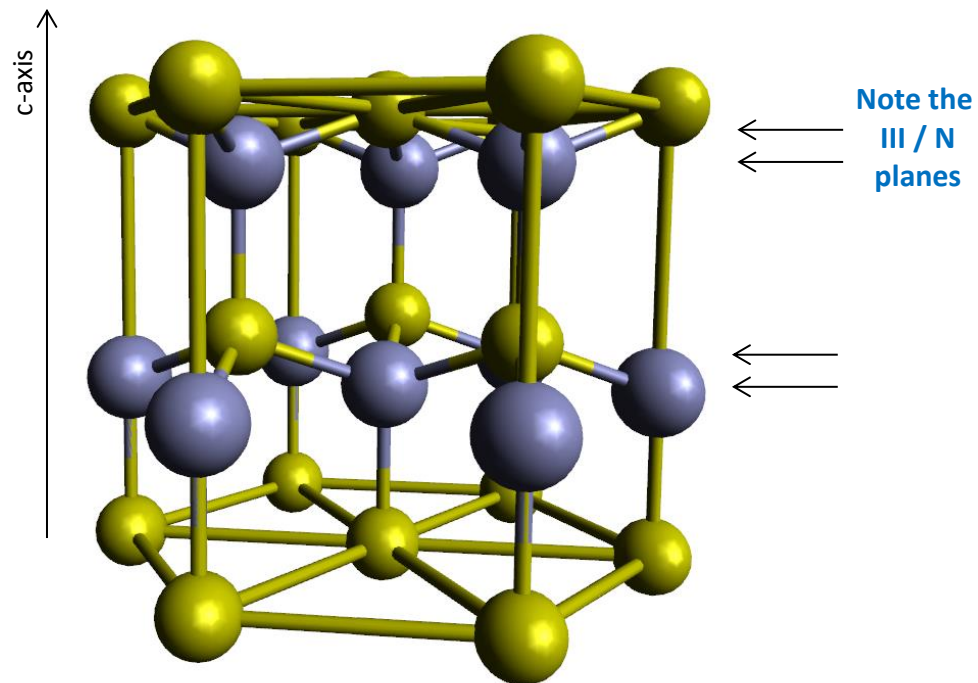
# Crystal structure of III-nitrides

Diamond lattice



Two interpenetrating FCC lattices displaced by  $a/4$  along the main diagonal

Wurtzite lattice  
Hexagonal GaN

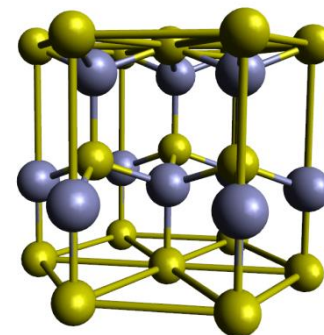


Named after French chemist Charles-Adolphe Wurtz



# *What causes polarization?*

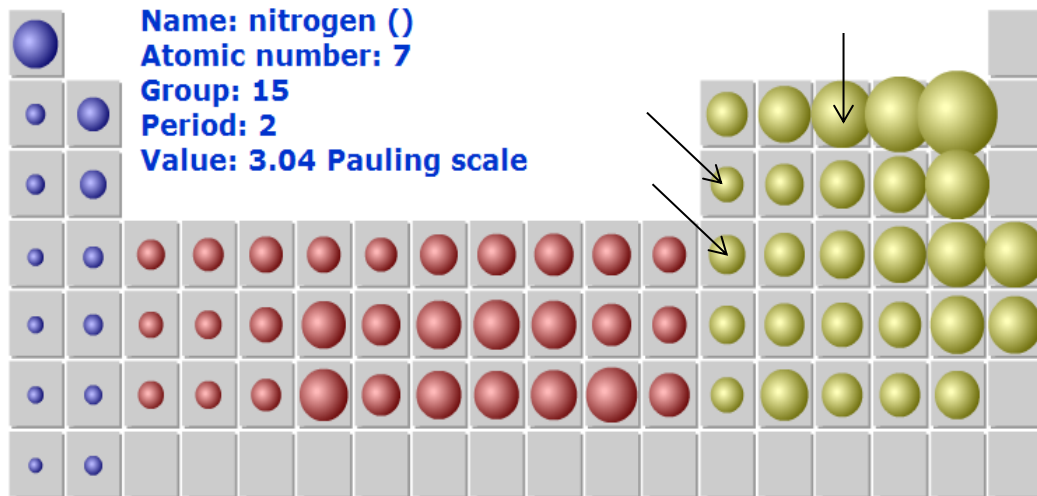
- There are two types of polarization in GaN
  - Piezoelectric (polarization with strain)
  - Spontaneous (polarization with no strain)
- Piezoelectricity requires the crystal to be non-centrosymmetric.  
In a centrosymmetric crystal, for every atom at location  $(x,y,z)$ , there is an indistinguishable atom at point  $(-x,-y,-z)$ .  
  
Crystals with centrosymmetry are not piezoelectric.  
Wurtzite/GaN is non-centrosymmetric.
- Spontaneous polarization occurs if the crystal is “naturally” distorted from the ideal shape. This happens due to the differently-sized constituent atoms, ex. Ga and N.



# Electronegativity / atomic radius

## Electronegativity (Pauling)

## WebElements



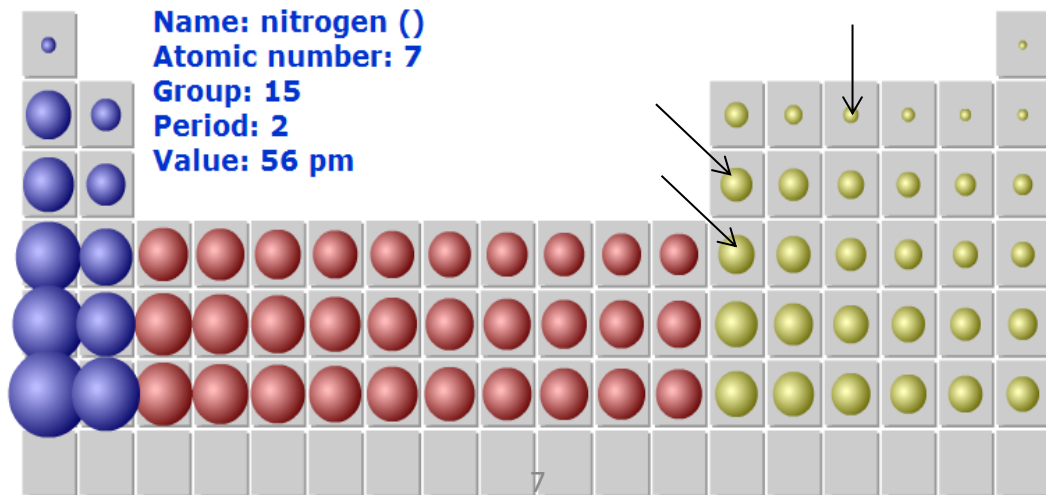
N: 3.04

Al: 1.61

Ga: 1.81

## Atomic radius

## WebElements



N: 56 pm

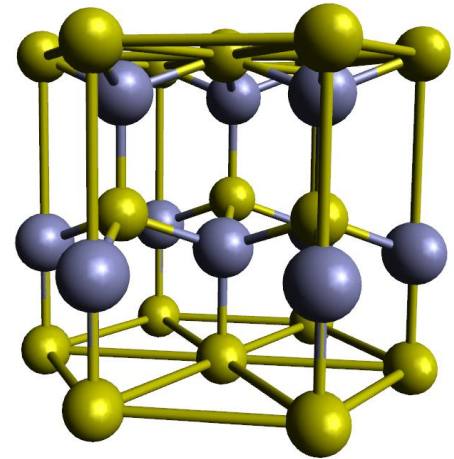
Al: 118 pm

Ga: 136 pm

# *Polarisation in AlGaN: Summary*

Let's put everything together:

- Non centrosymmetric crystal
- Large chemical differences between elements from III (Ga, In, Al) and V (N)



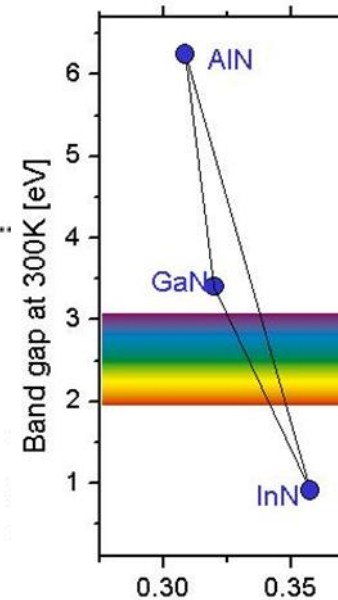
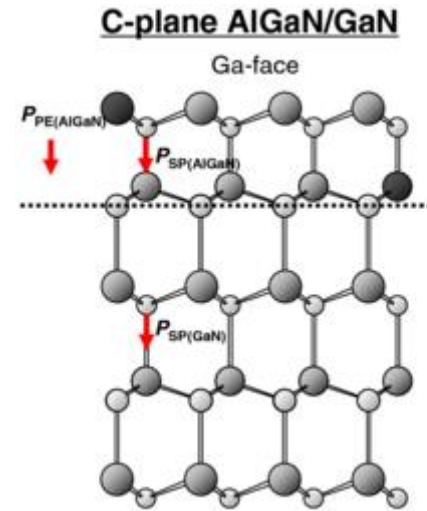
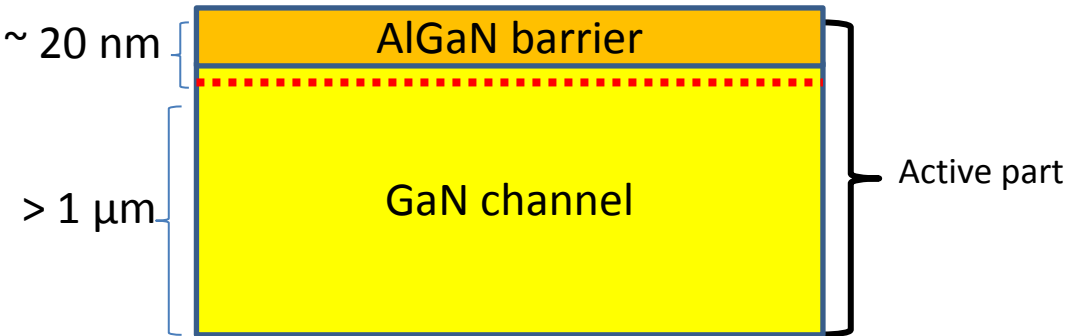
⇒ Charge separation along c-axis direction

Moreover :

- Alloys have different spontaneous polarisation:  
 $\text{pol}_{\text{AlN}} > \text{pol}_{\text{GaN}}$
- $E_{g,\text{AlN}} > E_{g,\text{GaN}}$



