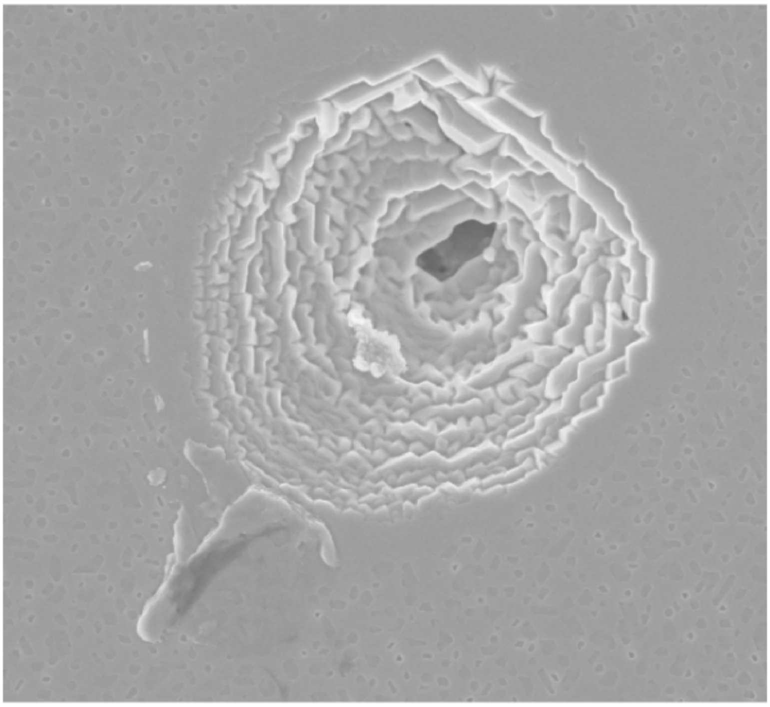
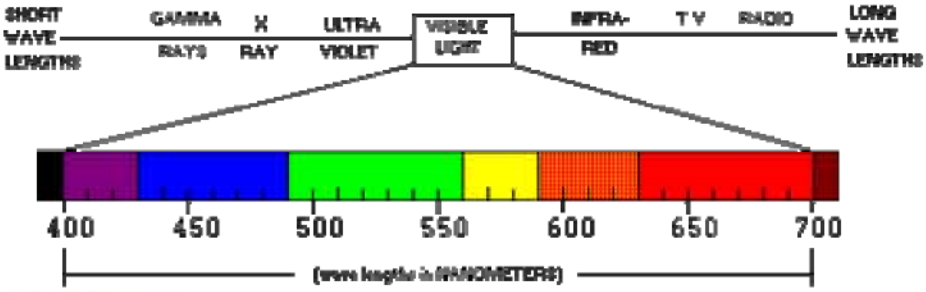
Basics of III-nitride materials



Not every poor growth leads to bad stuff ……

Semiconductor blue-light emitter
— a scientific novelty 10 years ago



- White light is made when the primary colors are added together “at equal intensities.”
- When looking at objects the object appears a certain color. This is the color that is being reflected off of the object, in reality, the object is every color but the color is appears to be.

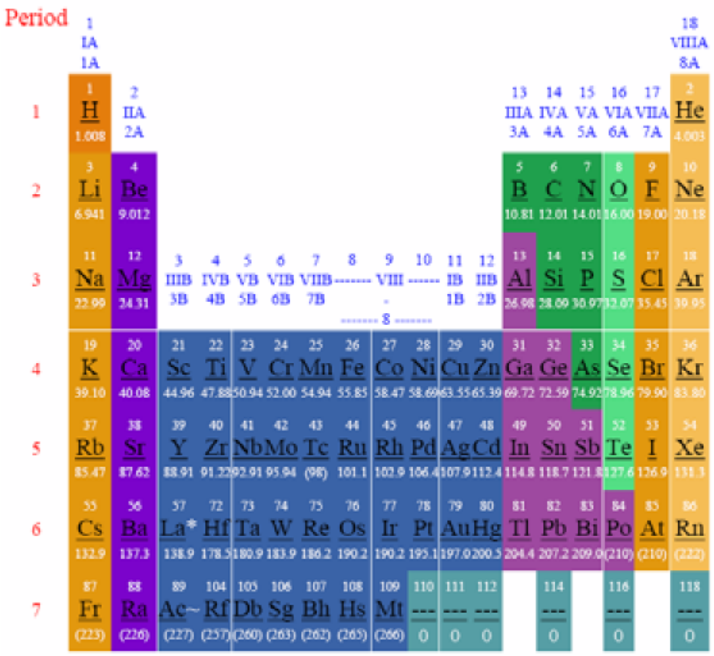
Why blue……?

Solid State Lighting

Blu-ray Disc

…up to 27 GB of data on a 12cm-CD-size disc using a 405nm blue-violet laser.

What is III-nitride material?



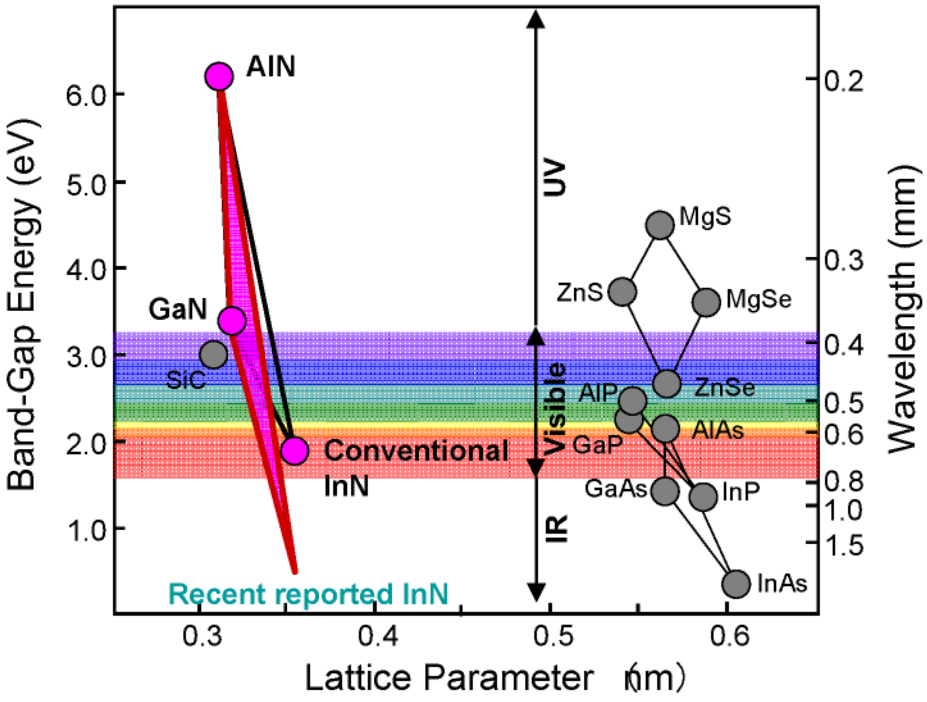
Period	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 -------	9 VIII - 8 -	10 -------	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 --- 0	111 --- 0	112 --- 0		114 --- 0		116 --- 0		118 --- 0

Silicon is not a universal material in semiconductor industry!!!

