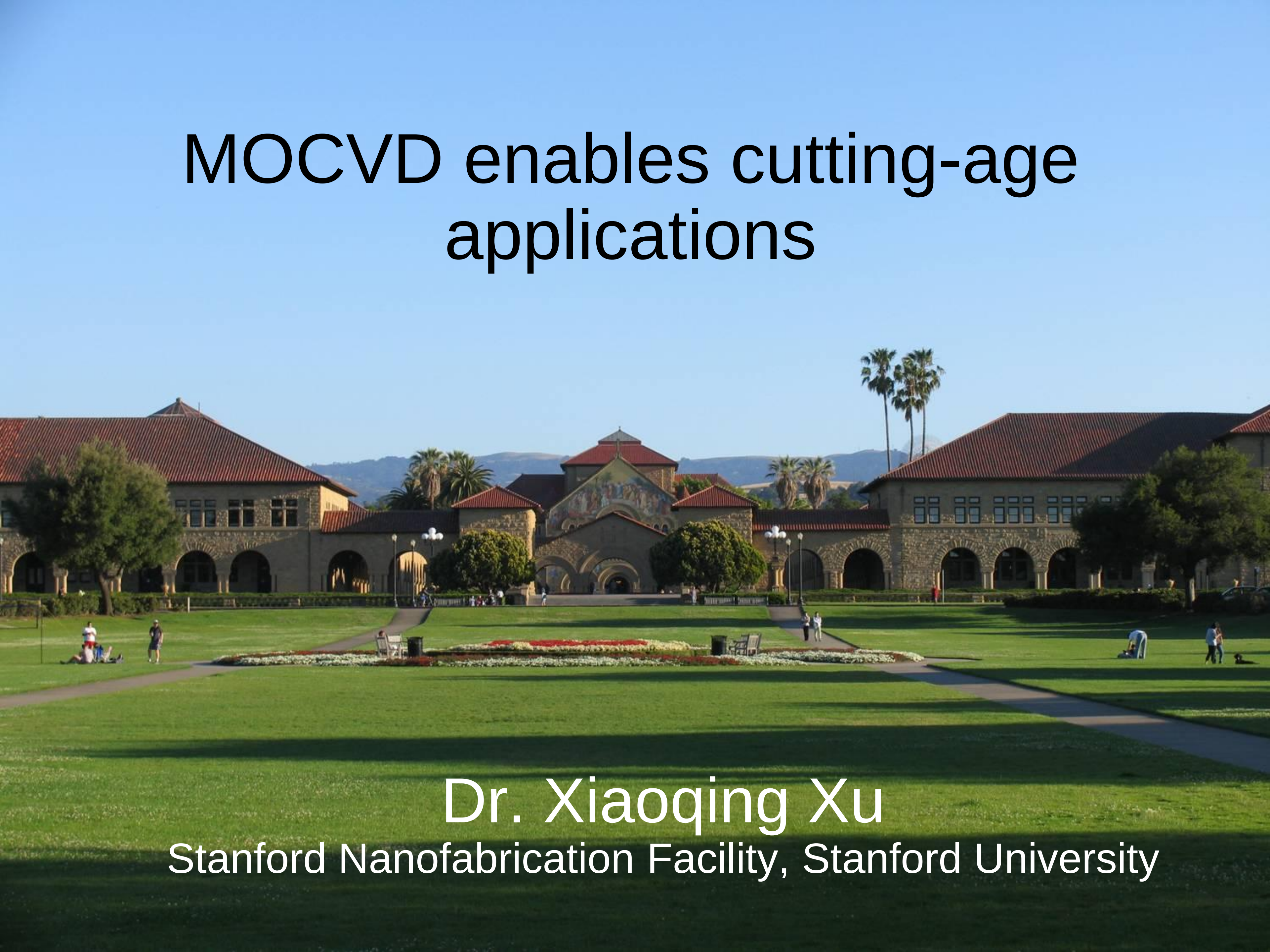
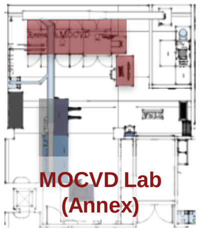
MOCVD enables cutting-age applications



Dr. Xiaoqing Xu
Stanford Nanofabrication Facility, Stanford University

Today's SNF is a collection of shared lab spaces



- The Cleanroom (green): "Classic" fab, Si CMOS process plus some "dirty" processes for flexibility.
- ExFab: Flexible/fast fab, beyond electronics, beyond silicon. 3D printing, microfluidic, advanced lito et al.
- ***MOCVD lab (left): GaAs and GaN, doped and intrinsic films/nanostructures on III-V, silicon and sapphire.***
- SPF (blue): Systems Prototyping facility for designing & assembling boards and systems.
- Wide Band Gap Lab: Construction is underway for WBG materials processing and characterization.
- Open to all, ~500 active users, ~70% from internal/external academia, ~30% from industry

No longer a monolithic cleanroom, today's SNF is a collection of lab spaces, enabling:

- Flexibility, by adapting spaces to meet dynamically changing research needs
- Experimentation, by tailoring spaces with capabilities & rates to serve different target audiences.

Outline

- **MOCVD introduction**
- **MOCVD enabled applications and related research at Stanford**
  - VCSEL (Vertical-Cavity Surface-Emitting Laser)
  - HEMT (High Electron Mobility Transistor)
  - LED (Light Emitting Diode)
  - Solar energy conversion
- **Emerging substrate techniques**
  - GaN and GaAs substrate challenges
  - Research on re-use substrates

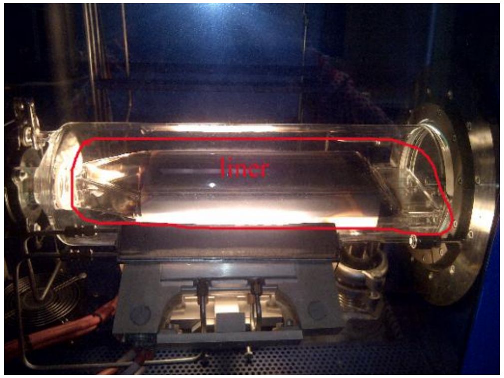
SNF MOCVD lab

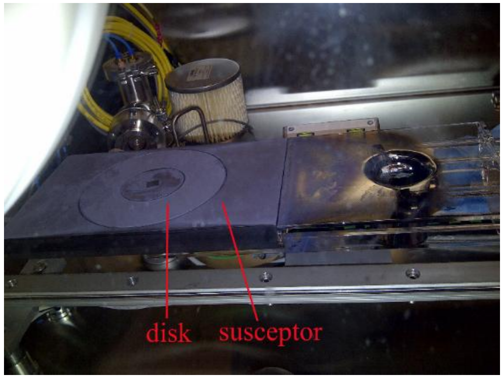
(986.9hr charged hours in 2018)

In,Al,Ga-As,P,(dilute nitride) epitaxial films and nanostructures, n-, p-type doing