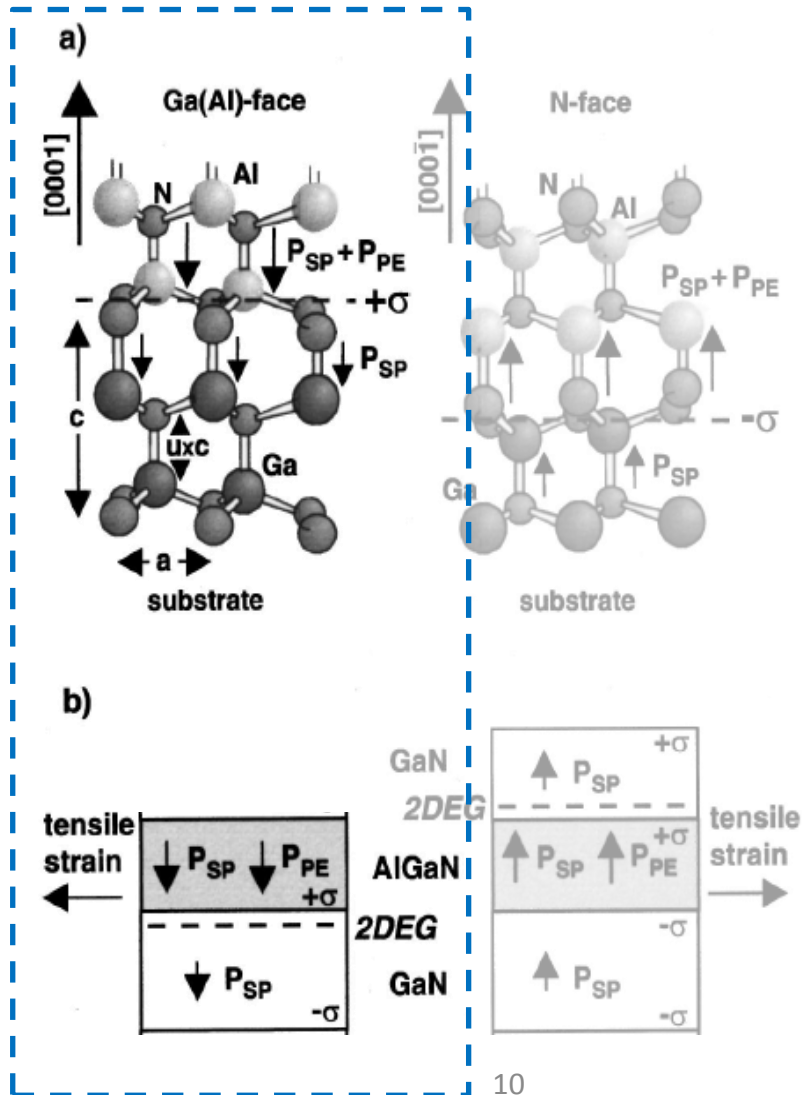
# CONSIDER THE FOLLOWING LAYER STACK



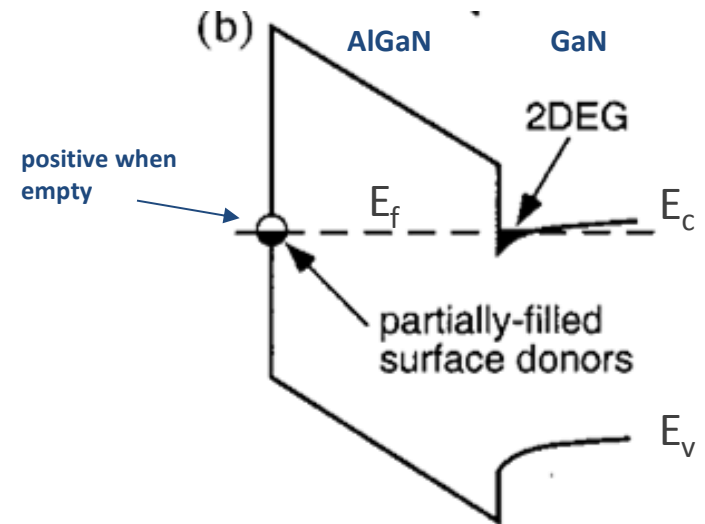
The AlGaN barrier:

- Thin layer is strained relative to thick GaN
- Has a higher bandgap than GaN
- Has a higher spontaneous polarisation than GaN

# AlGaN/GaN heterostructures

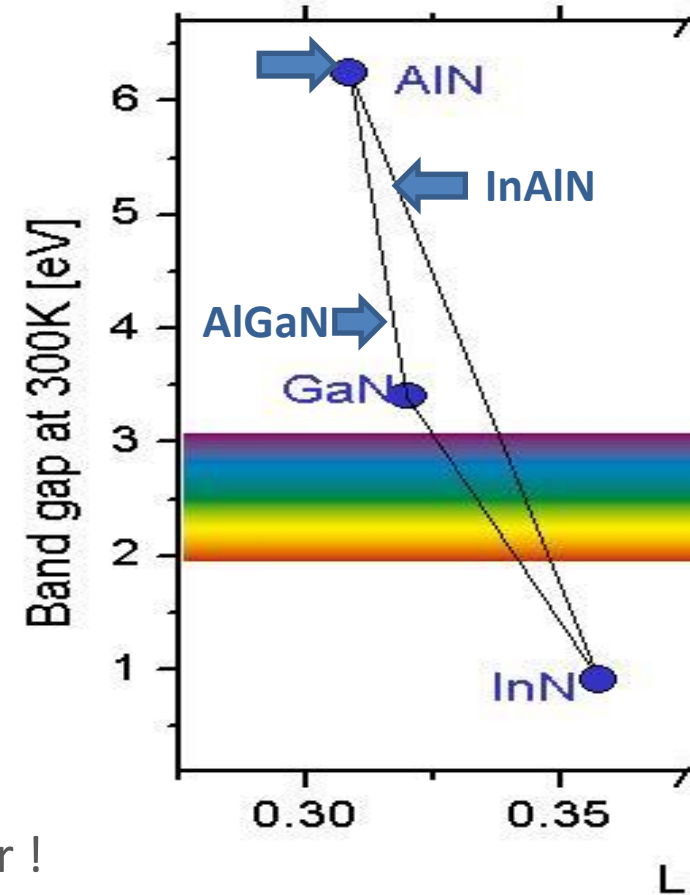
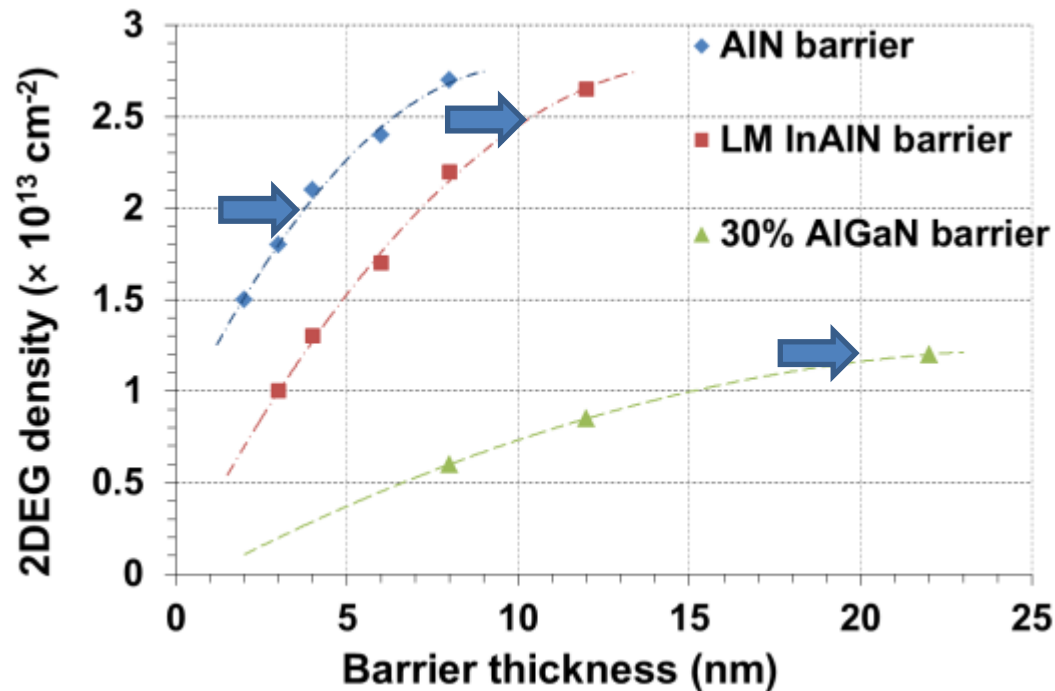


Band structure



**No impurity scattering  
=> high mobility**

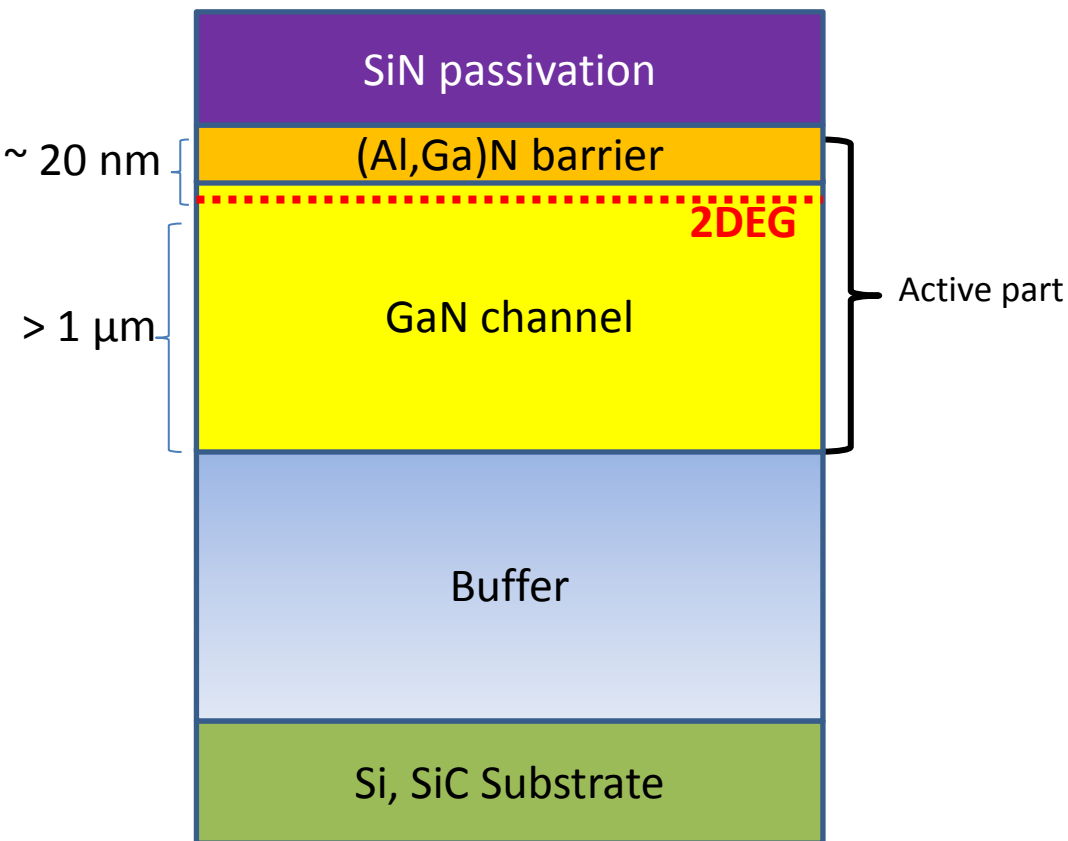
# Varying barrier layer to increase 2DEG density



- $N_s \sim 2 \times 10^{13} \text{ cm}^{-2}$  with only 4 nm thin AlN barrier layer !
- $N_s \sim 2.5 \times 10^{13} \text{ cm}^{-2}$  with only 12 nm InAlN barrier layer !

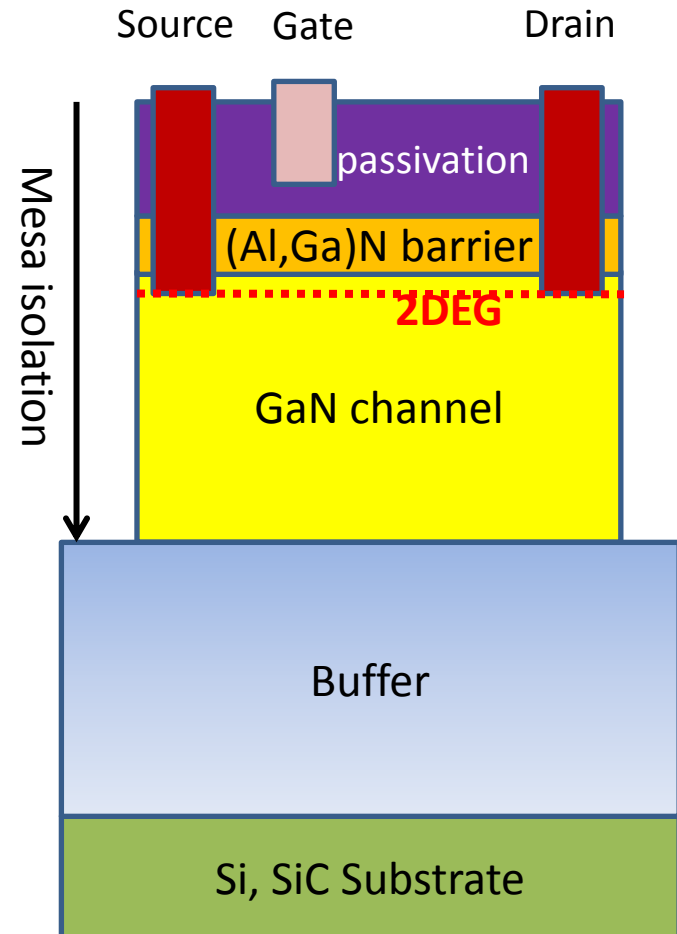
# GAN EPIAYER AND BASIC TRANSISTOR DEVICE

## Epiwafer



Creation of a 2DEG without any impurity doping!