III-nitrides include AlN, GaN, InN and their related ternary and quaternary.

Other wide-bandgap semiconductors include ZnO, diamond, SiC, ZnSe, BN…

Lattice parameter vs band-gap and wavelength of Important Semiconductors



Lattice constant of nitride compounds

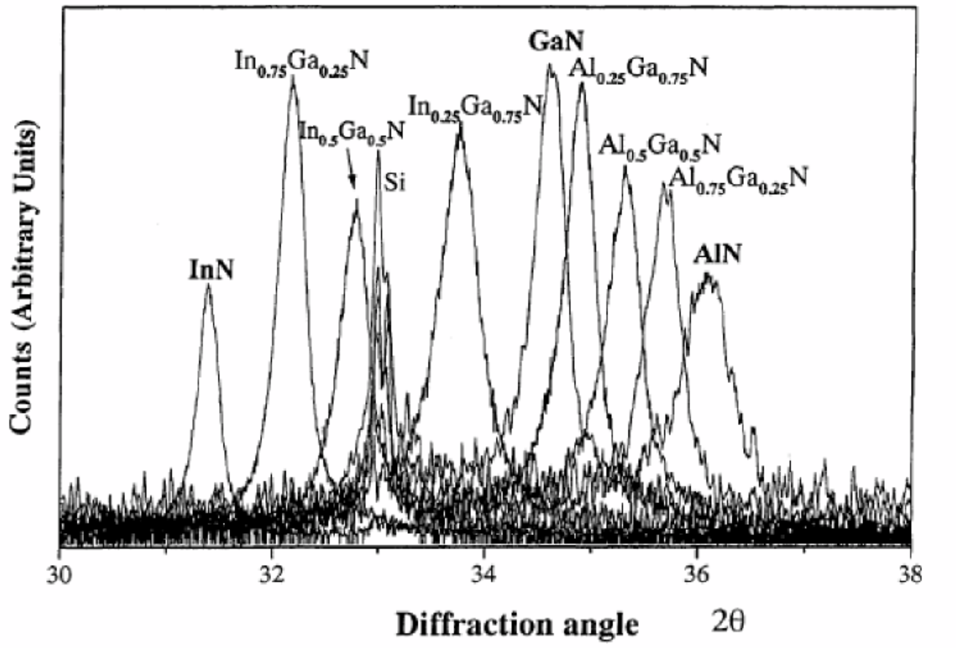


FIGURE 1 X-ray diffraction peak positions of the $(In/Al)_xGa_{1-x}N$ alloys grown by MBE.

The history…

For blue-light emitters,

Galium Nitride (GaN)

Vs.

Zinc Selenide (ZnSe)

Both materials have the right "bandgap" for blue light emission.

From middle1980s to early 1990s, most groups in universities and companies worked on ZnSe, since it is conventional wisdom in the international research community that GaN is useless as a LED material.

Why?

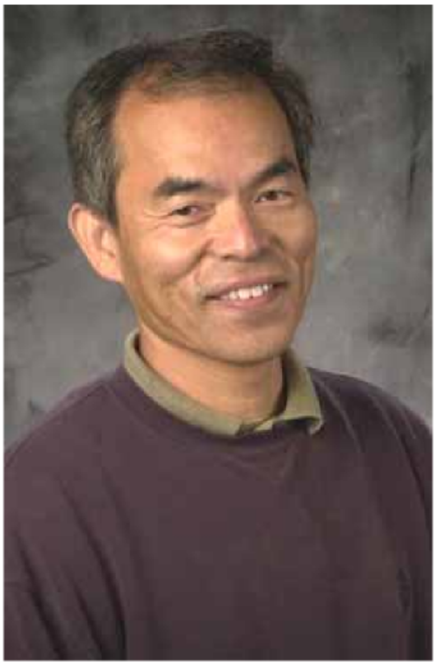
- The crystal quality of ZnSe had been very good, with dislocation density less than 1e4 cm-2, while GaN was more than 1e10 cm-2

- Some promising results based on ZnSe had been reported, while people knew little about GaN.

Only a small number of people at a few universities were working on GaN.

To follow the majority or not ???

Dr. Shuji Nakamura – the inventor of blue LEDs and LDs



1954	Born in Seto-cho, Nishiuwa-gun, Ehime Prefecture
1973-77	Majored in electronics at the University of Tokushima, Department of Engineering
1977-79	Master's Course at the University of Tokushima Graduate School of Technology
1979-88	Nichia Chemical Industries Co., Ltd.; research and development on infrared LED and crystal materials for LED
1988-89	Visiting Research Fellow at the University of Florida; research on crystal development of GaAs on Si
1989-99	Research and development on the blue, green LED and purple semiconductor laser
1994	Obtained PhD from the University of Tokushima
2000-	Professor, Department of Materials, University of California, Santa Barbara

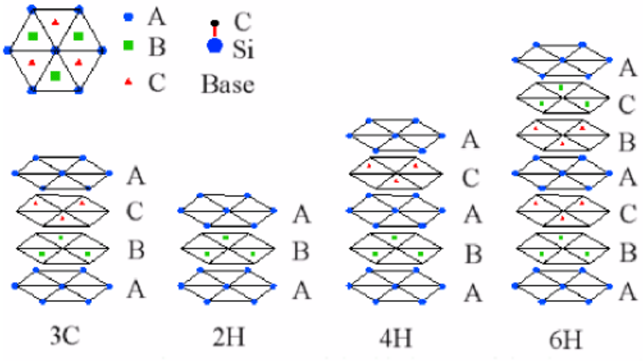
Crystal structure of GaN

Group-III nitrides occur in three common crystal stuctures: the wurtzite, zincblende, and rocksalt structures. Under ambient conditions, the thermodynamically stable structure is wurtzite for bulk aluminum nitride(AlN), gallium nitride and indium nitride (InN).