AIXTRON 200/4 III-V MOCVD

Temperature up to 800ºC

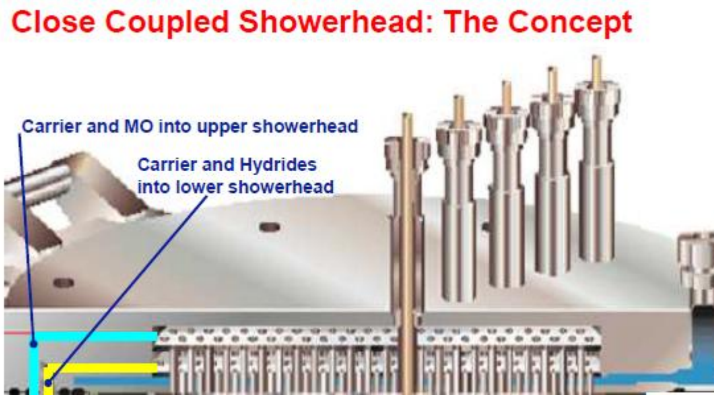




In,Al,Ga-N epitaxial films and n-, p-type doing

AIXTRON CCS III-N MOCVD

Temperature up to 1300ºC



VCSEL for mobile phone

iphone X started face ID

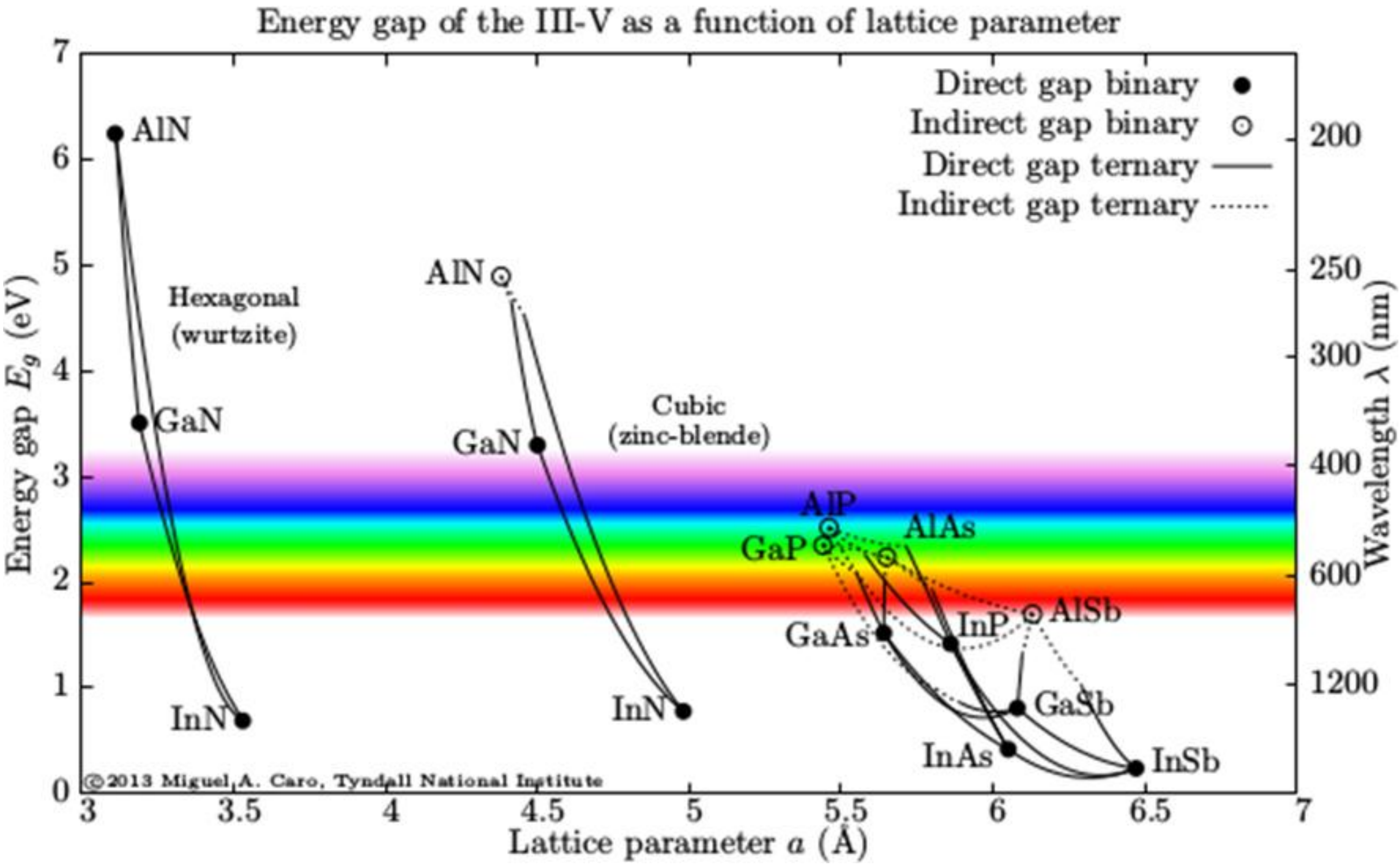
The **flood illuminator** shines infrared light at your face, which allows the system to detect whoever is in front of the iPhone, even in low-light situations or if the person is wearing glasses (or a hat). Then the **dot projector** shines more than 30,000 pin-points of light onto your face, building a depth map that can be read by the infrared camera

MOCVD ⇒ **GaAs based VCSEL** ⇒

(vertical-cavity surface-emitting laser)

https://www.computerworld.com/article/3235140/apples-face-id-the-iphone-xs-facial-recognition-tech-explained.html

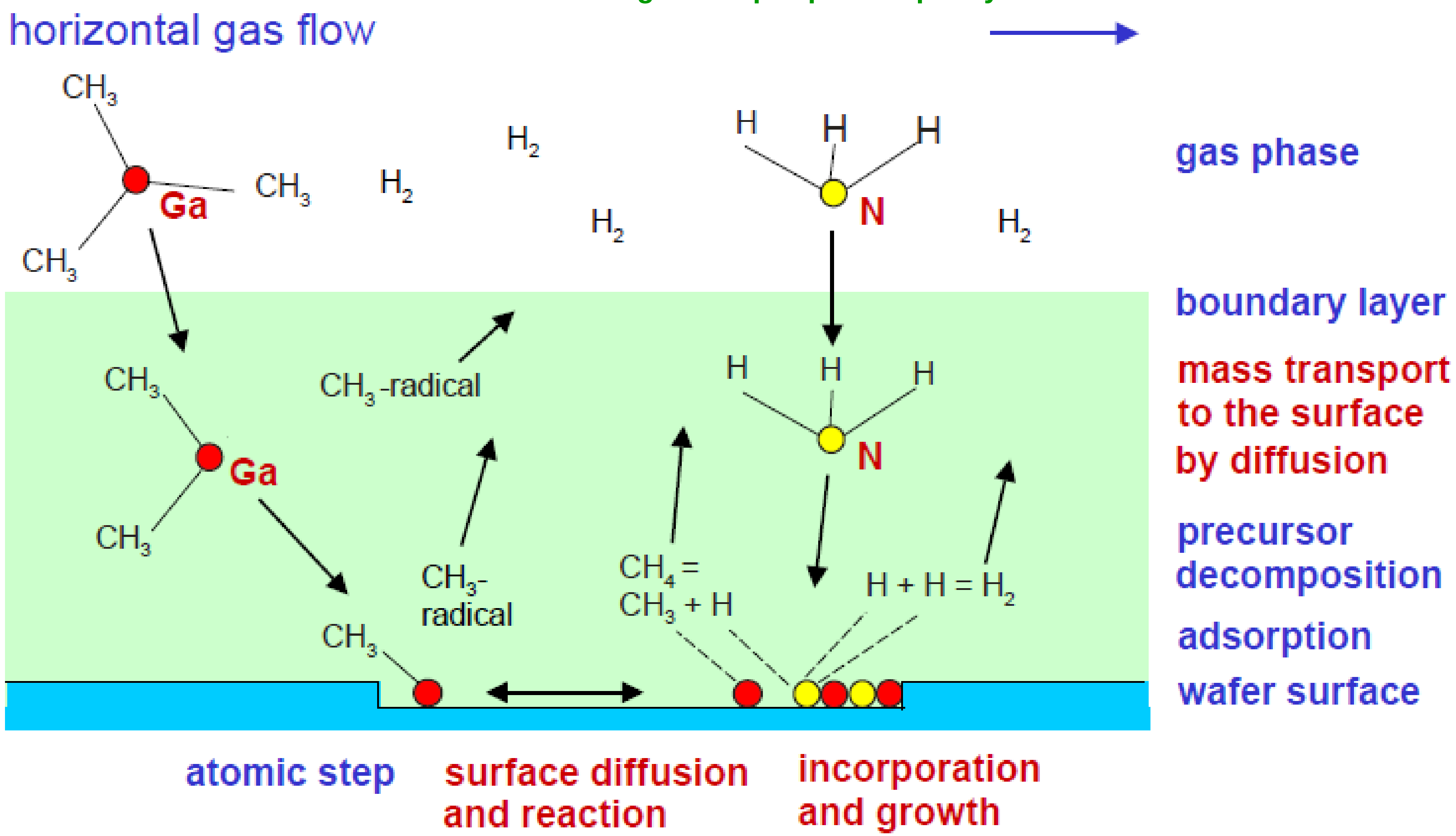
Material capability of MOCVD



MOCVD/MOVPE Growth Mechanisms

GaN for example:

MOCVD: metal organic chemical vapor deposition
MOVPE: metal organic vapor phase epitaxy



A simple example

Take GaN growth for example, the V and III precursors are TMGa and NH_3, respectively.