## Transistor Device



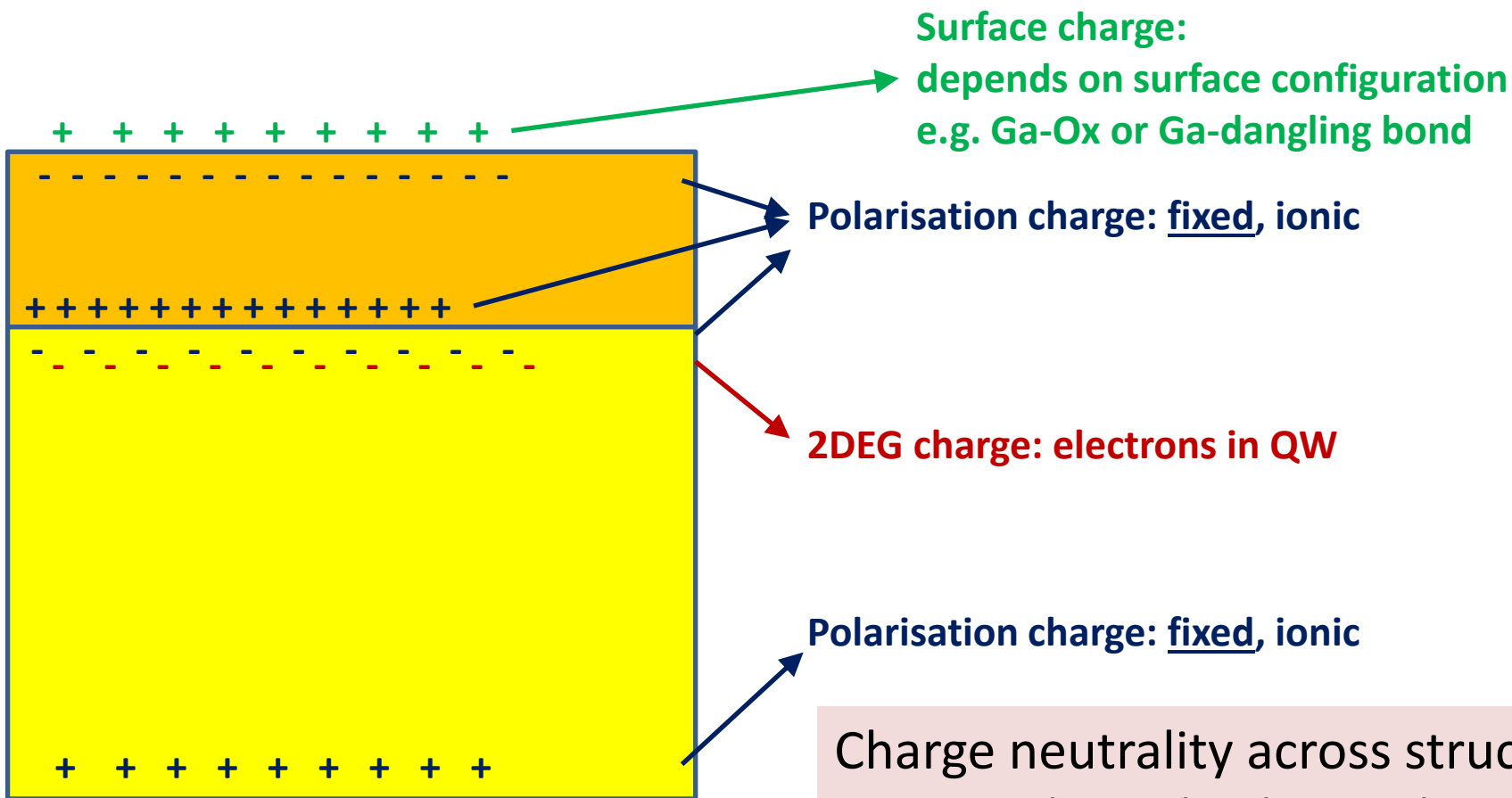
HEMT: High Electron Mobility Transistor



# HEMT = Surface Effects

## Charges in AlGaN/GaN HEMT (c-axis Ga-face)

REF: Ibbetson APL77-2 2000



Charge neutrality across structure!

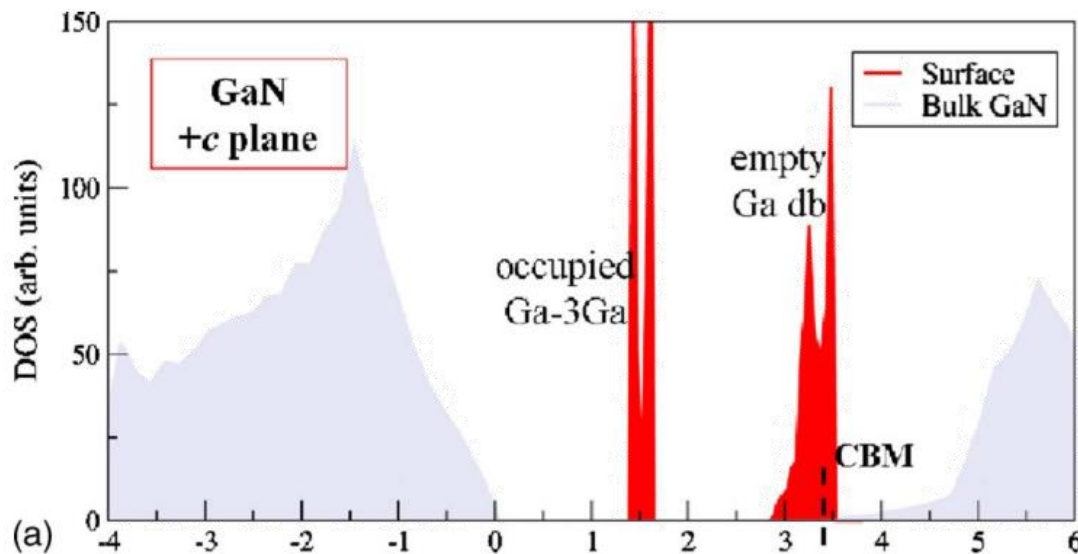
$$|\sigma_{\text{surf}}| \sim |\sigma_{\text{2DEG}}|$$



# Surface states

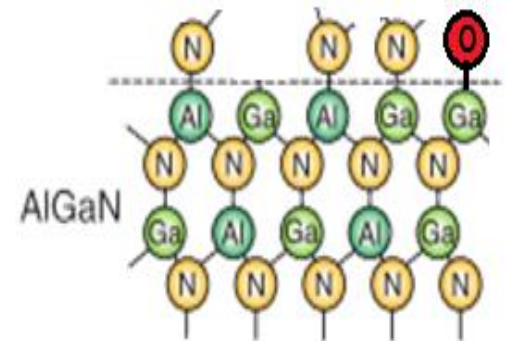
- Electrons in the 2DEG are supplied by the surface (not by thermalised impurities)

J. Appl. Phys. **101**, 081704 (2007)



REF: Van de Walle

Electron sources at the unpassivated surface:



# Dispersion / current collapse

- DC-to-RF dispersion!** (REF: Vetury, IEEE TED48-3 2001)

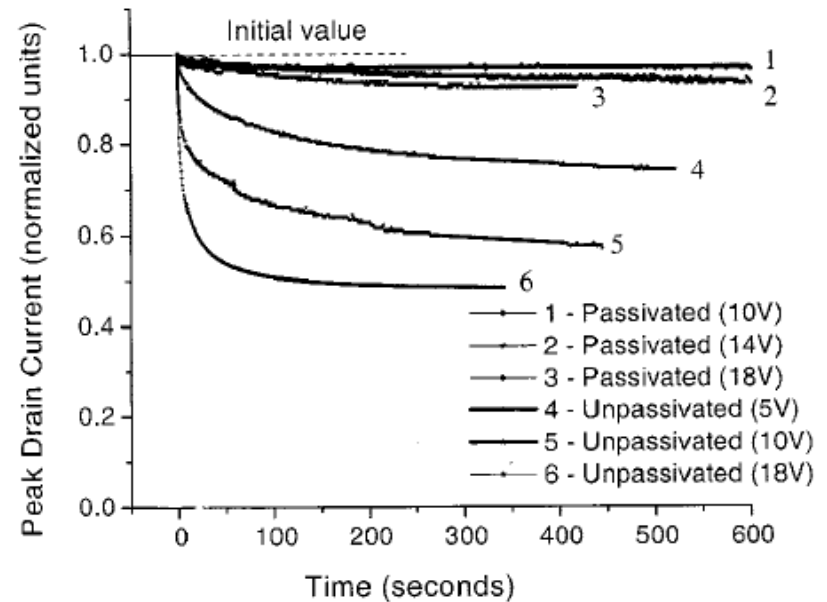
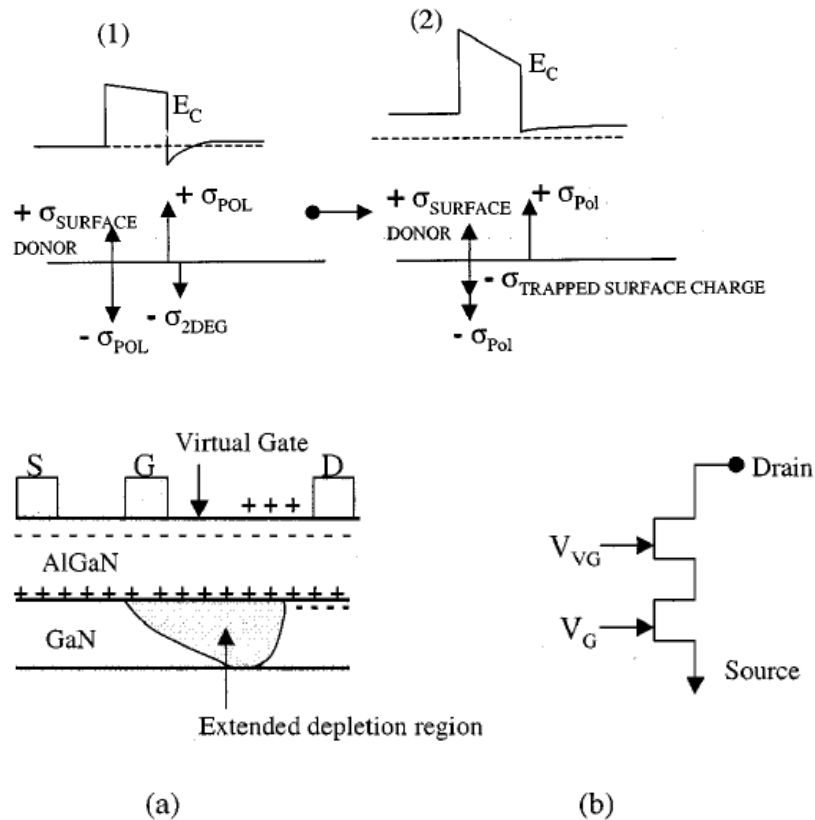


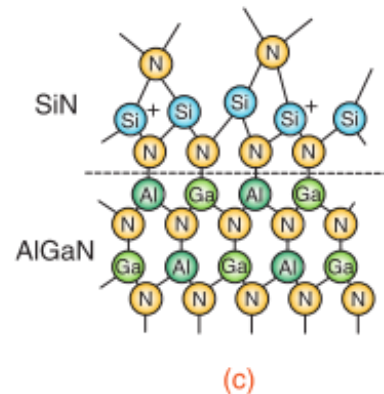
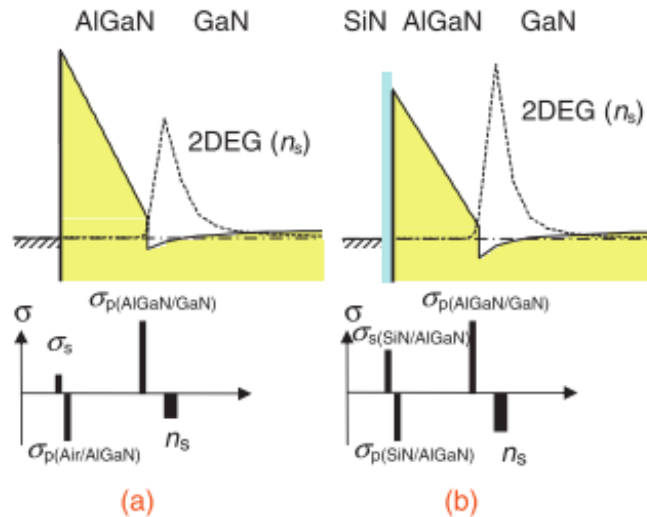
Fig. 3. Model of the device showing the location of the virtual gate and schematic representation of the device including the virtual gate.