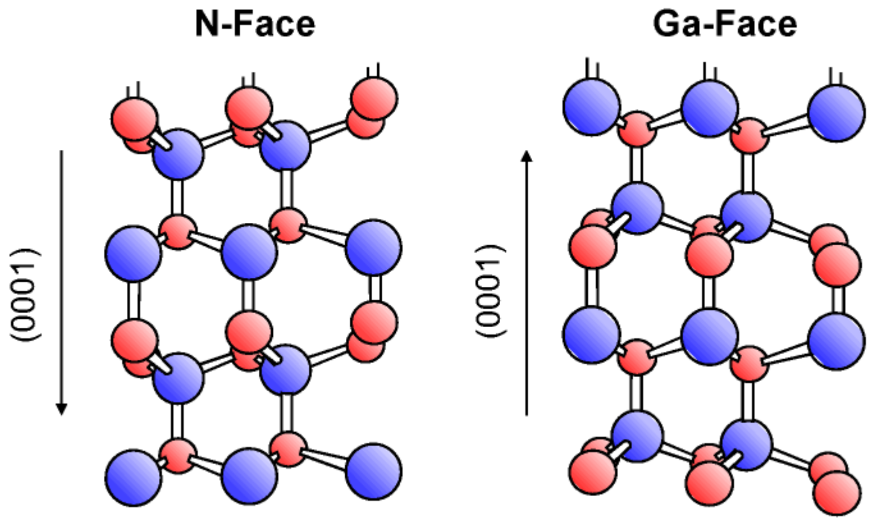
The stacking sequence of the closest packed diatomic planes seen in the wurtzite structure is different from that seen in zincblende. In the wurtizite structure the stacking sequence of the (0001) plane is ABABAB and in the <0001> direction. In the zincblende structure the stacking sequence of the (111) plane is ABCABC in the <111> direction.

The difference in the structures lies in the bond angle of the second nearest neighbors, and this difference is the key to the existence of spontaneous polarization effects seen in this material system compared to zincblende system

The case of GaN is very similar to that of SiC



Polarity of Wurtzite GaN



The [0001](by convention, the [0001] direction is given by a vector pointing from a Ga atom to a nearest neighbor N atom) direction is known as the Ga face and the [000-1] is known as the nitrogen face. It is important to note that polarity is a bulk property and not a surface property.

Ga face and N face GaN have very different physical and chemical properties.

Polarization of wurtzite GaN

Certain crystals have the property of developing an electric polarization when their temperature is changed. Alternatively, if a spontaneous polarization is already present, a change of temperature alters it. This phenomena is called pyroelectricity. All group III nitrides exhibit pyroelectric effects in the wurtzite structure.

The relative magnitudes of SP is more related to the non ideality of the cell parameter and the ionicity of the Gallium-Nitrogen bond. The source of the strong spontaneous polarization is that the metal nirogen bond forms a dipole and the dipole is stronger as we go from GaN to AlN.

Due to the tensor nature of the stress-strain relation (Hooke's law) in solids, it is interesting to note that the piezoelectric polarization along the c-axis is dependent on the relative change in the lattice constant along the a-axis.

SP

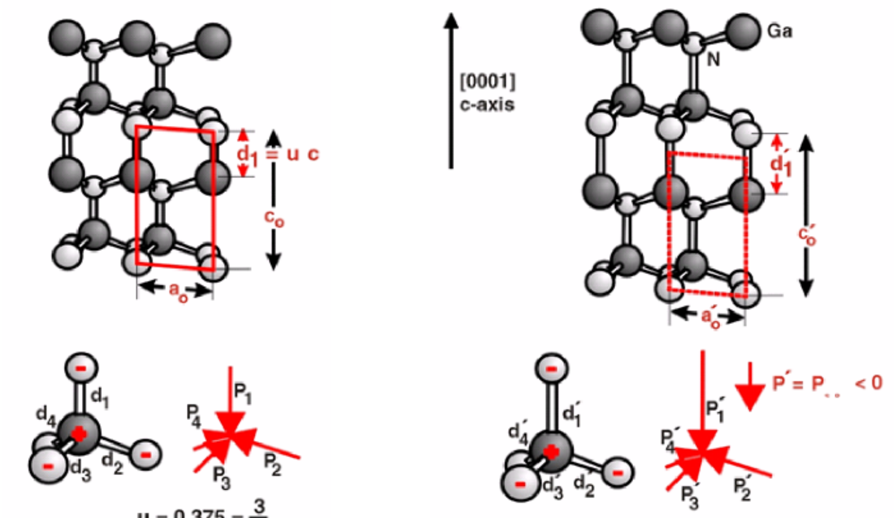
$$\begin{aligned}
P^{SP}_{ABN}(x) &= P_{AN^{SP}}x + P^{SP}_{BN}(1-x) + bx(1-x) \\
P^{SP}_{AlGaN}(x) &= -0.09x - 0.034(1-x) + 0.021x(1-x) \\
P^{SP}_{InGaN}(x) &= -0.042x - 0.034(1-x) + 0.037x(1-x) \\
u^{SP}_{AlInN}(x) &= -0.09x - 0.042(1-x) - 0.070x(1-x)
\end{aligned}$$

PE

$$P_{PZ} = 2\frac{a-a_0}{a_0}\left(e_{31} - e_{33}\frac{C_{13}}{C_{33}}\right)$$

$$\begin{aligned}
P^{pz}_{AlGaN/GaN}(x) &= [-0.0525x + 0.0282x(1-x)]Cm^{-2} \\
P^{pz}_{InGaN/GaN}(x) &= [0.148x - 0.0424x(1-x)]Cm^{-2} \\
P^{pz}_{AlInN/GaN}(x) &= [-0.0525x + 0.148x(1-x) + 0.0938x(1-x)]Cm^{-2}
\end{aligned}$$

Spontaneous polarization in wurzite GaN



$u = 0.375 = \frac{3}{8}$

ideal wurtzite structure: all bonds have the same length and bond angles are equal.

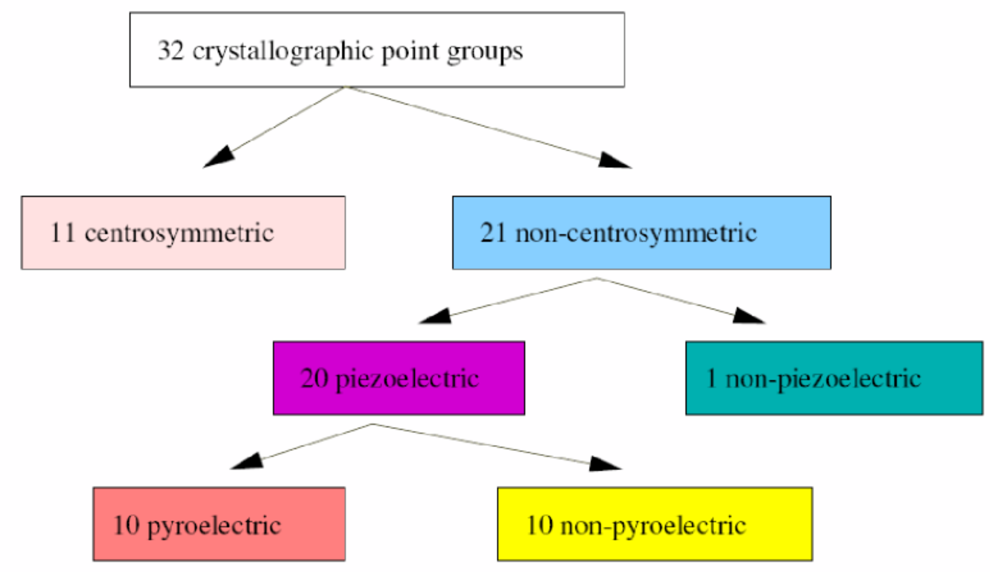
GaN, InN and AlN crystals have bonds along the c-axis which are longer than the other bonds, the bond angles deviate from the ideal value.