- Pyrolysis

$$Ga(CH_3)_3(v) \Rightarrow Ga(CH_3)_2(v) + CH_3(v) \tag{3}$$

$$Ga(CH_3)_2(v) \Rightarrow GaCH_3(v) + CH_3(v) \tag{4}$$

$$GaCH_3(v) \Rightarrow Ga(v) + CH_3(v) \tag{5}$$

$$NH_3(s/v) \Rightarrow NH(3-x)(s/v) + xH(s/v) \tag{6}$$

- Interface Reaction

$$GaCH_3(s/v) + NH(s/v) \Rightarrow GaN(s) + 1/2H_2 \tag{7}$$

- Adduct formation

$$TMGa + NH_3 \Rightarrow TMGa - NH_3 \tag{8}$$

MOCVD/MOVP-*Epitaxy* Schematic

Homoepitaxy

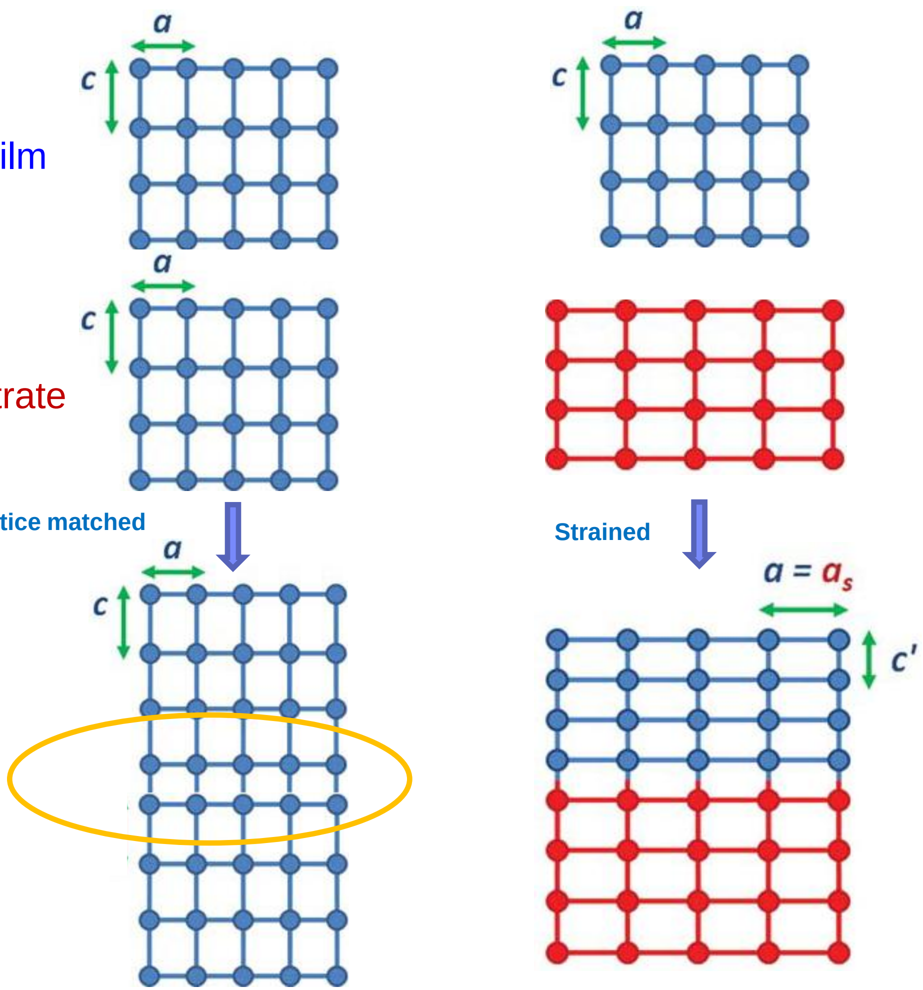
Heteroepitaxy

Epi-film

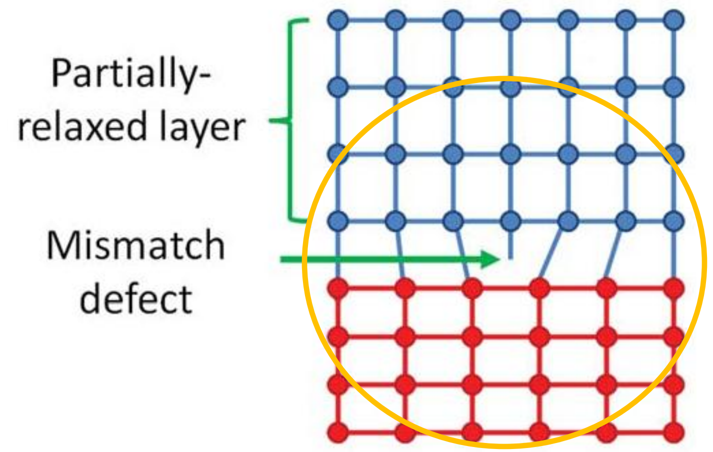
Substrate

Lattice matched

Strained



Defect (dislocation) form to relieve the strain



Adapted and modifieded from Muhammad Iqbal Bakti Utama, Nanoscale. 2013 May 7;5(9):3570-88

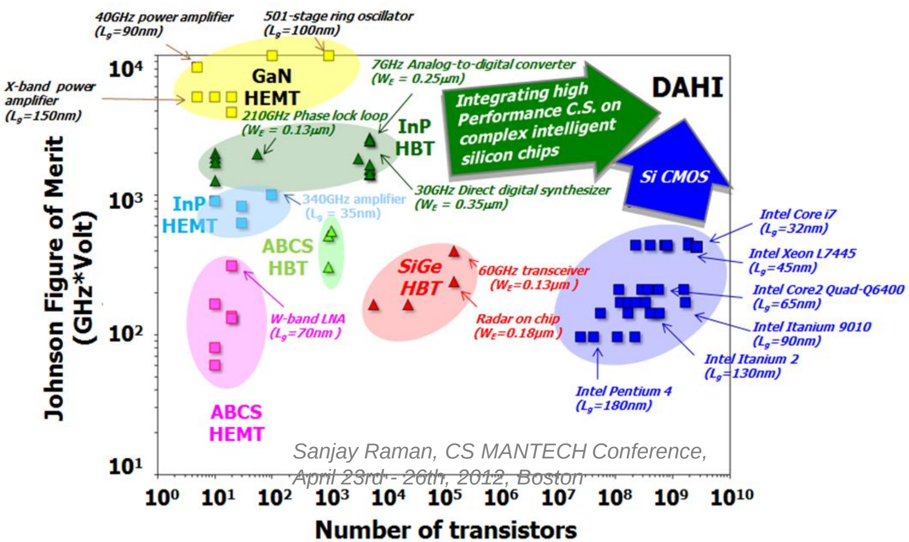
Device application background

LED

Laser

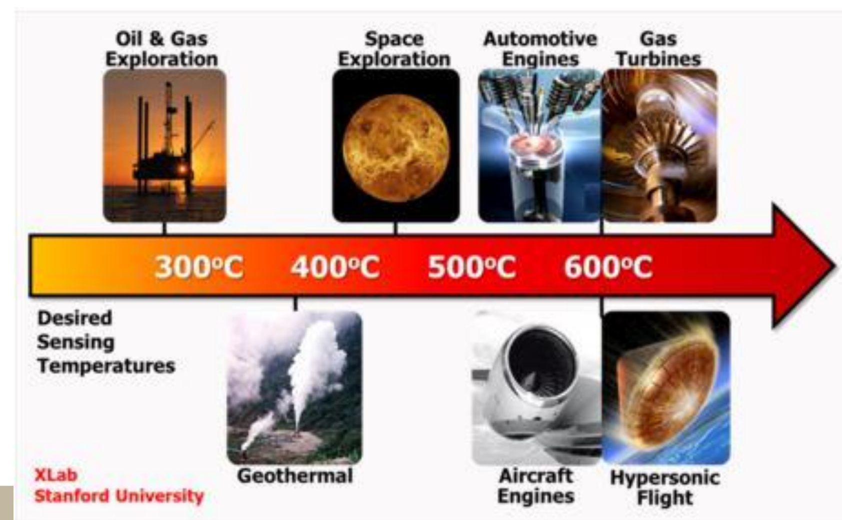
Solar cell

HBT (heterojunction bipolar transistor) &HEMT(High-electron-mobility transistor)