(For RF devices biased at 10 V – 50 V)

# HEMT Surface Passivation with SiN

REF: Onojima APEX1 -071101 2008

## Unpassivated surface:



## Atomic configuration matters!

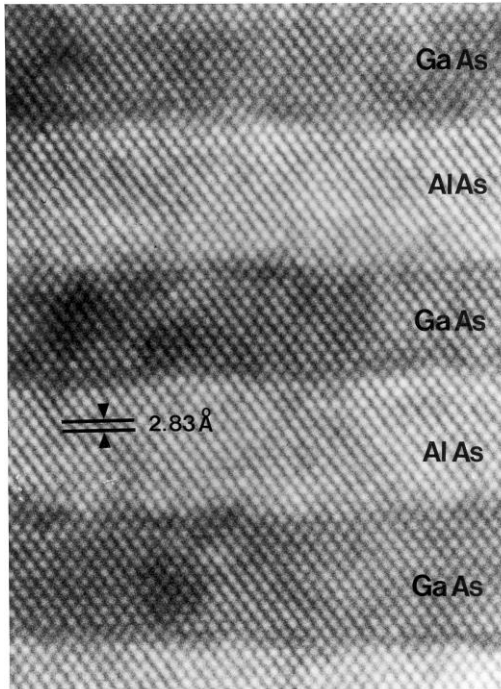
Cleaning procedures for GaN are based on nitridation ( $N_2$  plasmas,  $NH_3$  plasmas,  $(NH_4)_2S$ , Thermal treatments in  $N_2$  or  $NH_3$ )

**Fig. 1.** Schematic diagrams of the conduction band and charge distributions in the AlGaN/GaN heterostructure (a) without SiN passivation and (b) with SiN passivation. (c) Schematic model of the atomic arrangement at the SiN/AlGaN interface.

# Outline

- Properties of GaN
- Epitaxy of GaN
- GaN on Silicon

# Epitaxy



M.R.Leys et al, J.C.G. **68**(1983) 431

Google says:

**epitaxy**

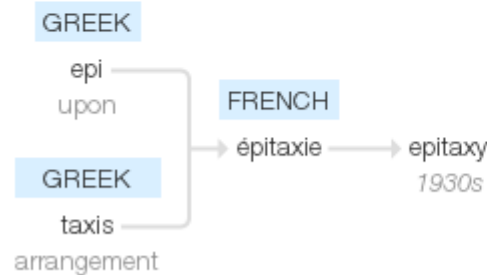
/ˈɛpɪtaksi/

noun CRYSTALLOGRAPHY

noun: epitaxy

the natural or artificial growth of crystals on a crystalline substrate that determines their orientation.

Origin



1930s: from French *épitaxie*, from Greek *epi* 'upon' + *taxis* 'arrangement'.

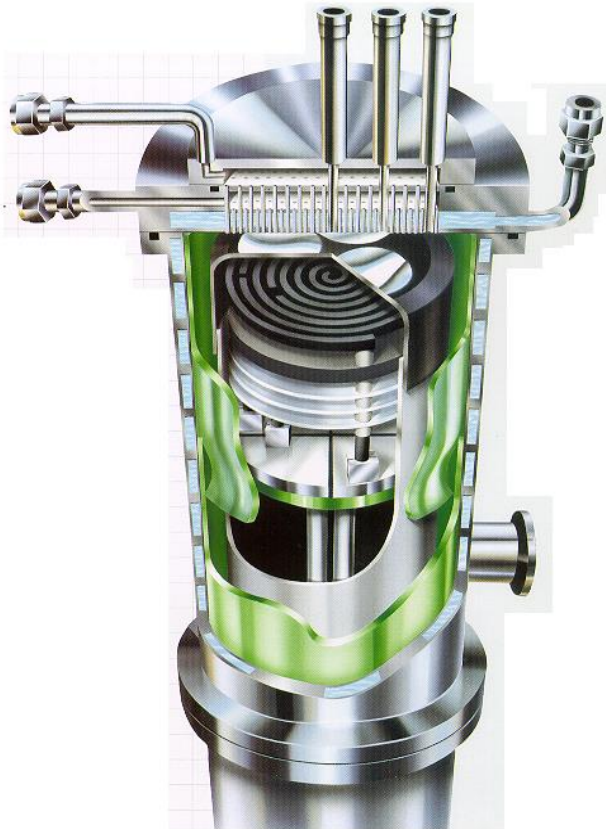
To “grow” a crystal

-> enlarge an existing crystal (substrate) with new (different) material



# Metal-Organic Chemical Vapour Deposition

## Or Metal-Organic Vapour Phase Epitaxy



- Heated  $> 1000^{\circ}\text{C}$  (for GaN)
- Rotating susceptor contains substrates
- Water cooled reactor vessel
- Reagent gases are introduced through 'showerhead'
  - Nitrogen: from  $\text{NH}_3$
  - Ga: from trimethyl-Gallium
  - Al: from trimethyl-Aluminium
  - In: from trimethyl-Indium
- In a 'carrier' flow:  $\text{N}_2$  or  $\text{H}_2$
- Controlled temperature, pressure, gas flows

# Other growth techniques for GaN

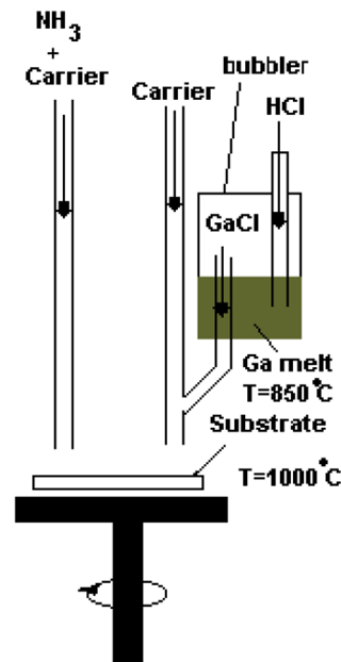
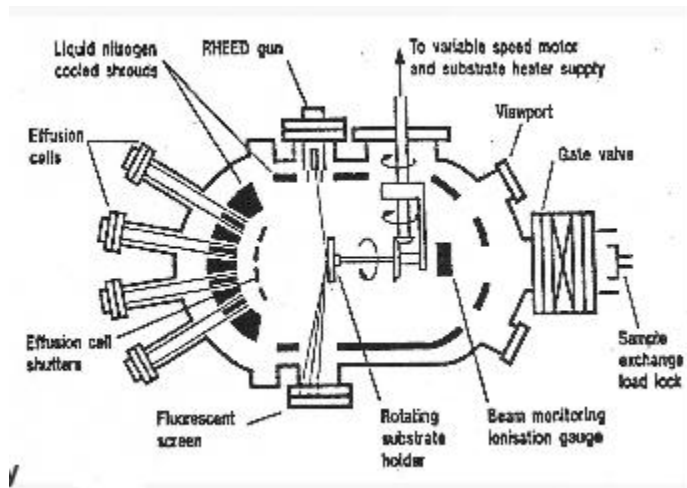
## Molecular Beam Epitaxy - MBE

Ultra High Vacuum

NH<sub>3</sub> or N<sub>2</sub> plasma sources

Research tool or for laser diodes

Not mass production technology



## Halide Vapor Phase Epitaxy HVPE

High growth rate (100-200 um/hr)

No pre-reactions; Carbon-free;

No possibility for abrupt interface, alloy => no heterostructures

Intrinsically n-type (no semi-insulating)

Used for thick bulk layers (pseudo-substrates, templates...)

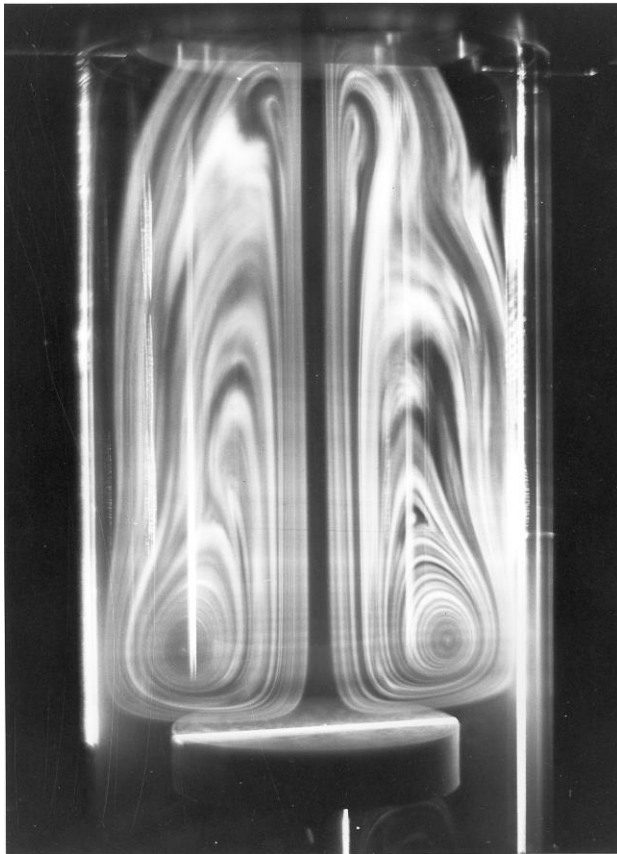
# *Advantages and disadvantages of MOCVD*

- + Good growth rates  $\sim 1$  to  $5 \text{ um/hr}$
- + Good crystal quality achievable
- + Abrupt interfaces possible
- + Easy fabrication of alloys
- + Production-compatible reactors available
- + High uniformity
- Intrinsic contamination (Carbon, Hydrogen)
- Scaling to batch reactors is tough
- No qualitative reagent precursors for “special” elements

# Things that matter for MOCVD: Fluid dynamics

Gasflow patterns visualized by  $\text{TiO}_2$  particles (smoke)

Vertical (pedestal) reactor, gasinlet at top



C.A.Wang, MIT, J.C.G. **77** (1986) 136

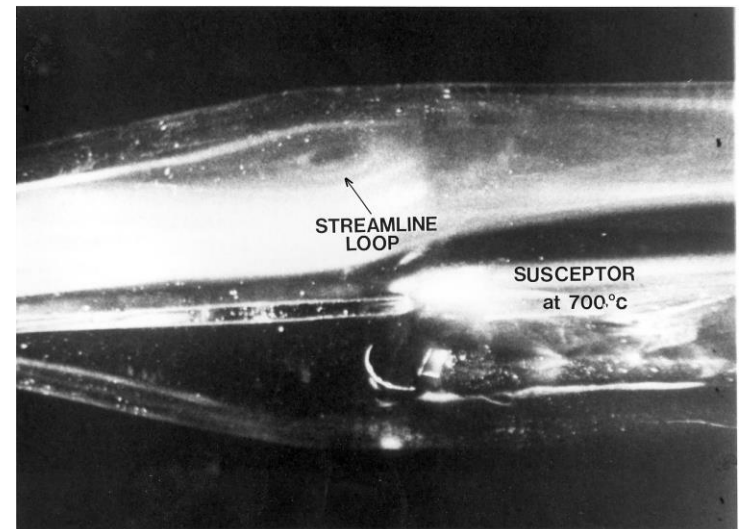
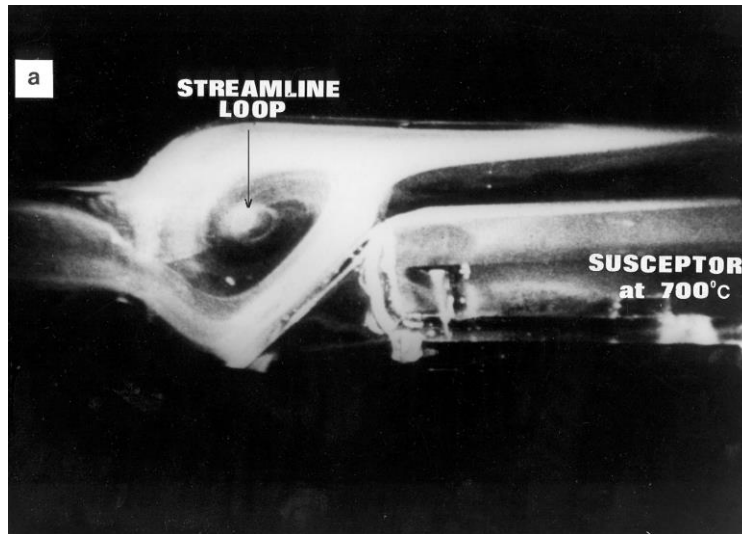
**Forced** convection due to a **pressure** difference between inlet and exhaust

**Free** convection due to a **temperature** difference between susceptor and surroundings

Here the two are in **opposing** directions.....

# Things that matter for MOCVD: Gas flow effects

In horizontal reactors forced and free convection are perpendicular



Note that immediately above the susceptor **no** particles are seen.