Metal-nitrogen bond has got a strong dipole moment.

(no inversion symmetry) Spontaneous polarization is possible.

The possibility of inorganic crystals being polar (pyroelectric or piezoelectric) is strictly a function of their point group symmetry

Neumann's principle:
The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal.



32 crystallographic point groups

11 centrosymmetric

21 non-centrosymmetric

20 piezoelectric

1 non-piezoelectric

10 pyroelectric

10 non-pyroelectric

Polarization induced surface and interface charges

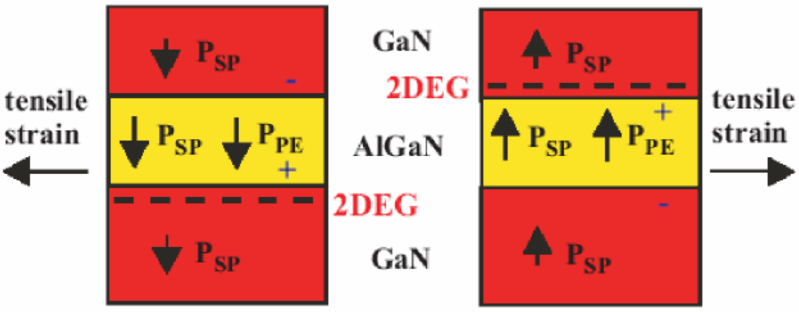


Figure Polarization vectors, bound charges and 2DEG formation in GaN/AlGaN/GaN structures. In Ga face material the 2DEG forms at the lower heterointerface and in N-face material the 2DEG forms at the upper heterointerface

$$\vec{\nabla}.\vec{\mathrm{P}} = -\rho_{bound}$$

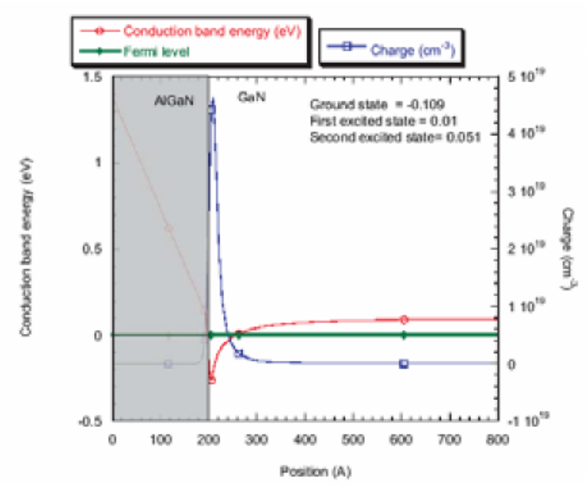
$$\sigma_{ABN} = \mathbf{P}_{ABN} = \mathbf{P}^{SP}_{ABN} + \mathbf{P}^{PZ}_{ABN}, \text{ for surfaces}$$

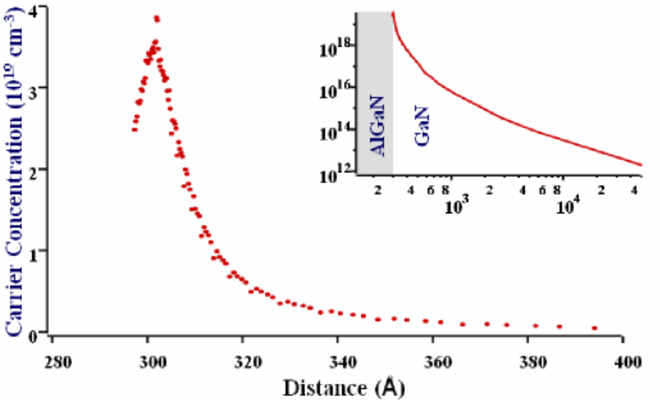
$$\sigma_{ABN/GaN} = \mathbf{P}_{GaN} - \mathbf{P}_{ABN}$$

$$= \left(\mathbf{P}^{SP}_{GaN} + \mathbf{P}^{pz}_{GaN}\right) - \left(\mathbf{P}^{SP}_{ABN} + \mathbf{P}^{pz}_{ABN}\right), \text{ for interfaces}$$

Dividing the $\mathbf{P}$ by e (1.6×10^{-19}), we get the sheet charge in m^{-2}.

2DEG in AlGaN/GaN heterojunction





If we have surfaces of these semiconductors exposed to air, the discontinuity of the polarization vector would cause a bound charge to form on the surface.
The surface charge is positive(negative) for material with N-face (Ga-face) polarity. As the bound charge is on the surface of the semiconductors, a host of screening effects due to surface charges through defects or adsorbed charges from the environment can occur. This would make it difficult to measure these charges.

Various substrate materials for GaN

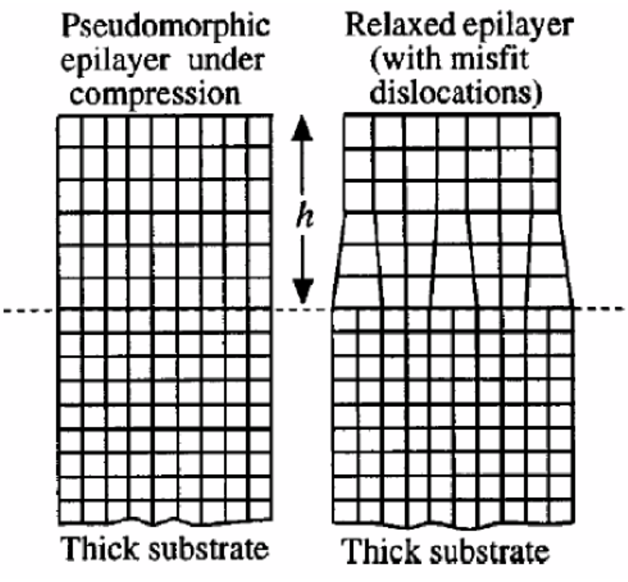
主要白光LED公司	所用衬底材料
Nichia	蓝宝石 (sapphire)
Lumileds	蓝宝石 (sapphire)
Toyota Gosei	蓝宝石 (sapphire)
Rohm	蓝宝石 (sapphire)
Osram	碳化硅 (SiC)
Cree	碳化硅 (SiC)