Sanjay Raman, CS MANTECH Conference, April 23rd - 26th, 2012, Boston

New sensor systems for extreme harsh environments



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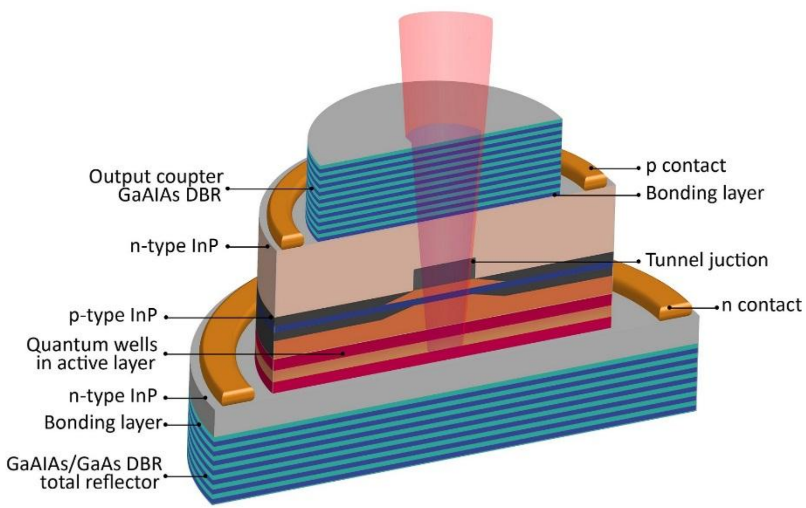
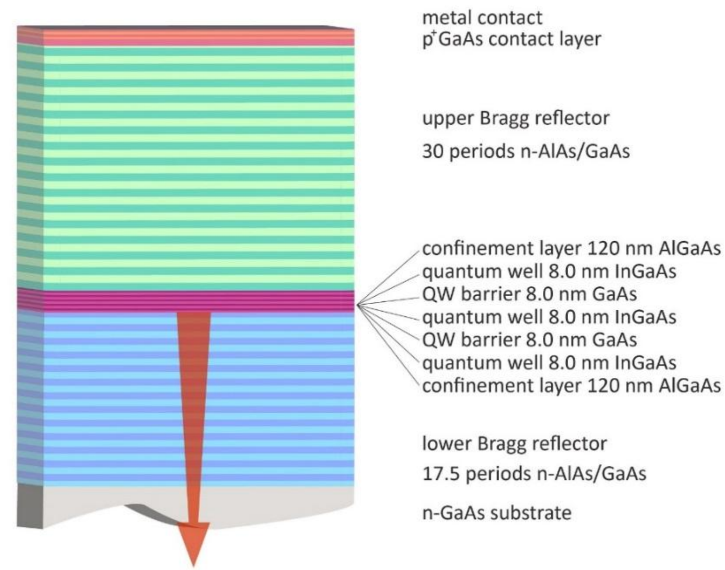
MOCVD hot field-1. VCSEL