This is due to the **thermoforetic** effect: particles move **away** from a **hot** surface

**Existence of a “boundary layer” with:**

temperature gradient

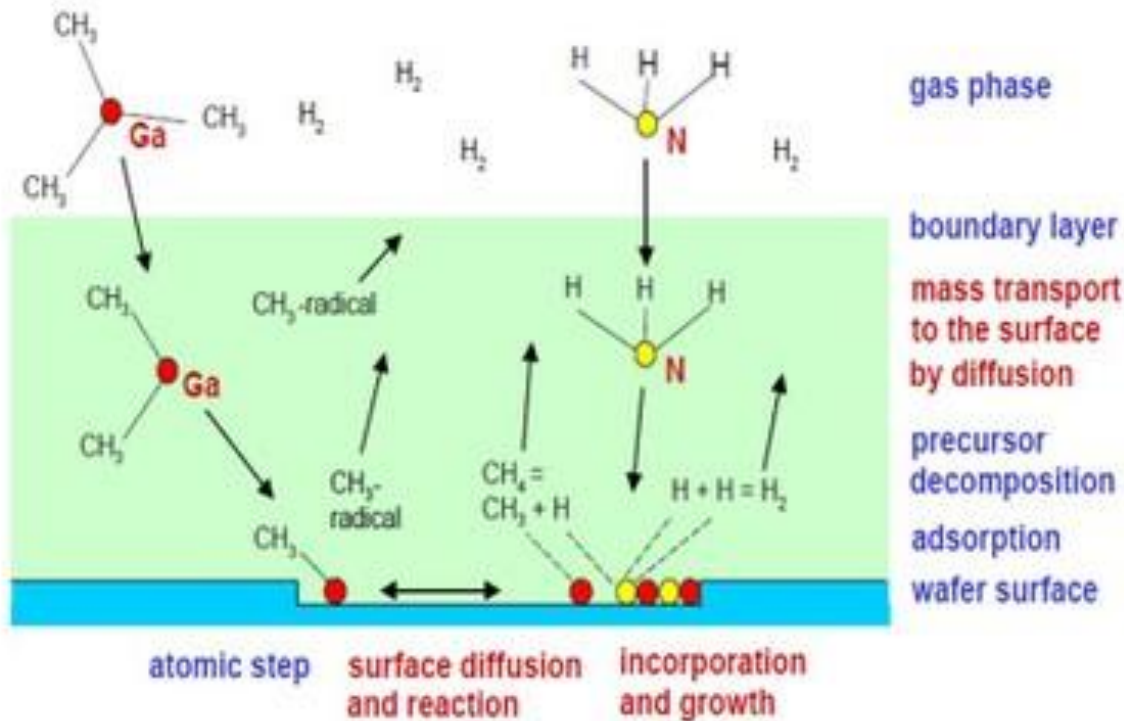
velocity gradient

concentration gradient

composition gradient



# Things that matter for MOCVD: Chemical reactions



In the gas-phase:  
Pyrolysis of TMGa/TMA/TMI  
and NH<sub>3</sub>

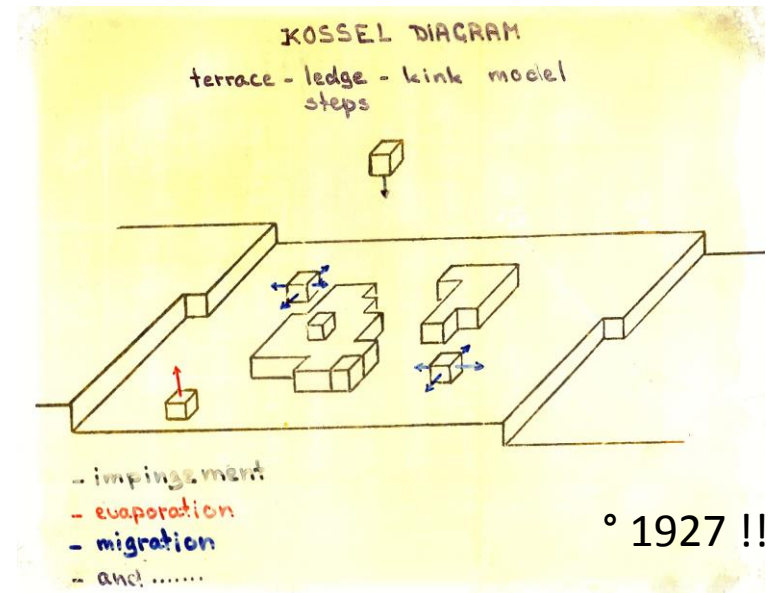
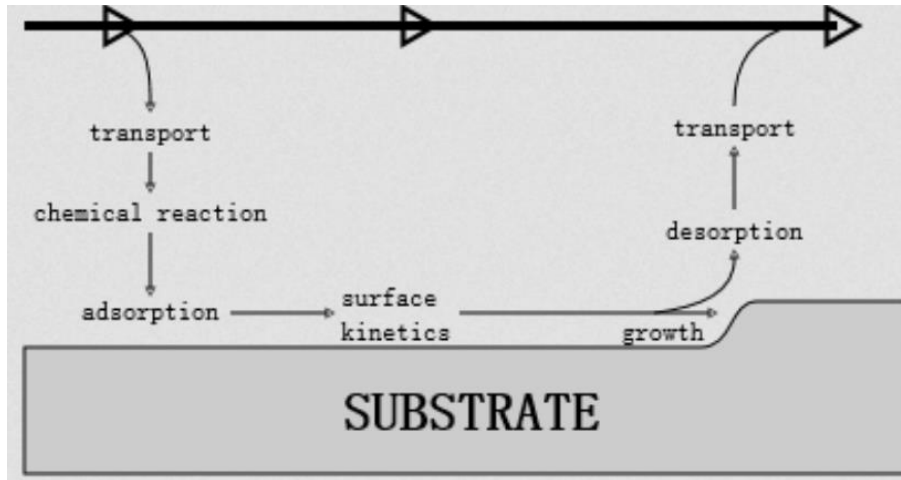


At the surface:  
 $\text{CH}_3\text{-Ga} + \text{NH}_3 \rightleftharpoons \text{GaN} + \text{CH}_4 + \text{H}_2$

Temperature-, (vapour-)  
pressure- dependent  
equilibrium reaction

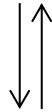
The equilibrium is dynamic!!!

# Things that matter for MOCVD: Kinetics



Another (dynamic) equilibrium between:

- Adsorption / desorption of reaction species on the surface



- Incorporation: Lateral migration towards nucleated island or crystal step

Consequence: Growth on a foreign substrate requires a good nucleation technique

# Where does it go? ...Thermodynamics

## Energy, heat and work

**THE FIRST LAW:**  $\Delta U = q + w$ ;  $dU = dq + dw$

$$c_v = \left( \frac{\partial U}{\partial T} \right)_v$$

At constant volume

$$c_p = \left( \frac{\partial H}{\partial T} \right)_p$$

At constant pressure

**Enthalpy:**  $H = U + pV$

**IMPORTANT:** Gibbs energy:  $G = H - TS$

S is **entropy**

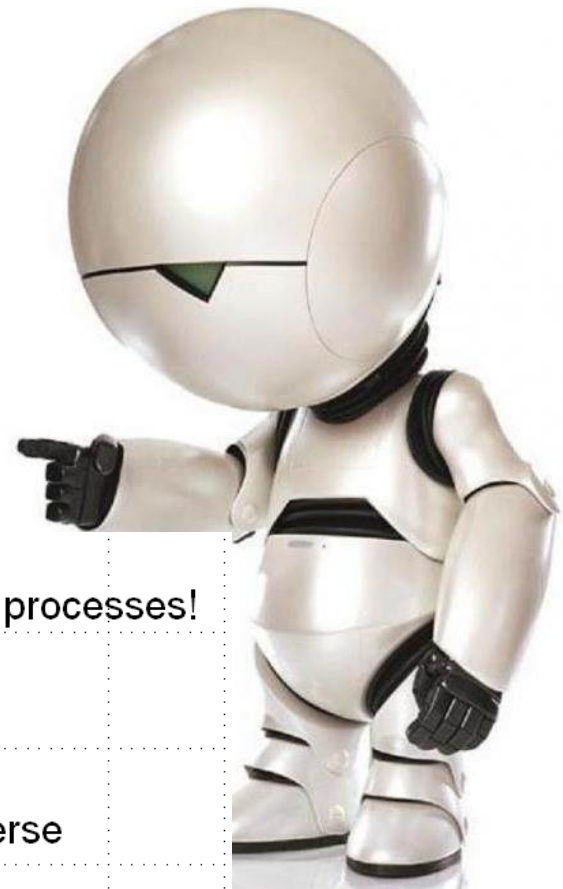
**definition!** At  $T = 0$ ,  $S = 0$ . This applies for pure, crystalline substances

# DON'T PANIC

**THE SECOND LAW :**  $dS = \frac{dq_{ev}}{T}$  For **reversible** processes!

In general  $dS \geq \frac{dq}{T}$

Due to **irreversible** processes the entropy of the universe continuously **increases**



# Description of a closed system with state functions

There are four state functions:  $U(V, T)$ ,  $A(V, T)$ ;  $H(p, T)$ ,  $G(p, T)$

We prefer pressure and temperature as variables

Enthalpy  $H$ , **Gibbs Energy  $G$**

The standard state: at 298.15K, 1 bar :  $\Delta H^0$ ,  $\Delta G^0$

Definition of the chemical potential  $\mu = \left( \frac{\delta G}{\delta n} \right)_{p, T}$  Molar Gibbs energy

In general:  $\mu = \mu^o + RT \ln \frac{p}{p^o}$  **THIS ONE IS IMPORTANT!**

**At equilibrium:** the chemical potential is equal everywhere and constant

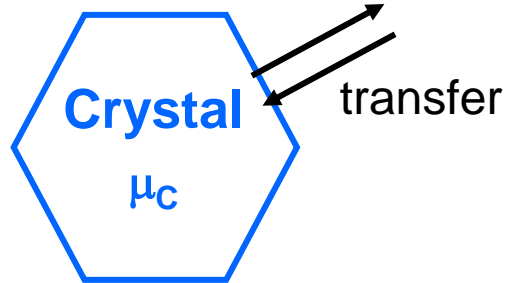
**Change:**  $d\mu = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$

Either the number of particles,  $n$

Or the Gibbs energy, i.e. pressure **p** and/or temperature **T**

# As always, it depends on the Gibbs free energy

Surroundings, ambient,  $\mu_A$



If  $\mu_C = \mu_A$  : equilibrium

If  $\mu_C < \mu_A$  : growth

if  $\mu_C > \mu_A$  : etching

**A system tends to its low(est) Gibbs energy**

Gibbs energy ( $\mu$ ) is a function of **p, T**

Change:

$\bar{p} - p_{eq} = \Delta p$ , positive, **supersaturation**

$T - T_{eq} = \Delta T$ , negative, **undercooling**

Definition of the chemical potential  $\mu = \left( \frac{\delta G}{\delta n} \right)_{p,T}$  Molar Gibbs energy

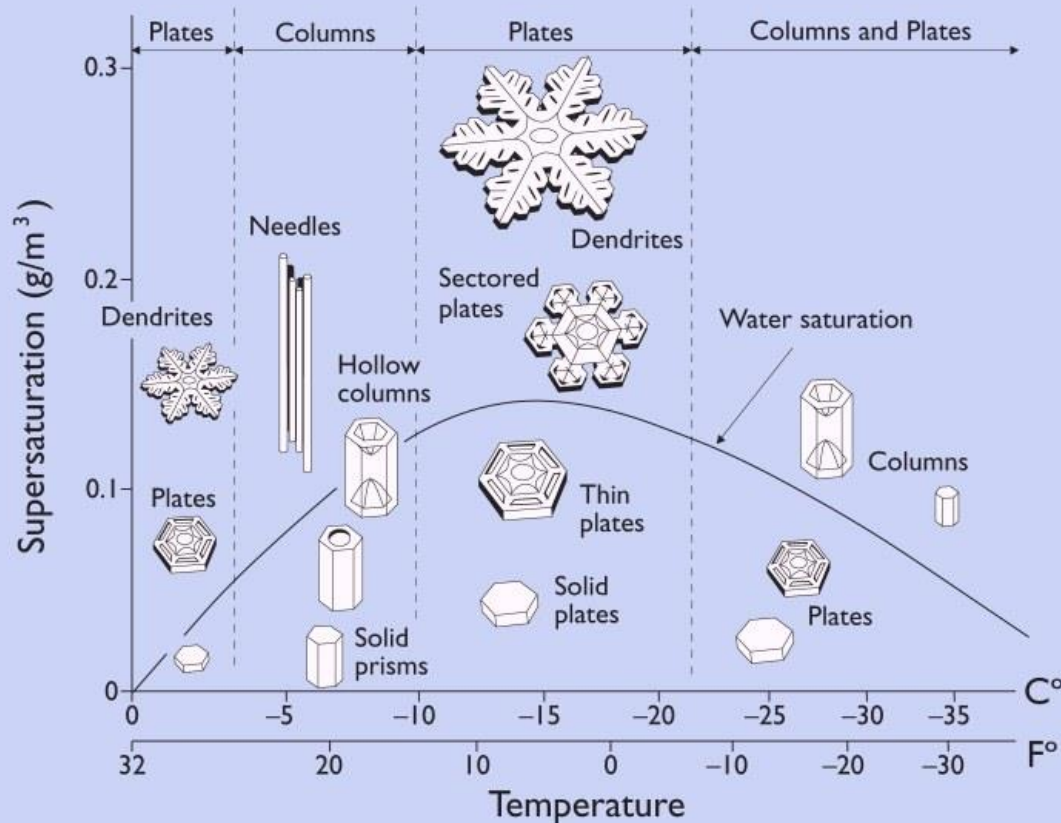
In general:  $\mu = \mu^o + RT \ln \frac{p}{p^o}$