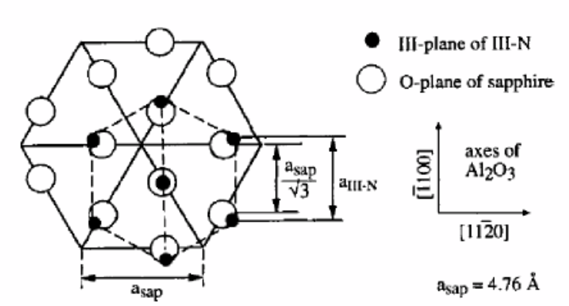
自支撑GaN衬底

- Sapphire
- SiC
- Silicon substrate
- Substrate materials for non-polar GaN, like r-plane GaN, LiAlO3, m-plane SiC
- Bulk GaN, GaN template, bulk AlN
- ZnO as well as other materials ever tried.
- Patterned substrate, LEO-related techniques

GaN hetero-epitaxial growth

How is lattice mismatch defined? $f_m = \frac{a_l - a_{sub}}{a_{sub}}$

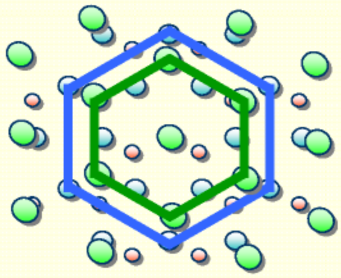
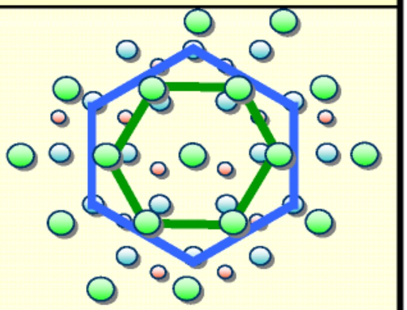




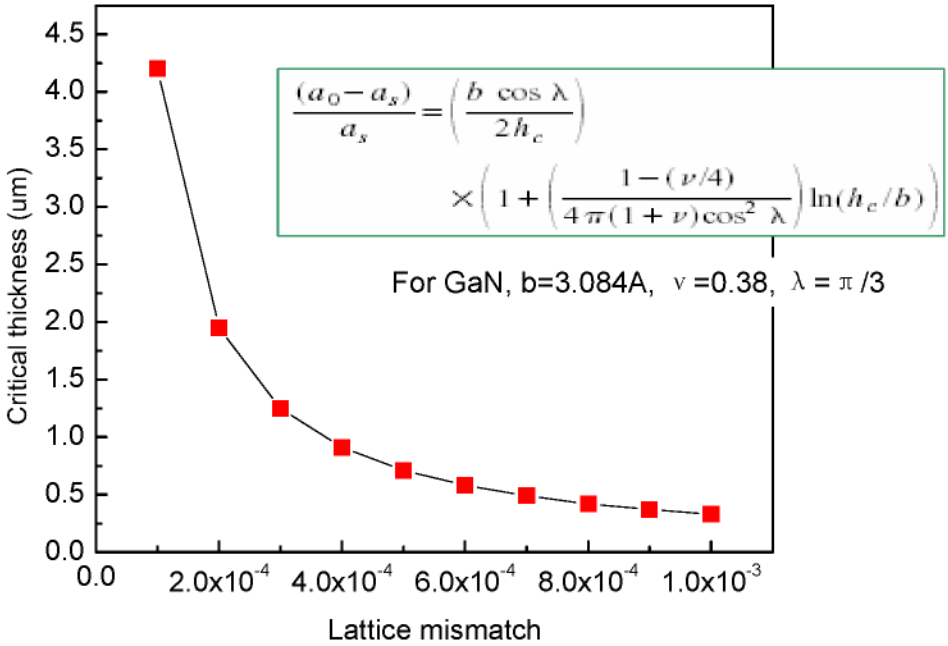
Growth of III-nitrides on sapphire

Theoretically SiC should be a better substrate for GaN than sapphire due to smaller lattice mismatch. SiC also has superior thermal properties. However, sapphire has better transparency for UV light, which is important for UV emitter applications.

Lattice Mismatch between III-Nitrides and Sapphire Substrate

	$[11\text{-}20]_{III\text{-}N}//[11\text{-}20]_{Sap}$ 0° Rotation	$[11\text{-}20]_{III\text{-}N}//[10\text{-}10]_{Sap}$ 30 ° Rotation
Atomic arrangement		
AlN a=3.112 Å	-34.6%	+13.3%
GaN a=3.189 Å	-33.0%	+16.1%
InN a=3.548 Å	-25.4%	+29.2%

Critical thickness of GaN epilayer on foreign substrate

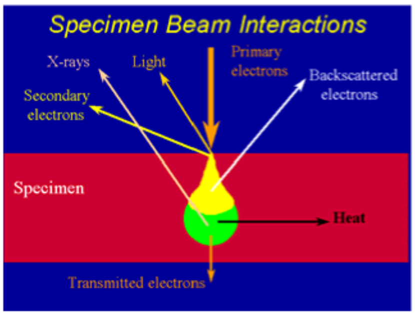


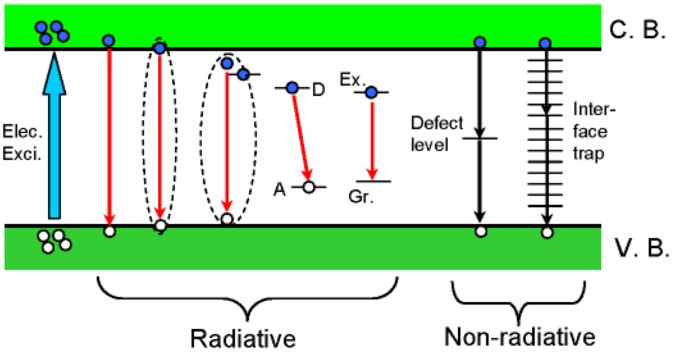
$$\frac{(a_0-a_s)}{a_s}=\left(\frac{b\ \cos\lambda}{2h_c}\right)\times\left(1+\left(\frac{1-(\nu/4)}{4\pi(1+\nu)\cos^2\lambda}\right)\ln(h_c/b)\right)$$

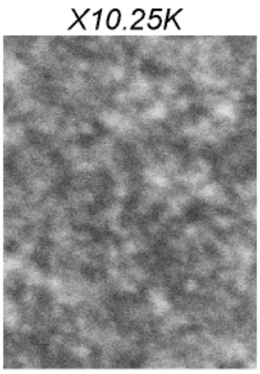
For GaN, b=3.084A, ν =0.38, $\lambda = \pi/3$

When growing GaN on sapphire, optimized nucleation layer is super important. Also, whether the final film is in compressive or tensile strain is a complex case, which depends on many factors.