Structure diagram of VSCEL

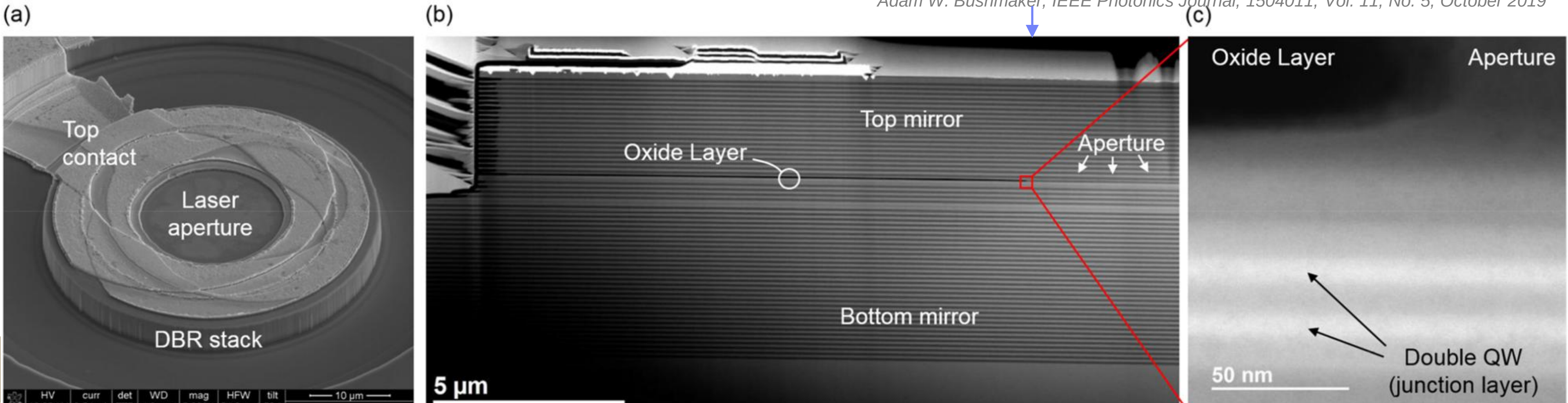


https://www.enlitechnology.com/show/semiconductor.htm

Structure of DBR

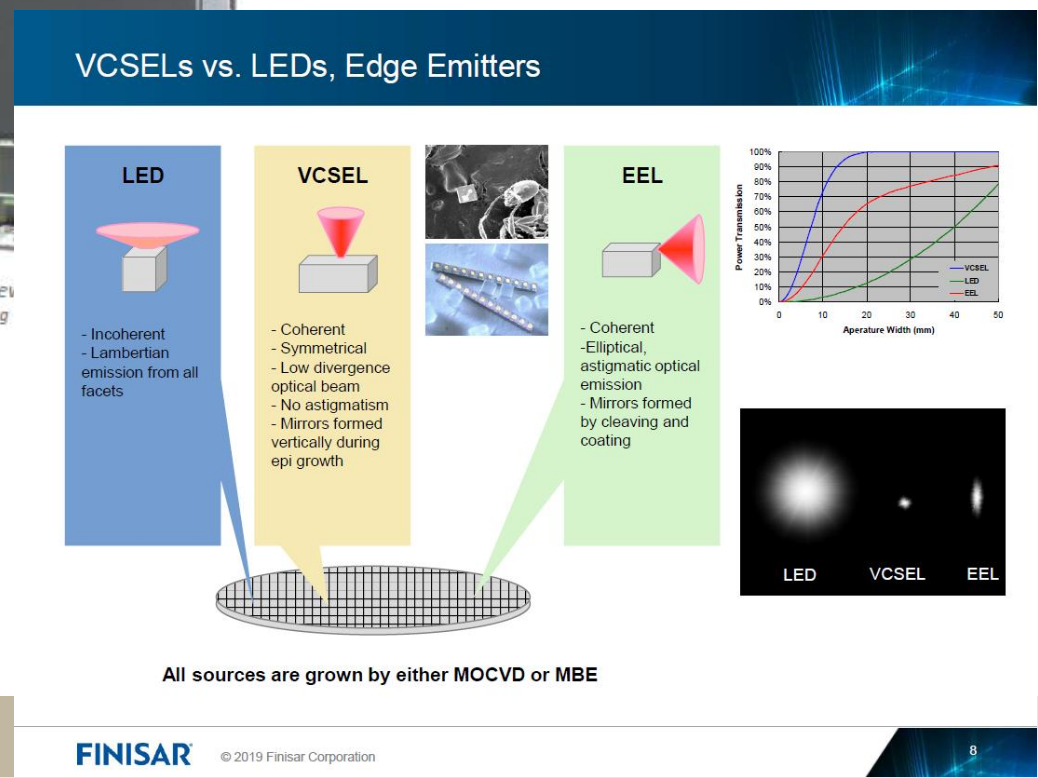


Adam W. Bushmaker, IEEE Photonics Journal, 1504011, Vol. 11, No. 5, October 2019

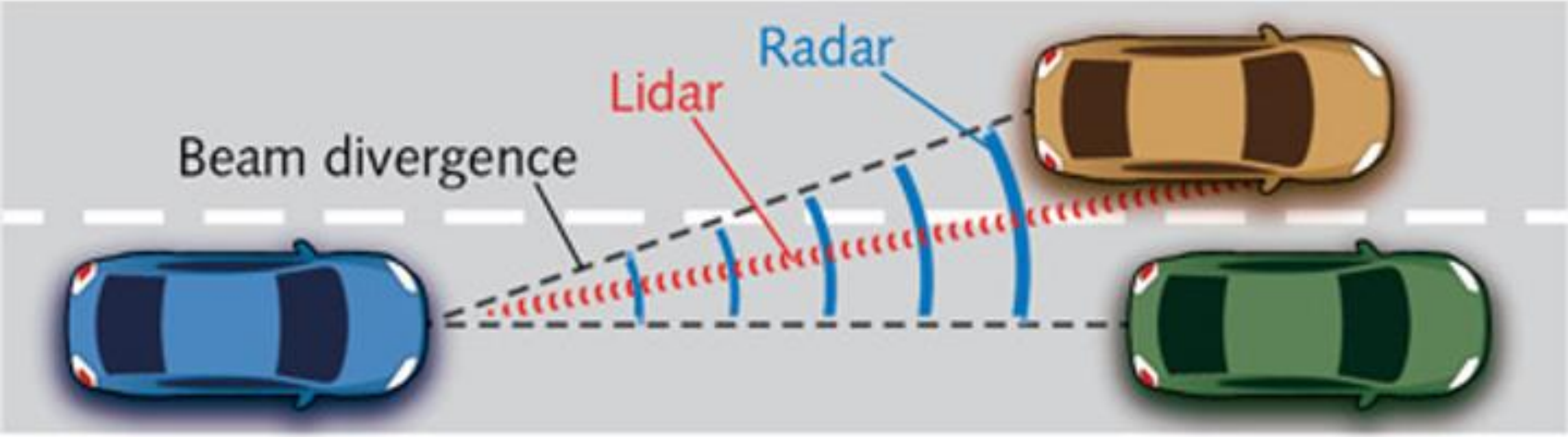


VCSEL for mobile phone

Apple iPhone X Opened Vie
©2018 by System Plus Consulting



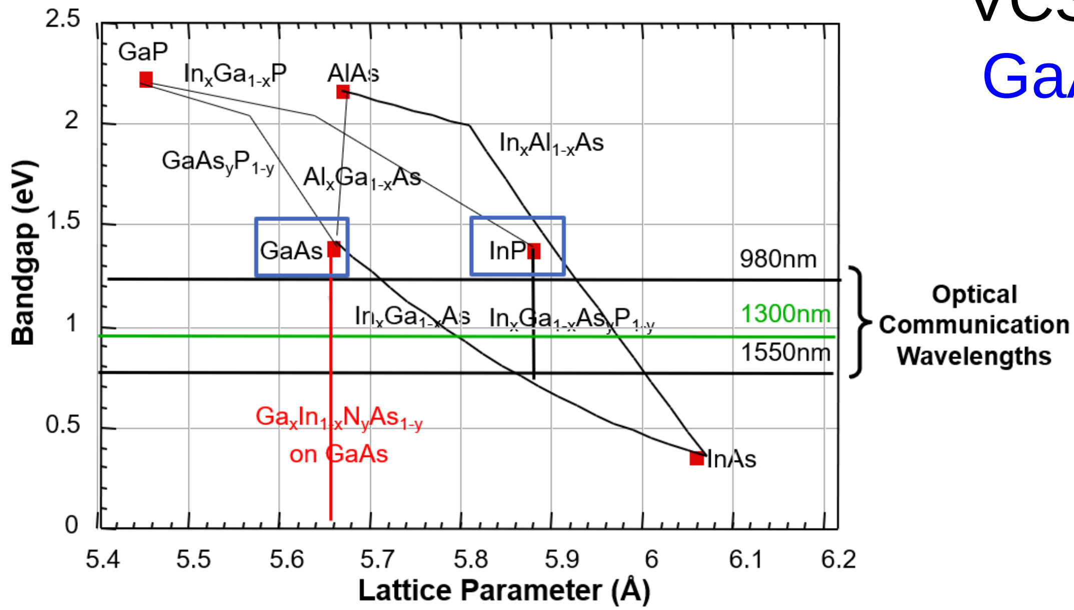
VCSEL for Lidar

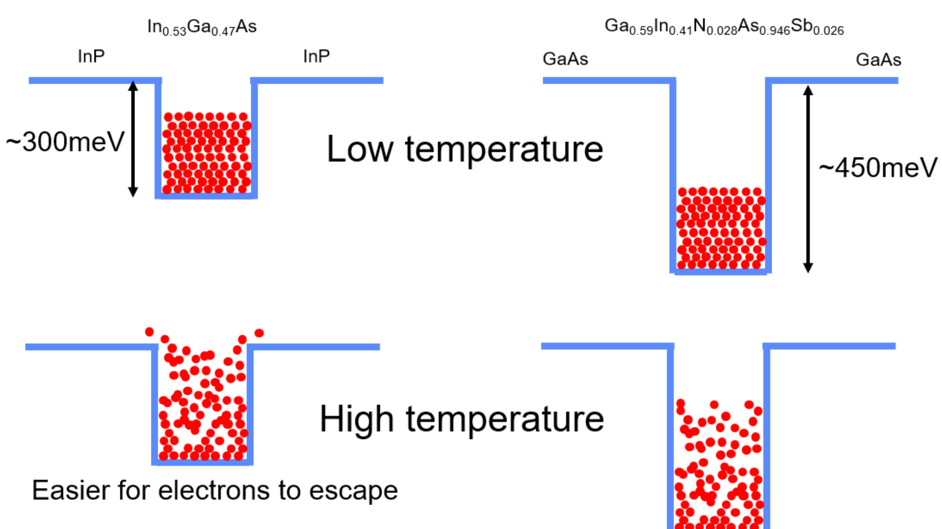


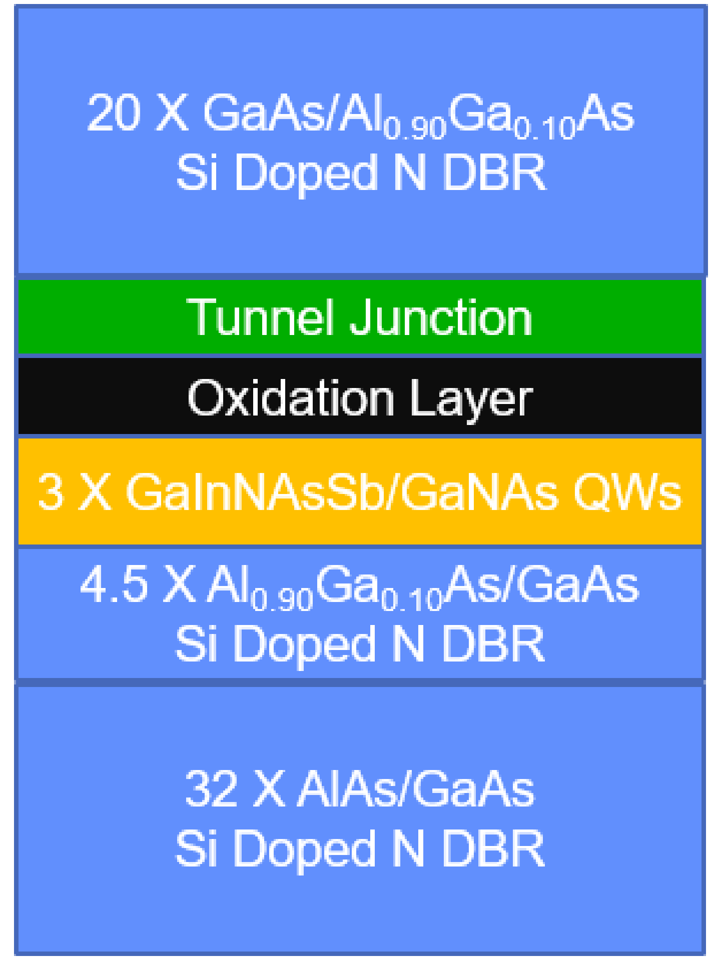
Parameters	LiDAR	RADAR	Camera
Range	High	High	Very Low
Field of View	High	Low	Very Low
3D Shape	High	Low	Very Low
Obj. Rec @ Long Range	High	Low	Very Low
Accuracy	High	Low	Low
Rain, Snow, Dust	High	High	Low
Fog	Medium	High	Low
Night time	High	High	Low
Read Signs & See Color	Medium	Low	High

https://automotive.electronicspecifier.com/sensors/what-is-driving-the-automotive-lidar-and-radar-market