# Crystal growth: an example from nature

## Nakaya diagram, 1954

Supersaturation as density,  
partial (over)pressure of H<sub>2</sub>O in air



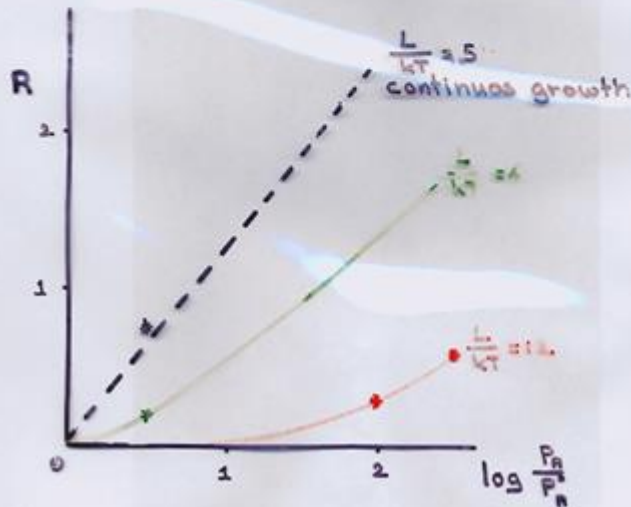
Ukichiro Nakaya (?-1962)  
Worked in Hokkaido/Sapporo  
1932-

snowflakes may be called  
"letters sent from heaven"

# Movie time!

$\log \frac{P_A}{P_A^0}$	$r^*$ (no. of atoms)	$\frac{L}{kT}$
2.6	3 to 4	12
2	5 to 6	12
0.4	9	6
0.5	3 dimens.	4.5

$L = \text{bulk lattice binding energy} = 3 \phi_{AA}$



Things to look for

Movie 1:

Nucleation island formation

Critical island size

Lateral coalescence of islands

Movie 2:

Effect of precursor partial pressure

Movie 3:

Contaminants

Movie 4:

Step bunching

G. H. GILMER  
K. C. KNOWLTON  
H. J. LEAMY  
K. A. JACKSON  
  
BELL TELEPHONE  
LABORATORIES

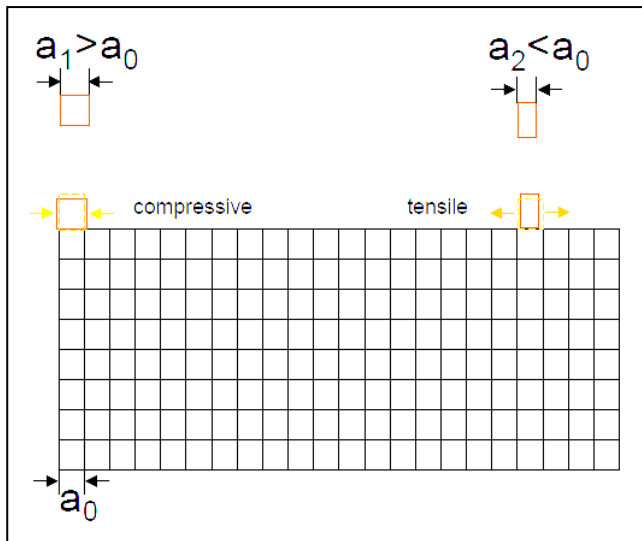
*From the late 70s*

# *Homo-epitaxy versus hetero-epitaxy*

- Homo-epitaxy:
  - E.g. doped Si on Si, GaN on GaN
  - Requires native substrate
- Hetero-epitaxy
  - When there is no native substrate
  - To form hetero-junctions →
    - Critical for QWs, lasers, HEMTs, ...
  - Strain management

Nobel Prize Physics 2000  
Alferov & Kroemer

# Strain in heteroepitaxy



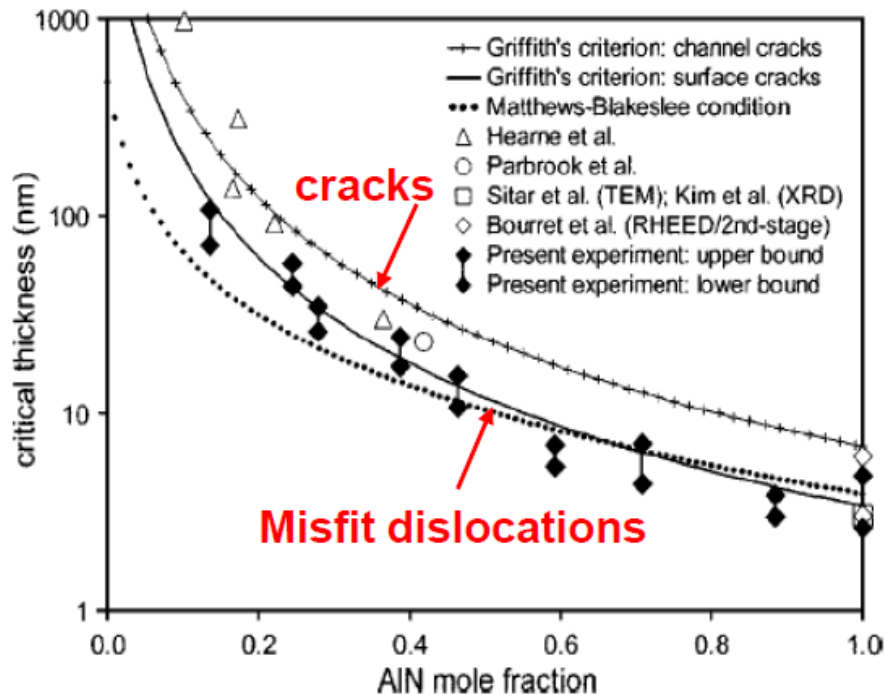
$$\text{Elastic strain: } \varepsilon_0 = \frac{(a_s - a_f)}{a_f}$$

$$\text{Stress: } \sigma = \varepsilon_0 \cdot E$$

with E, the elastic biaxial modulus

- Lattice mismatch between the lattice constant of the film ( $a_f$ ) and the lattice constant of the substrate ( $a_s$ ) gives rise to stress in the film,  $\sigma$ .
- The stress can be either **tensile** or **compressive**.
- In cubic system, strain relaxation occurs through dislocation formation.

# Lattice Mismatch – critical thickness



In a growing mismatched layer, strain builds up (**elastically strained**) until it reaches a critical energy and it **plastically deforms**

Put differently: these two regimes are separated by a “critical thickness”

# Strain relaxation in cubic lattices

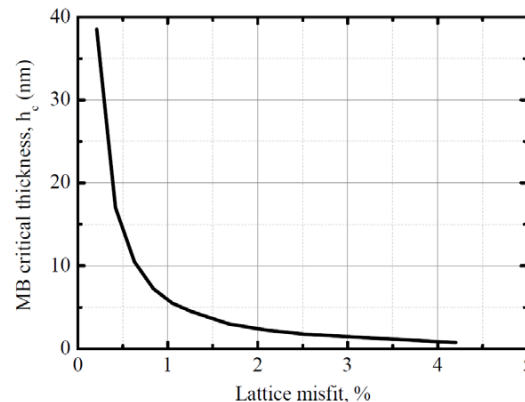
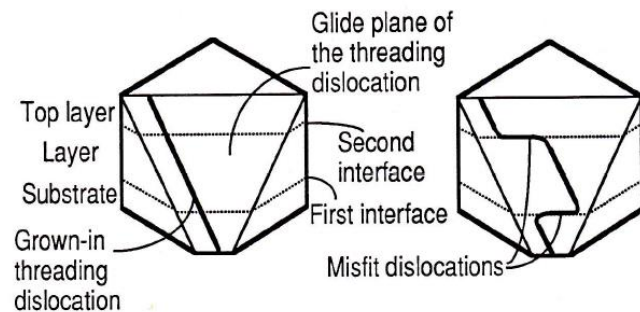
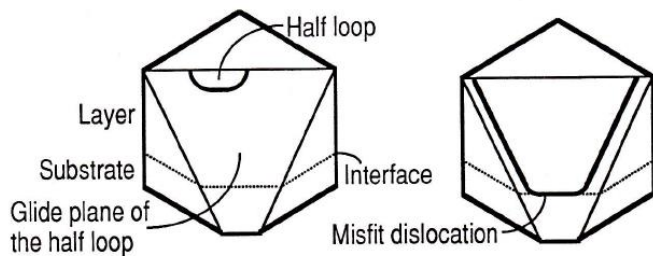
Lattice mismatch builds up strain, relaxation is by dislocation formation

A plane with weak interatomic bonding serves as slip (glide) plane

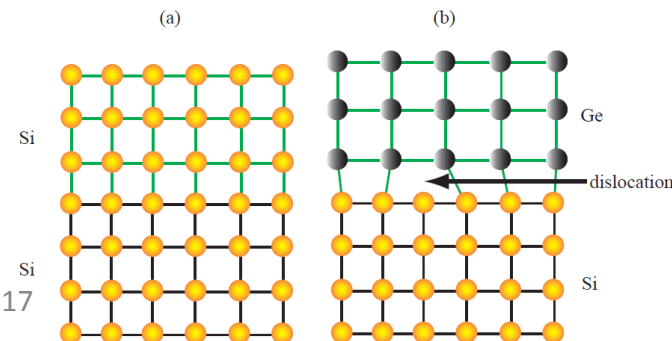
In cubic lattices this is mostly  $\{111\}$

An array of misfit (edge) dislocations is formed at the interface

Matthews and Blakeslee (1975) :  
critical layer thickness vs misfit dislocation formation



$$h_c \sim 2\text{nm at } 2\%$$

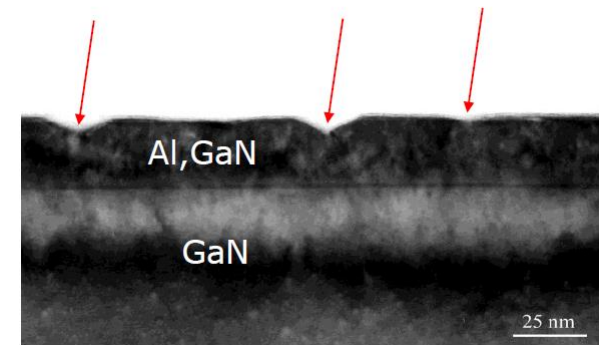
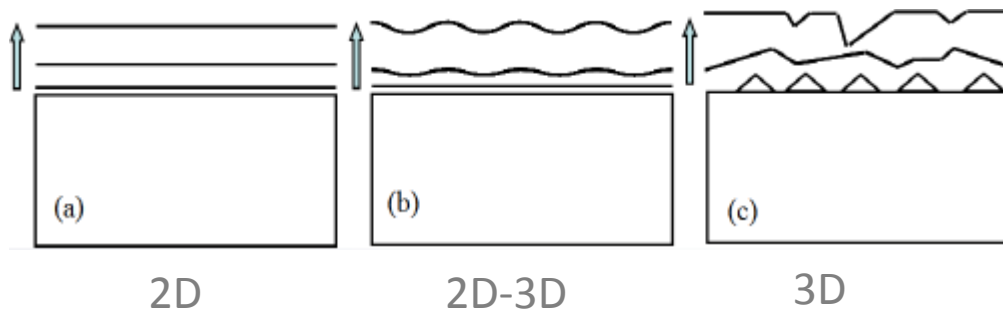