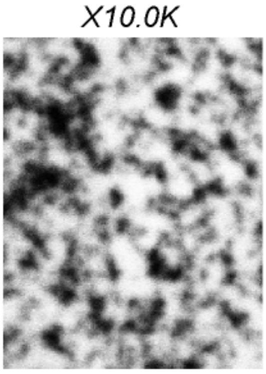
Cathodluminescence mapping for defect characterization



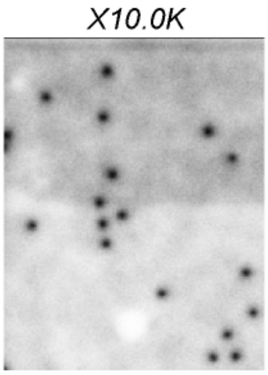




Nitronex GaN on silicon



GaN on sapphire (SUNY)

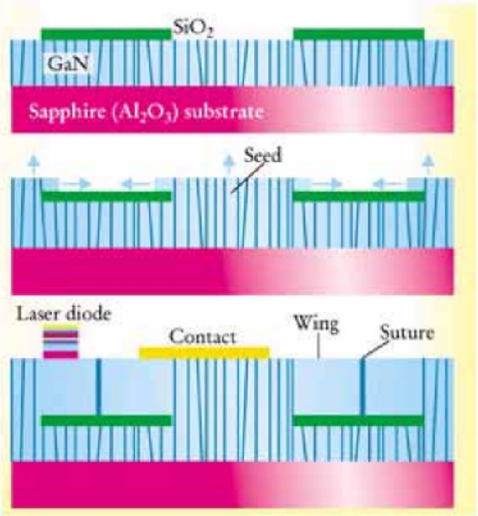


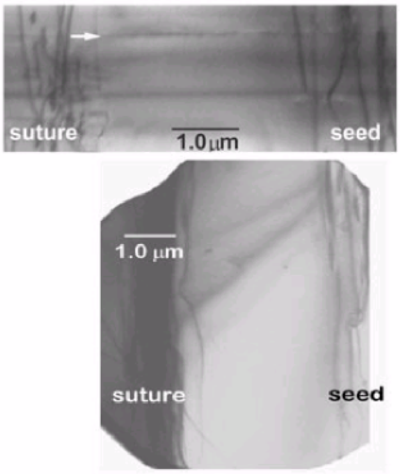
Cree HVPE GaN substrate

The advantage of bulk GaN for HB-LED applications

衬底材料	Sapphire	SiC	Si	GaN
晶格失配度	差	中	差	优
界面特性	良	良	良	优
化学稳定性	优	优	良	优
导热性能	差	优	优	优
热失配度	差	中	差	优
导电性	差	优	优	优
光学性能	优	优	差	优
机械性能	差	差	优	中
价格	中	高	低	高
尺寸	中	中	大	小

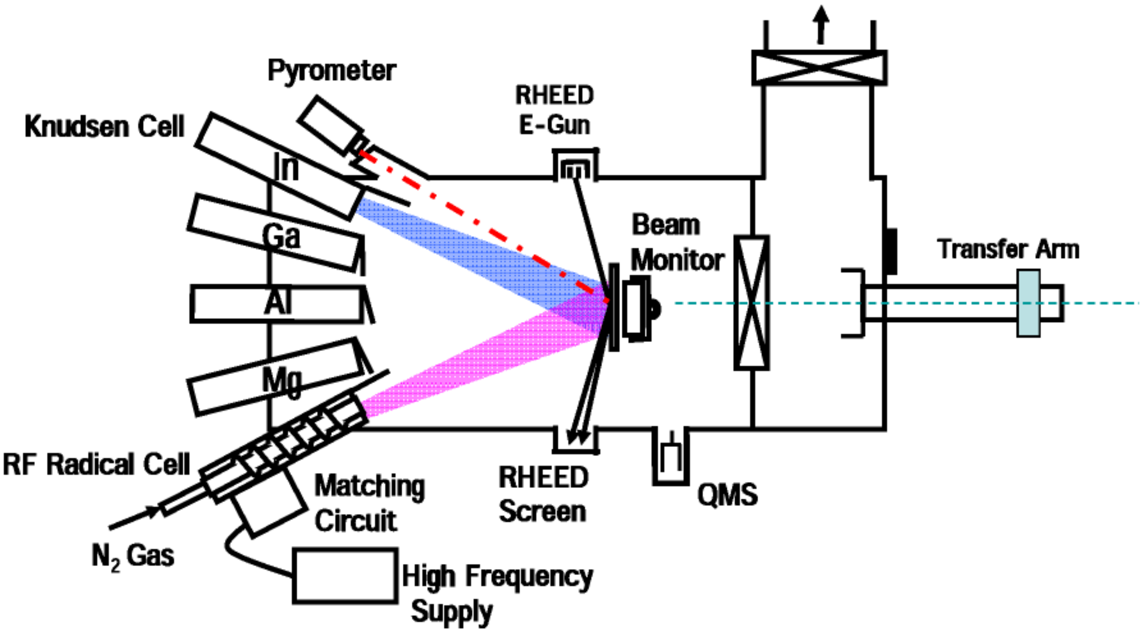
Lateral epitaxial overgrowth (LEO) growth of GaN





Major GaN growth techniques: MOCVD and MBE

RF MBE system for III-nitride growth



Background pressure 1e-10 Torr; Conventional effusion cells;
EPI unibulb r.f. plasma source

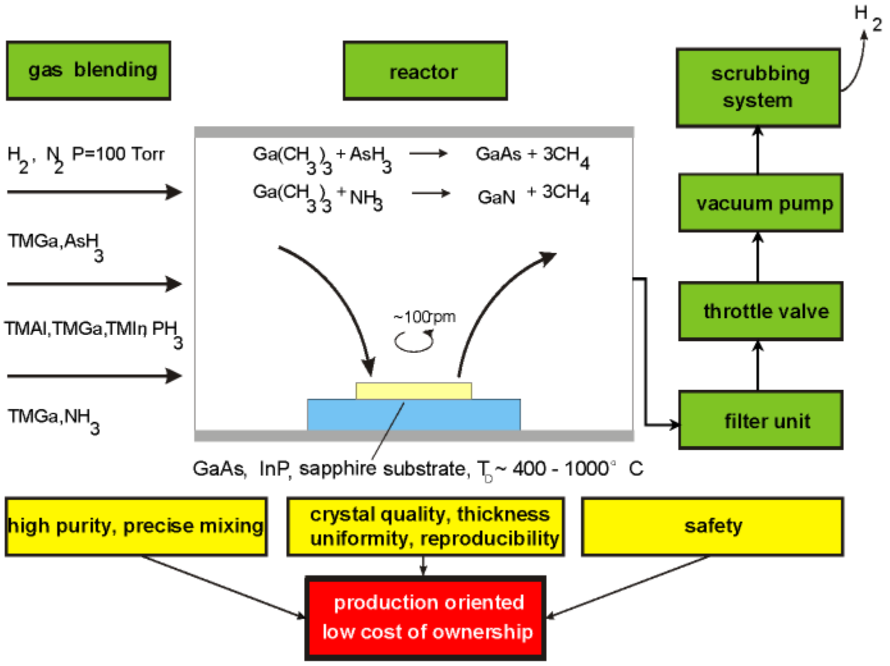
Thomas Swan MOCVD reactor for high-quality nitrides

MOCVD/MOVPE/OMVPE

- MOCVD: Metal Organic Chemical Vapor Deposition
- MOVPE: Metal Organic Vapor Phase Epitaxy
- OMVPE: Organo Metallic Vapor Phase Epitaxy
  - Often all three expressions are used interchangeably

Note: although MOCVD is the dominant growth technique for the nitride industry, the technique is not very successful in growing InN and In-rich nitrides. Currently MBE produces better In-rich nitrides.