VCSEL Research at Stanford:
GaAs based long wavelength VCSELs







Li Zhao, PhD thesis, Stanford University, 2019

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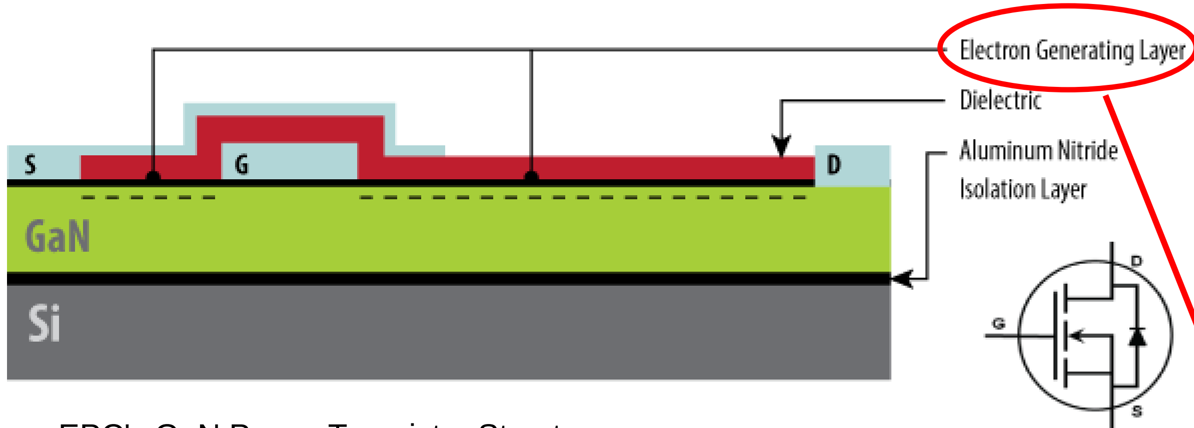
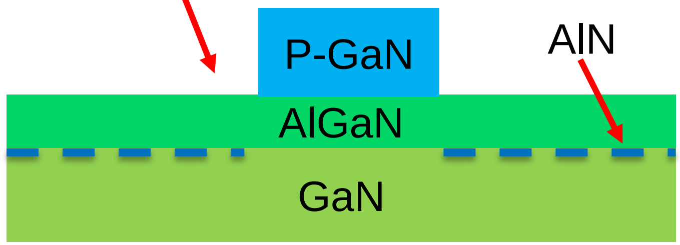
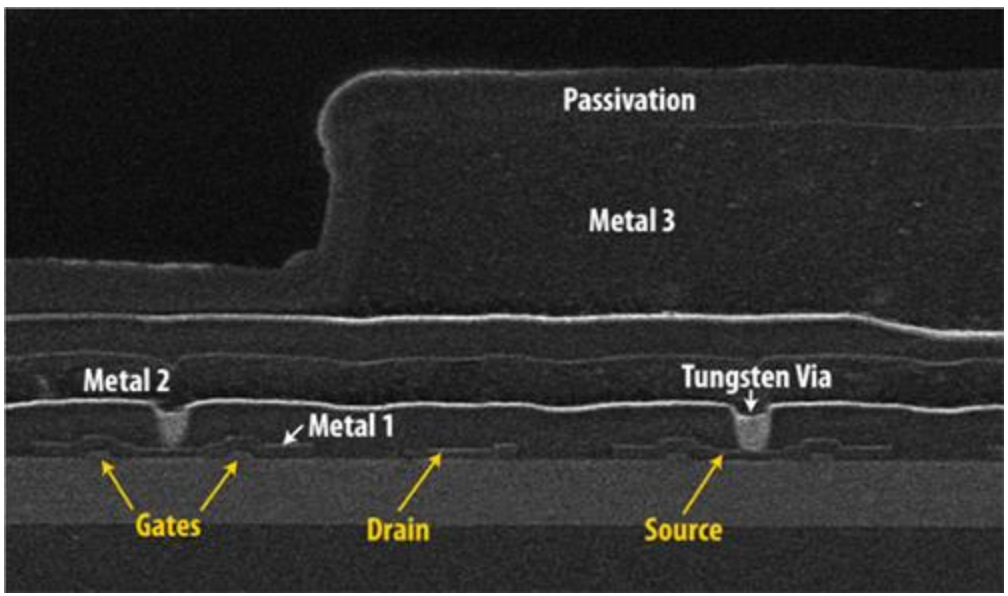
MOCVD hot field-2. HEMT



EPC's GaN Power Transistor Structure



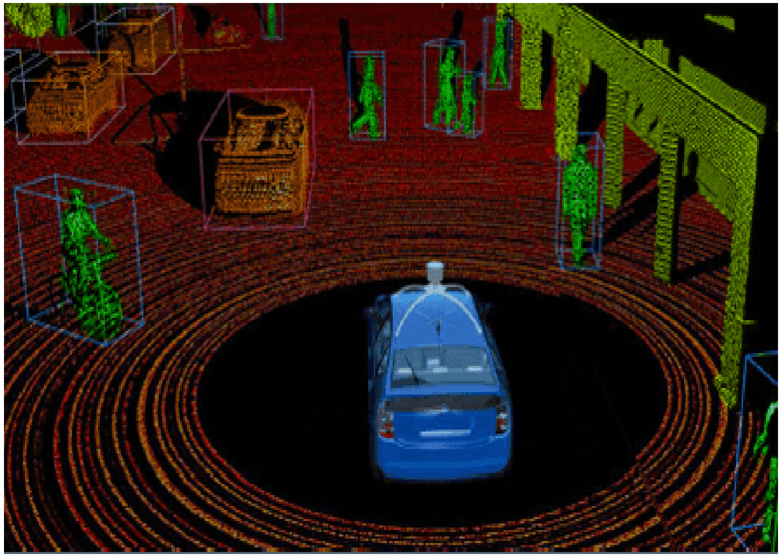


Scanning electron micrograph cross section of an eGaN FET

GaN HEMT for lidar

Si power switch

GaN power switch



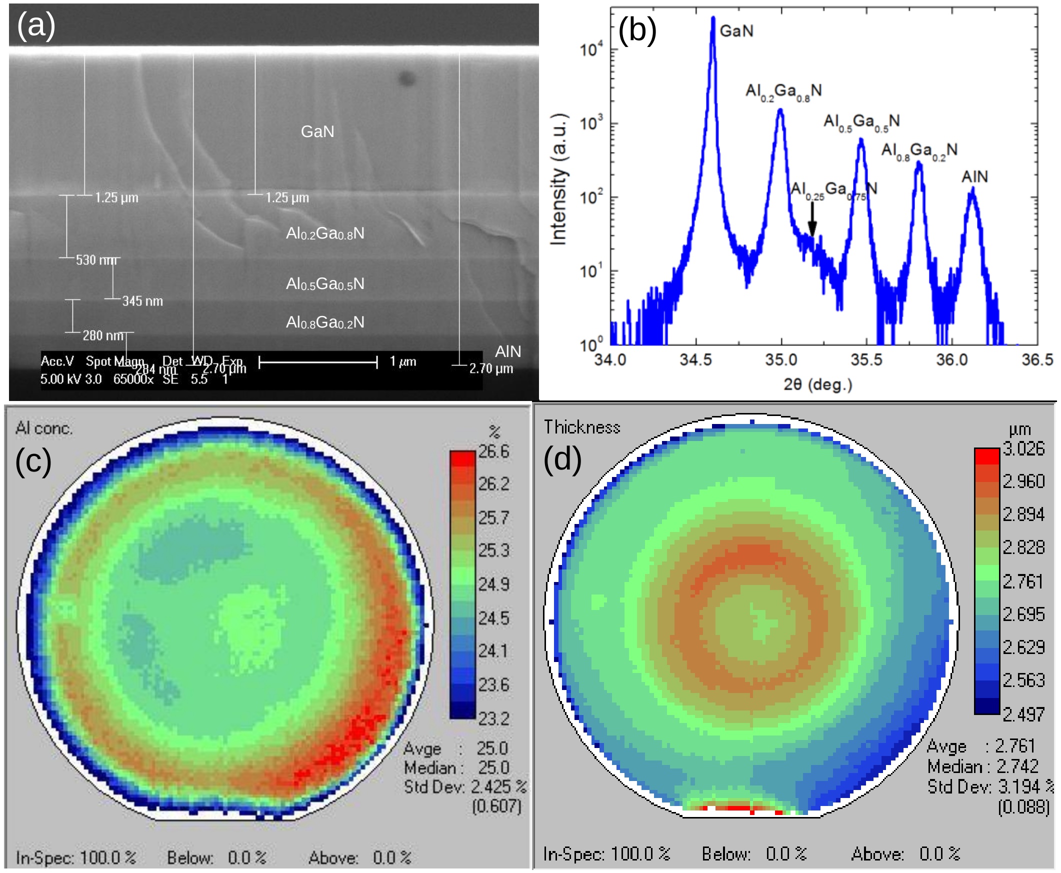
Alex Lidow, "How eGaN FETs and IC Technology Improves Lidar performance", 2018 APEC

GaN HEMT for smaller charger

GaN HEMT for wireless charging

HEMT Research at Stanford:

1. D-mode AlGaN/GaN HEMT on Si



(a) SEM cross section and (b) XRD pattern of the HEMT structure; (c) the PL mapping of the $Al_xGa_{1-x}N$ barrier and (d) the thickness mapping of the full HEMT structure.