# *Different stress relaxation mechanisms*

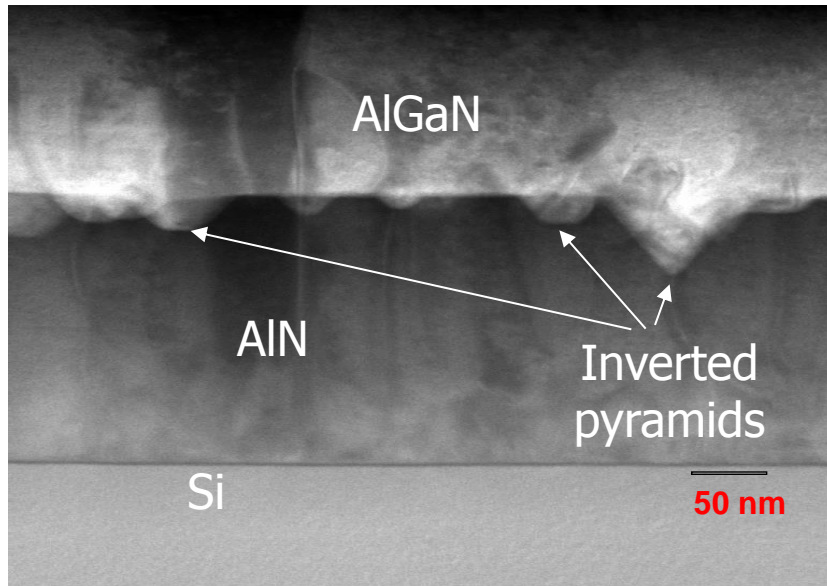
(Nitrides (wurtzite) does not have slip planes)

- Misfit dislocation formation
- Dislocation bending
- Surface roughening (from 2D to 3D growth mode)
- Grooves formation and/or surface cracking



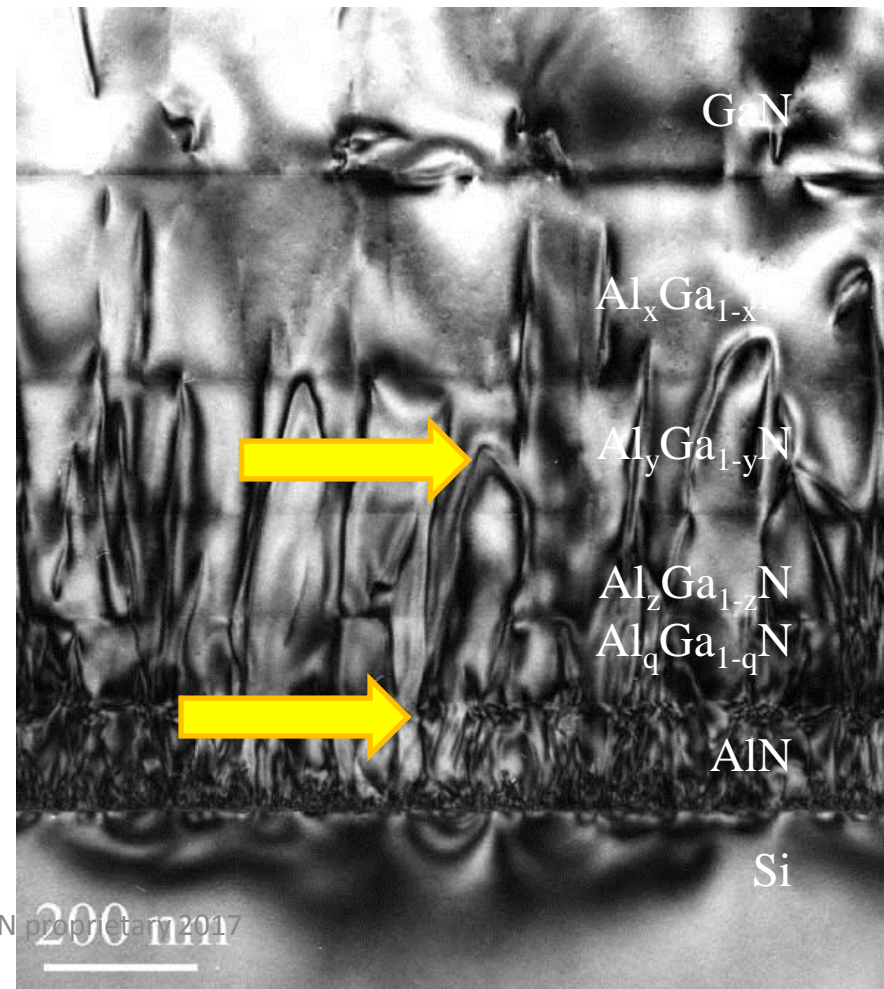
# TEM cross section AlN/Al,GaN/GaN on Si (0002) two-beam diffraction condition

Mosaicity at AlN/Si interface, the result of nucleation via domains



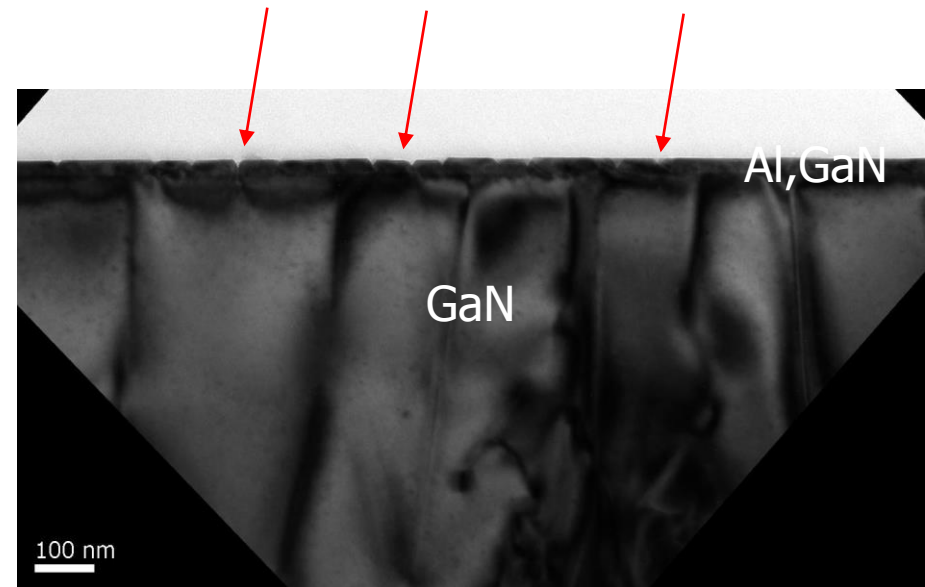
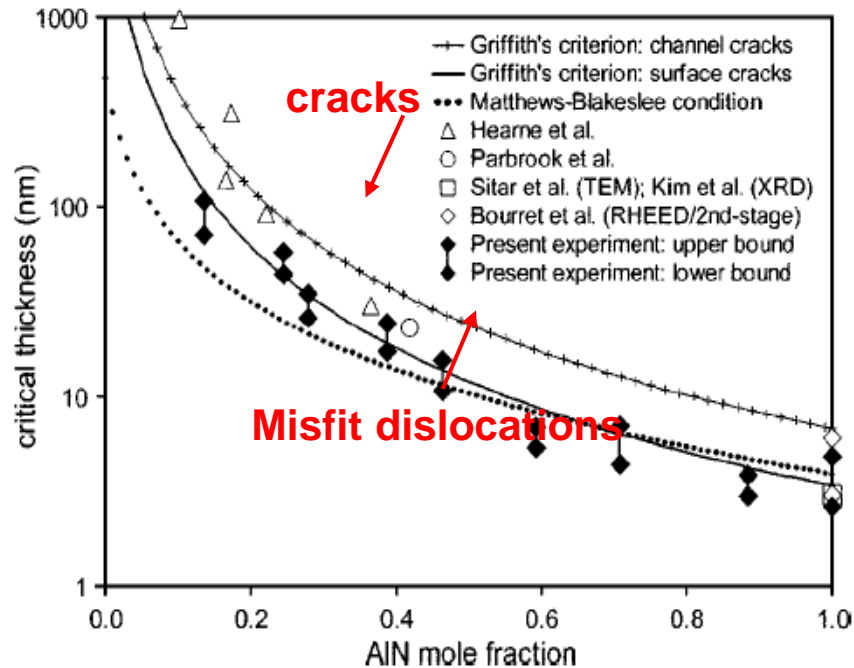
AlN has pyramidal holes

On AlN: 4 Al,GaN interlayers:  
Lattice mismatch: dislocations, bending



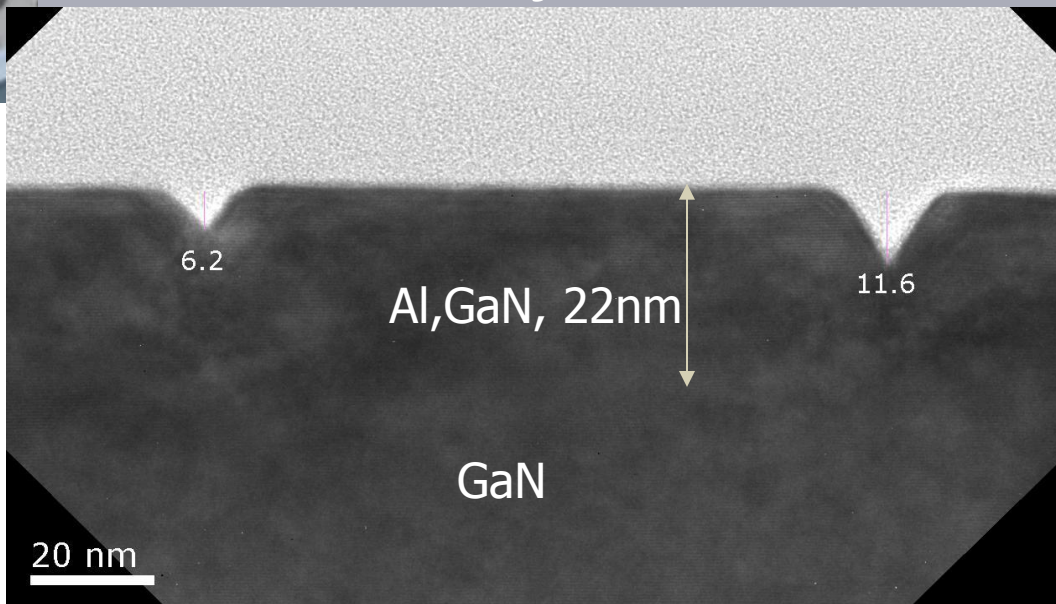
# There are “mechanical” limitations to the top Al,GaN of the HEMT

A lattice mismatched system has to **elastically** strain or **plastically** deform



At a certain thickness  
the surface becomes **unstable**, undulating  
At convex regions inclined facets appear  
leading to **cracks**  
Below cracks, strain is relieved, 2DEG interrupted

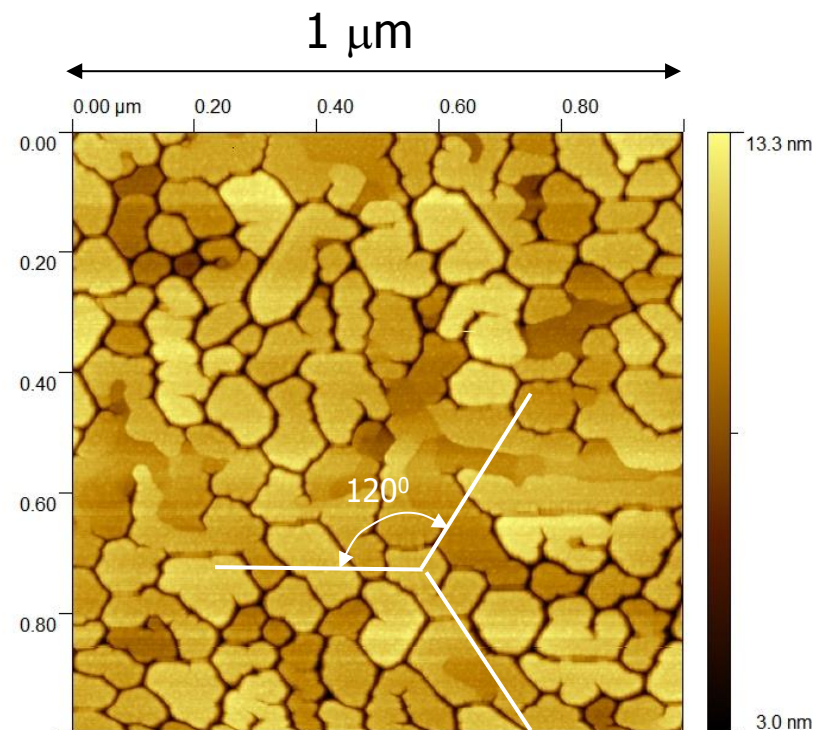
## TEM and AFM of AlGaN barriers



The “cracks” do not seem to correspond to threading dislocations in the GaN layer. Also, they are less deep than the layer thickness i.e. they do not propagate down to the AlGaN/GaN interface