Principle of LP-MOVPE



gas blending

reactor

scrubbing system

H_2

vacuum pump

throttle valve

filter unit

H_2, N_2 P=100 Torr

TMGa,AsH_3

TMAl,TMGa,TMIn PH_3

TMGa,NH_3

$Ga(CH_3)_3 + AsH_3 \longrightarrow GaAs + 3CH_4$

$Ga(CH_3)_3 + NH_3 \longrightarrow GaN + 3CH_4$

~100 rpm

GaAs, InP, sapphire substrate, T_D ~ 400 - 1000° C

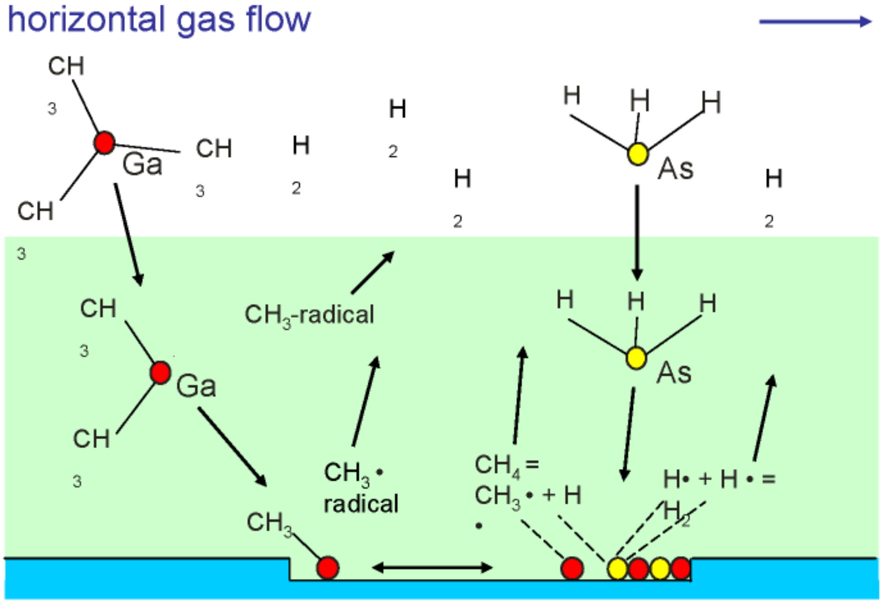
high purity, precise mixing

crystal quality, thickness uniformity, reproducibility

safety

production oriented low cost of ownership

MOVPE Growth Mechanisms (simplified)



gas phase

boundary layer

mass transport to the surface by diffusion

precursor decomposition

adsorption

wafer surface

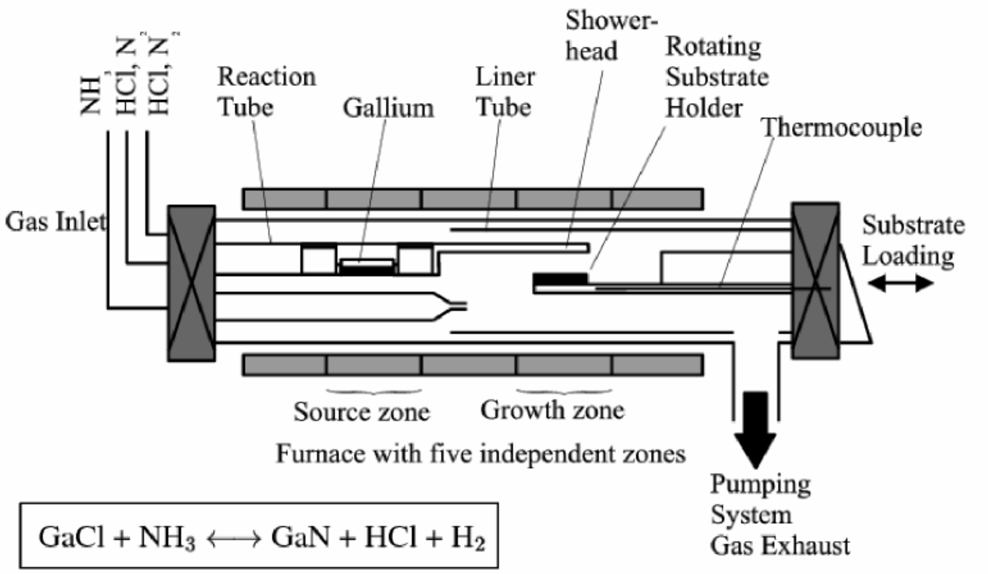
atomic step

surface diffusion and reaction

incorporation and growth

Hydride Vapor Phase Epitaxy (HVPE) growth of thick GaN film

- Aixtron HVPE system has been commercilized.
- Typical growth rate is between 100 to 200 um/hour.
- HVPE growth usually starts on MOCVD GaN template.

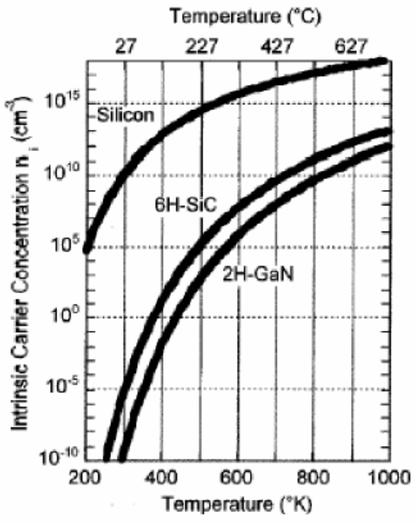


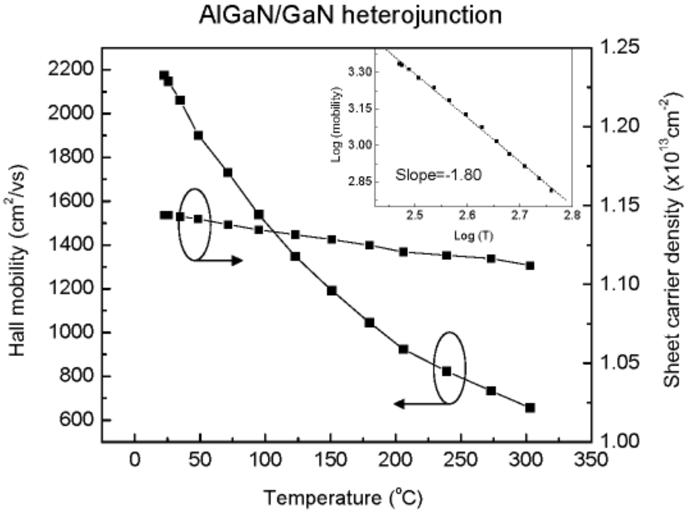
$$GaCl + NH_3 \longleftrightarrow GaN + HCl + H_2$$

Fig. 1. Schematic diagram of the HVPE reactor of AIXTRON AG

Electrical properties of GaN

- RT electrical mobility ~ 500 cm2/Vs is already a very good number for n-GaN
- Hole mobility is normally very low ~10 cm2/Vs.
- Mobility of 2DEG can be al high as 2000 cm2/Vs. But mobility is not the only thing for HEMT structure, sheet resistance is the key quality factor.