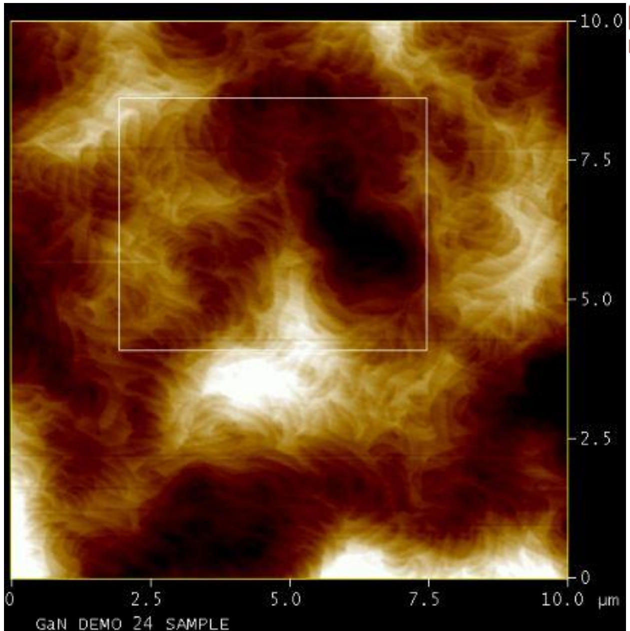


Image Statistics 1x1µm

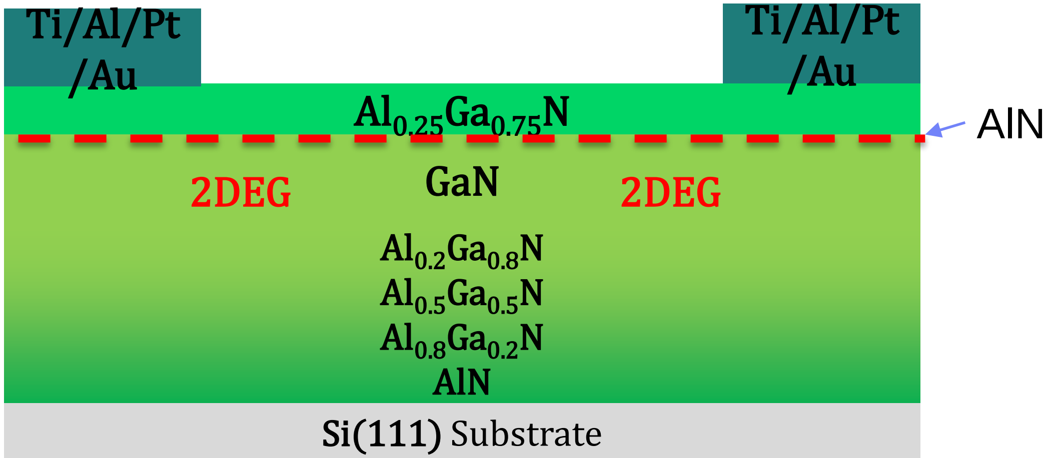
Img. Z range	1.099 nm
Img. Rms (Rq)	0.130 nm
Img. Ra	0.104 nm
Img. Rmax	1.099 nm
Img. Srf. area	1.000 µm²
Img. Srf. area diff	0.028 %

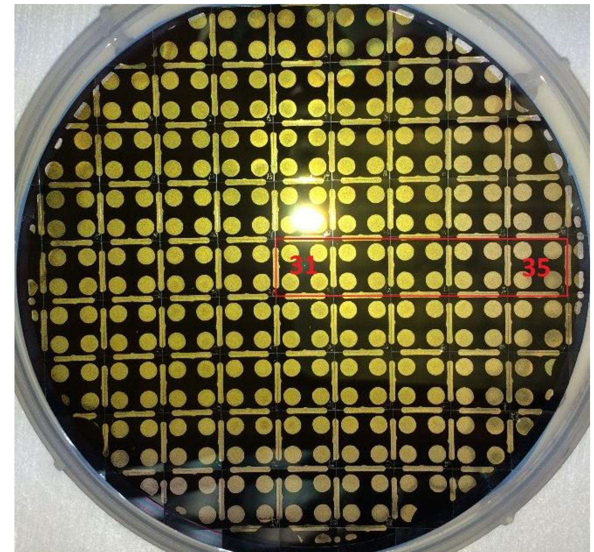
Image Statistics 10x10µm

Img. Z range	6.259 nm
Img. Rms (Rq)	0.822 nm
Img. Ra	0.650 nm
Img. Rmax	6.259 nm
Img. Srf. area	100.00 µm²
Img. Srf. area diff	0.0008 %