Chemical analysis shows the areas near the grooves are Ga-rich

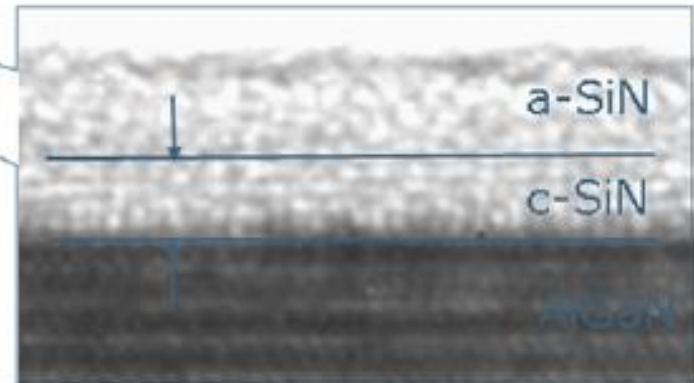
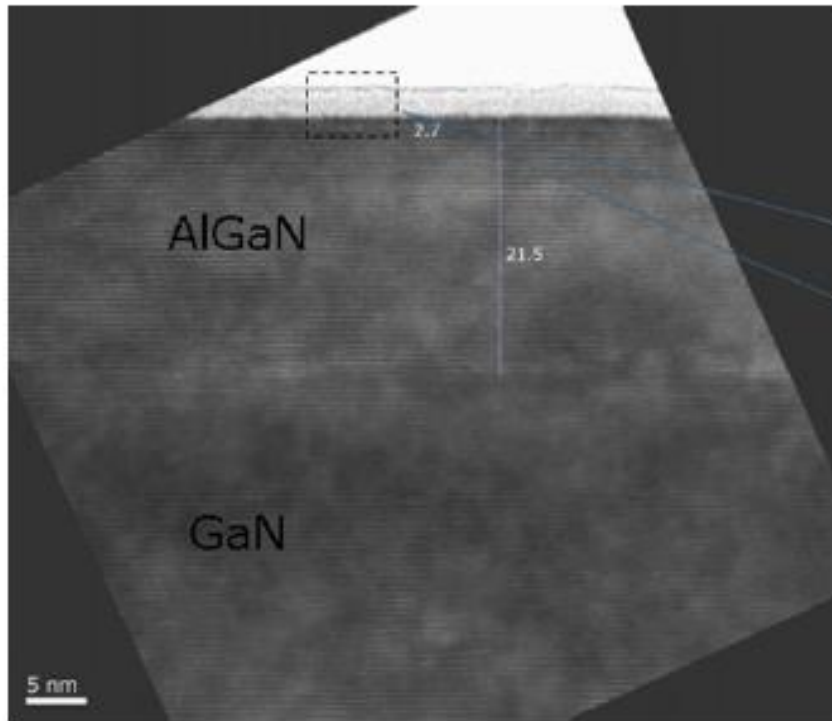
Crack depth in nm



AFM image

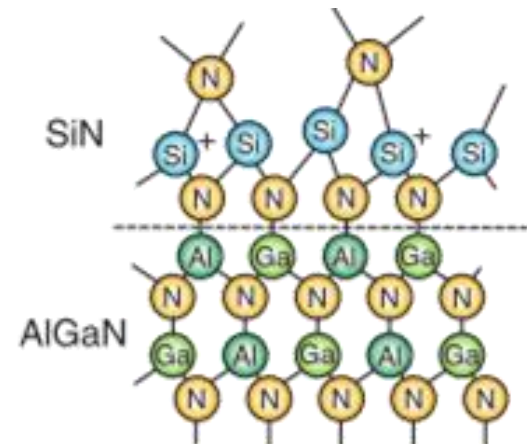


# *In-situ SiN*



SiN deposited in the MOCVD tool

- clean interface
- crystalline interface
- Relaxation prevention

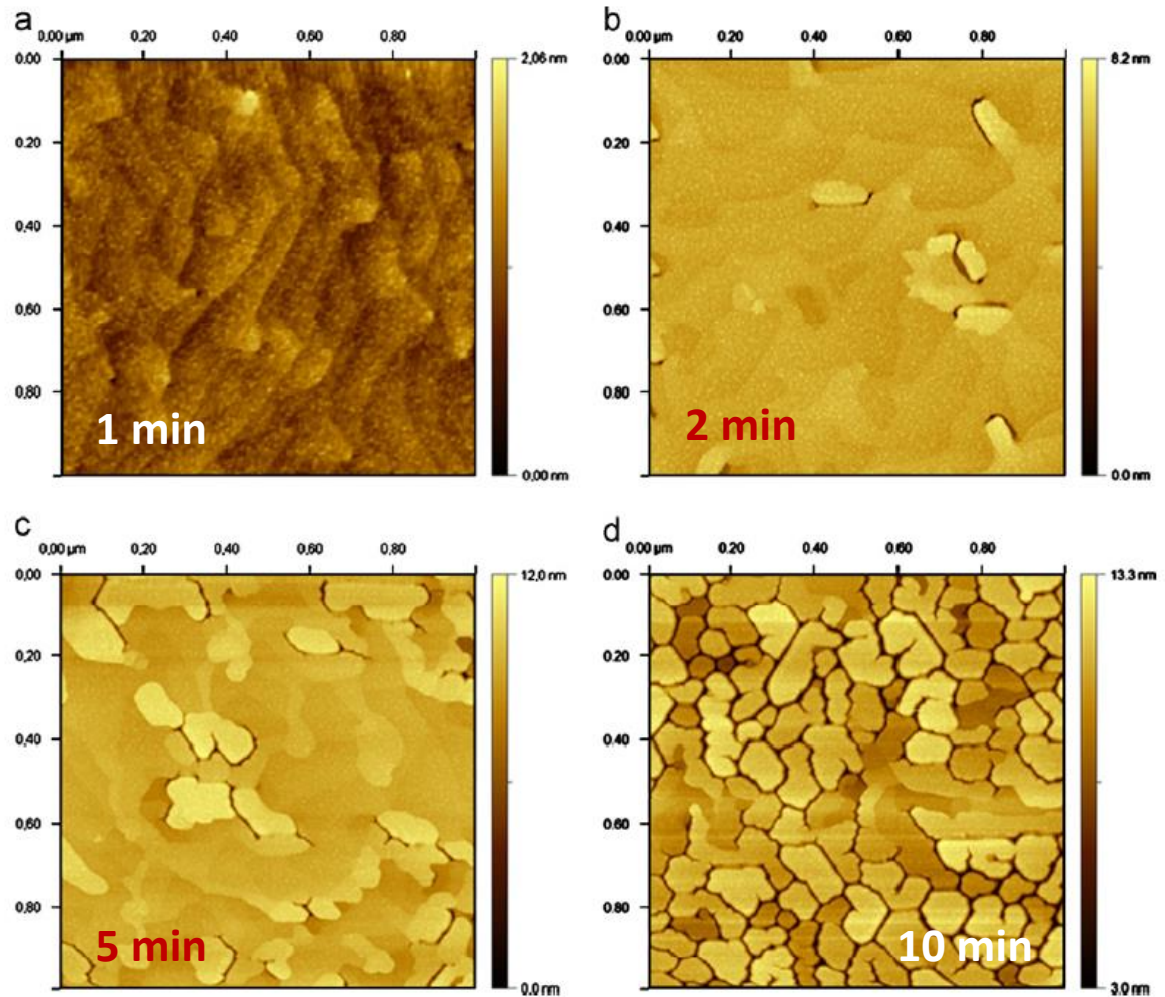


**AN**

# *Protect your barrier with in-situ SiN*

Capping the barrier with  
1 monolayer of SiN

Ref. Cheng JCG 353  
(2012) pp88-94





# *Outline*

- Properties of GaN
- Epitaxy of GaN
- GaN on Silicon

# Choose a substrate for GaN

- GaN crystals do not exist in nature  
=> hetero-epitaxy required
- Choice of the substrate

Material		Lattice mismatch GaN/substrate (%)	Thermal mismatch GaN/substrate (%)	Wafer Size Availability	Cost
GaN		-	-	2"	Prohibitive
SiC	s.i.	3.5	25	2" - 4", 150mm	Very High
	Cond.			2" - 4"; 150mm	High
Sapphire		16	-34	2" - 4"; 150mm; 200mm	Medium
Si		-17	54	2" --> 300 mm	Low

Although technically the most challenging,  
GaN on Si is the **only economical solution**

# Why choose GaN on Si?

GaN on Si is the only **cost-efficient** WB technology

- Cheap substrates (200mm Si: 30\$ vs. 4" SiC: 2000\$)

- Large wafer size
  - Up to 200mm today
- Si-fab compatible
  - Contamination aspects solved
  - Existing volume-production fabs:  
Fully depreciated fab or  
side-by-side with existing Si products

Substrate Properties	Si (111)	Al <sub>2</sub> O <sub>3</sub> (100)	6H-SiC	GaN (0001)
Lattice mismatch (%)	-17	-33	3.5	-
Thermal mismatch (%)	54	-23	24	-
Thermal conductivity (W cm <sup>-1</sup> K <sup>-1</sup> )	1.5	0.5	4.5	1.3
Wafer size	2"→12"	2"→8"	2"→6"	2"
Price	low	medium	very high	extremely high

Substrate choices

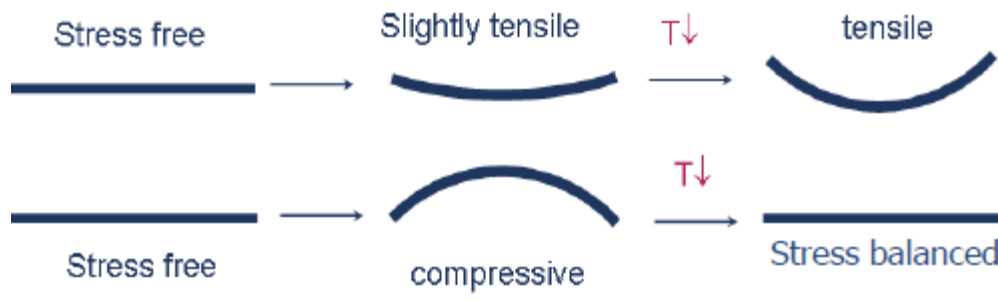
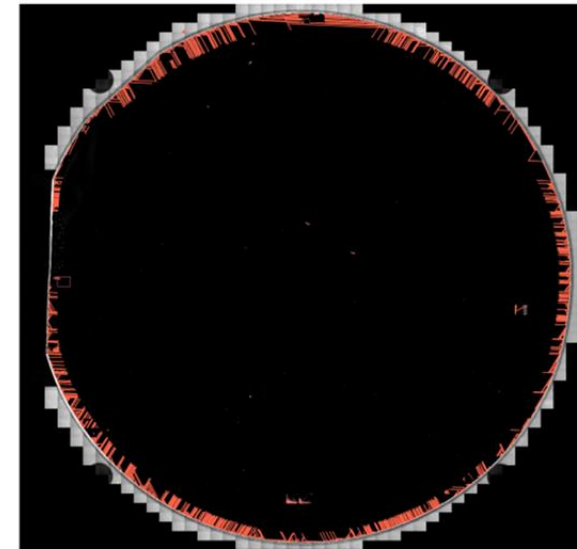
- Integration possible with Si CMOS

# Thermal stress in GaN on Si

Total stress:  $\sigma_{tot} = \sigma_{intrinsic (lattice)} + \sigma_{thermal}$

$$\sigma_{thermal} = \frac{E_f}{(1-\nu_f)} \cdot \Delta\alpha \cdot \Delta T = \frac{E_f}{(1-\nu_f)} (\alpha_{III-N} - \alpha_{Si}) (T_{growth} - T_{room})$$

Coefficient of thermal expansion      Growth Temperature



In GaN on Si, the tensile thermal stress is around 1.4GPa!!

Stress leads to wafer bow!

Wafer bow must be limited (typ. max 50  $\mu\text{m}$ ) for manufacturing (litho alignment).

# *In-situ curvature as monitoring tool*