N-type doping of III-nitrides

- Silicon is commonly used for n-type doping of GaN. Electron concentration up to e21-e22 has been reported for Si-doped GaN.

- Comparatively controllable low dose doping of n-type GaN is difficult to achieve.

- Growth of n+ AlGaN is also getting difficult as Al-content goes up.

- Growth of low carrier density In-rich nitrides is very difficult. Dislocations might be donor-like in InN.

- Impurities, like oxygen, are donors in GaN.

P-type doping of III-nitrides

- Mg is the most commonly used p dopant in GaN with a high ionization energy around 200 meV. At RT, only around 1% Mg atoms are ionized. 5e17 hole concentration is a good number.

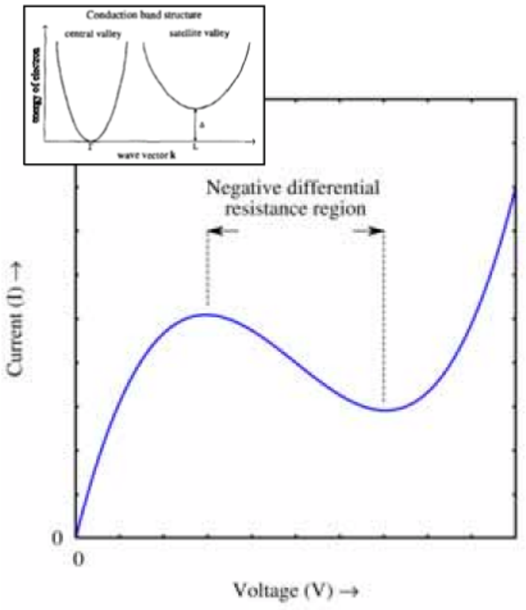
- Due to the formation of Mg-H complex, MOCVD Mg-doped GaN needs to be annealed for dopant activation. E-beam or thermal annealing techniques can be used.

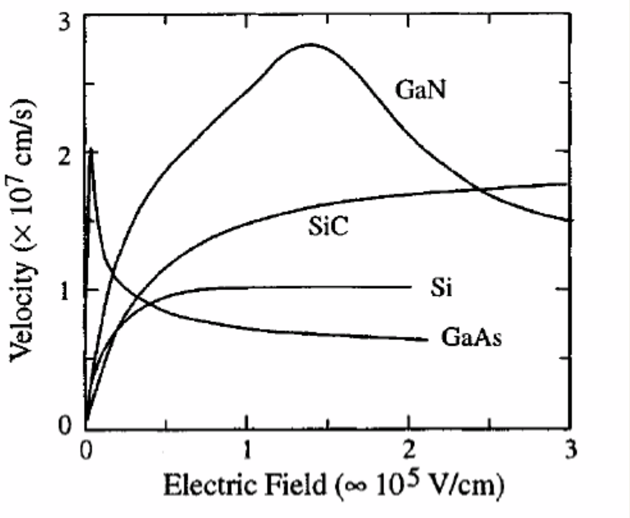
- Be, C and Zn were also tried for p-type doping of GaN but with very limited success.

- P-type doping of AlGaN is very challenging.

- P-type doping of In-rich nitrides is intriguing.

High field transport properties of GaN

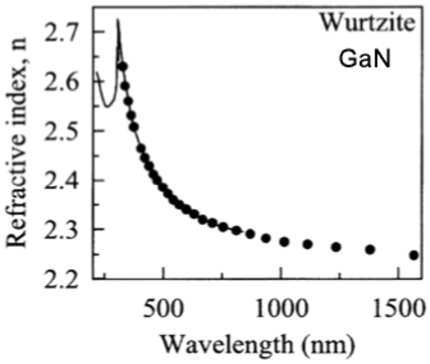




- Wide-bandgap energy related high breakdown electrical field.
- High electron saturation velocity
- High electron overshoot velocity

Optical properties of GaN-related materials

- GaN has a high refractive index, which is a disadvantage for light extraction.



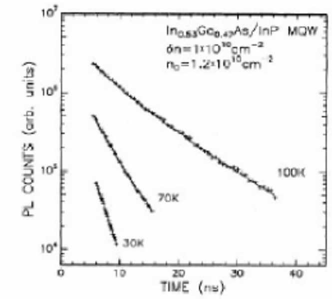
The refractive index of sapphire is ~1.7-1.8 and is ~2.6-2.8 for SiC.

- Besides band-edge emission, a defect or impurity-related yellow band around 550nm is commonly observed.

- Light emission from InGaN is surprisingly efficient considering such a high defect density, which is believed to be related to carrier localization in in-rich regions. However, most dislocations are certainly non-radiative recombination centers. Low-defect density GaN epilayer is essential for GaN LD applications.

The quality of GaN epilayer characterized by time-resolved PL

PL decay time of high-quality GaN can be up to 1 ns, while that of InGaN/GaN QWs can be up to tens of ns.



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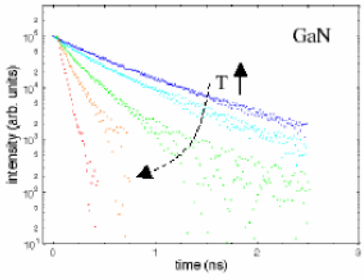

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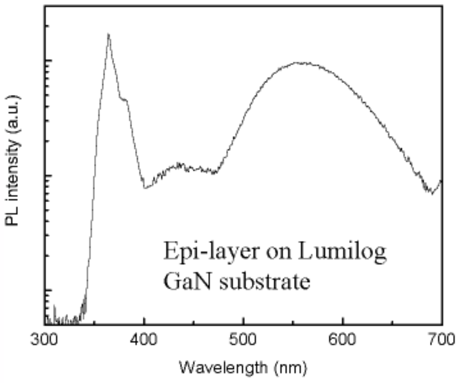

$$\frac{1}{\tau_{PL}(T)}=\frac{1}{\tau_{rad}(T)}+\frac{1}{\tau_{non-rad}(T)}$$

$$\eta_{\text{int}}(T)=\frac{\tau_{non-rad}(T)}{\tau_{rad}(T)+\tau_{non-rad}(T)}$$