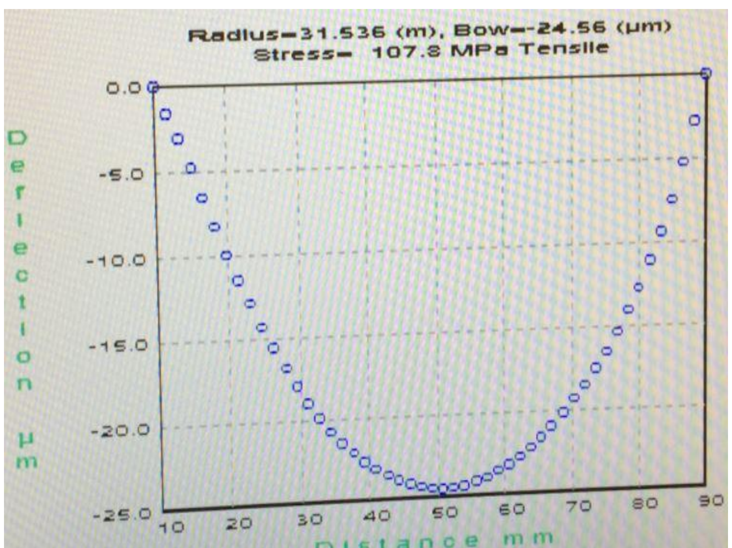
AFM image of GaN on Si

Wafer scale high uniformity





Wafer Bow

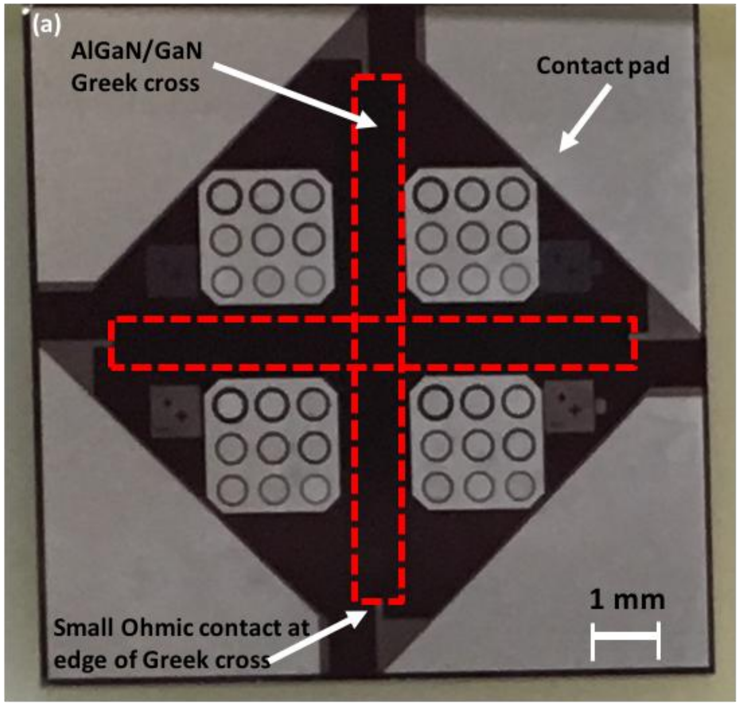


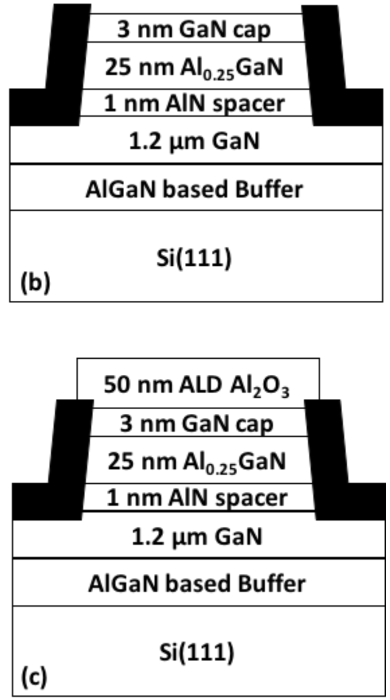
2DEG Mobility

	#1	#2	#3	#4	#5	Average (cm²/Vs)	Stdev%
μ_1 (cm²/Vs)	1205.7	1218.1	1217.8	1206.4	1230.6	--	--
μ_2 (cm²/Vs)	1210.5	1207.7	1206.6	1206.4	1226.2	--	--
μ (cm²/Vs)	1208.1	1212.9	1212.2	1206.4	1228.4	1213.6	0.72%

Xiaoqing Xu et al., AIP Advances 6, 115016 (2016)

Degradation of 2DEG transport properties after 600° C annealing





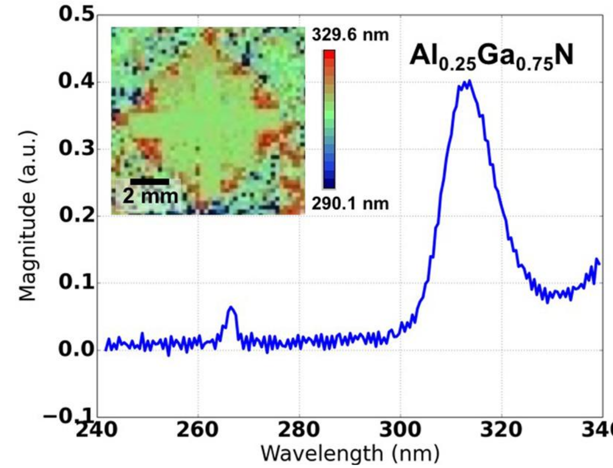
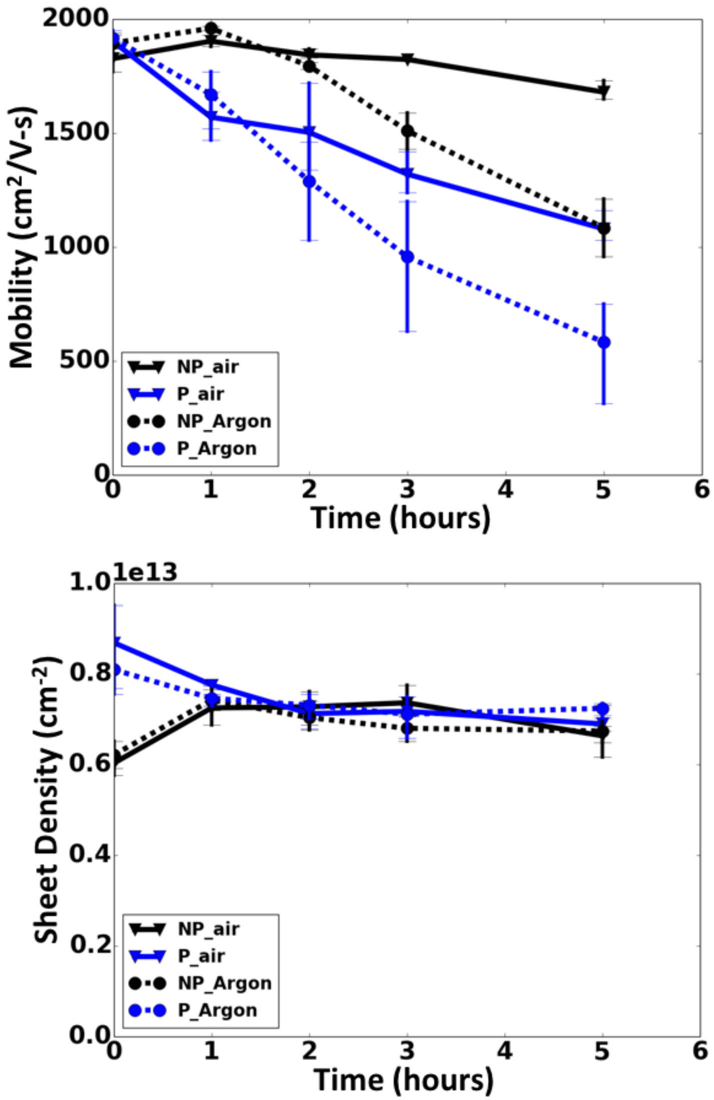


Table: PL peak of $Al_{0.25}Ga_{0.75}N$ barrier for samples w/o Al_2O_3 passivation, before and after anneal in air/Argon

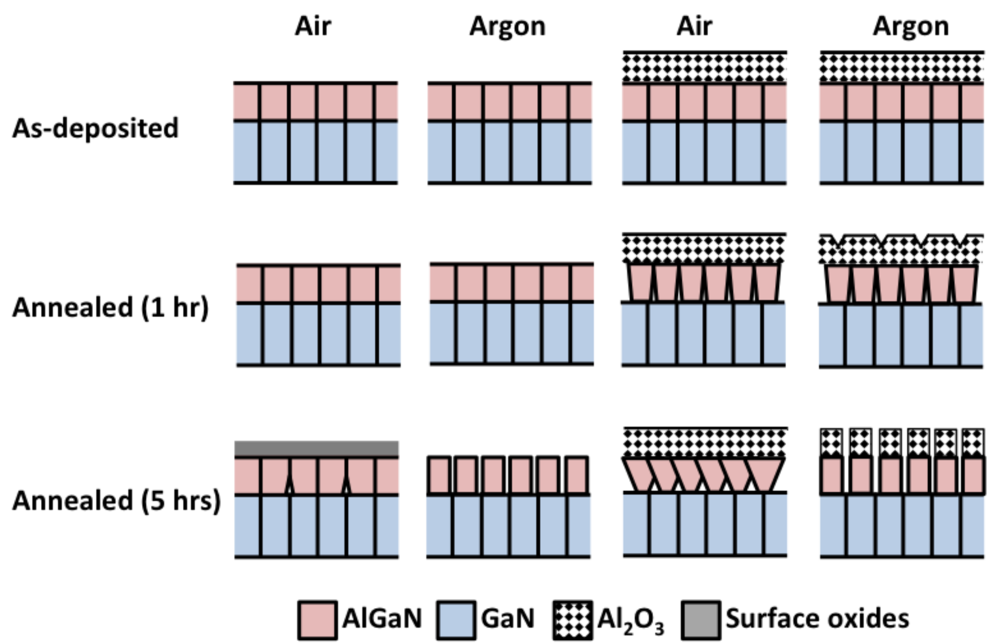
Sample	PL peak (nm)
No passivation, no anneal	316.4
Al_2O_3-passivated, no anneal	316.8
NP_air	317.4
NP_Argon	311.0
P_air	313.3
P_Argon	313.6

*Hou, Minmin, Sambhav R. Jain, Hongyun So, Thomas A. Heuser, **Xiaoqing Xu**, et al., Journal of Applied Physics 122, 195102 (2017).*

Degradation of 2DEG transport properties after 600° C annealing



Electron mobility (a) and sheet density (b) measured in the four groups of AlGaN/GaN samples over 5 hours of annealing

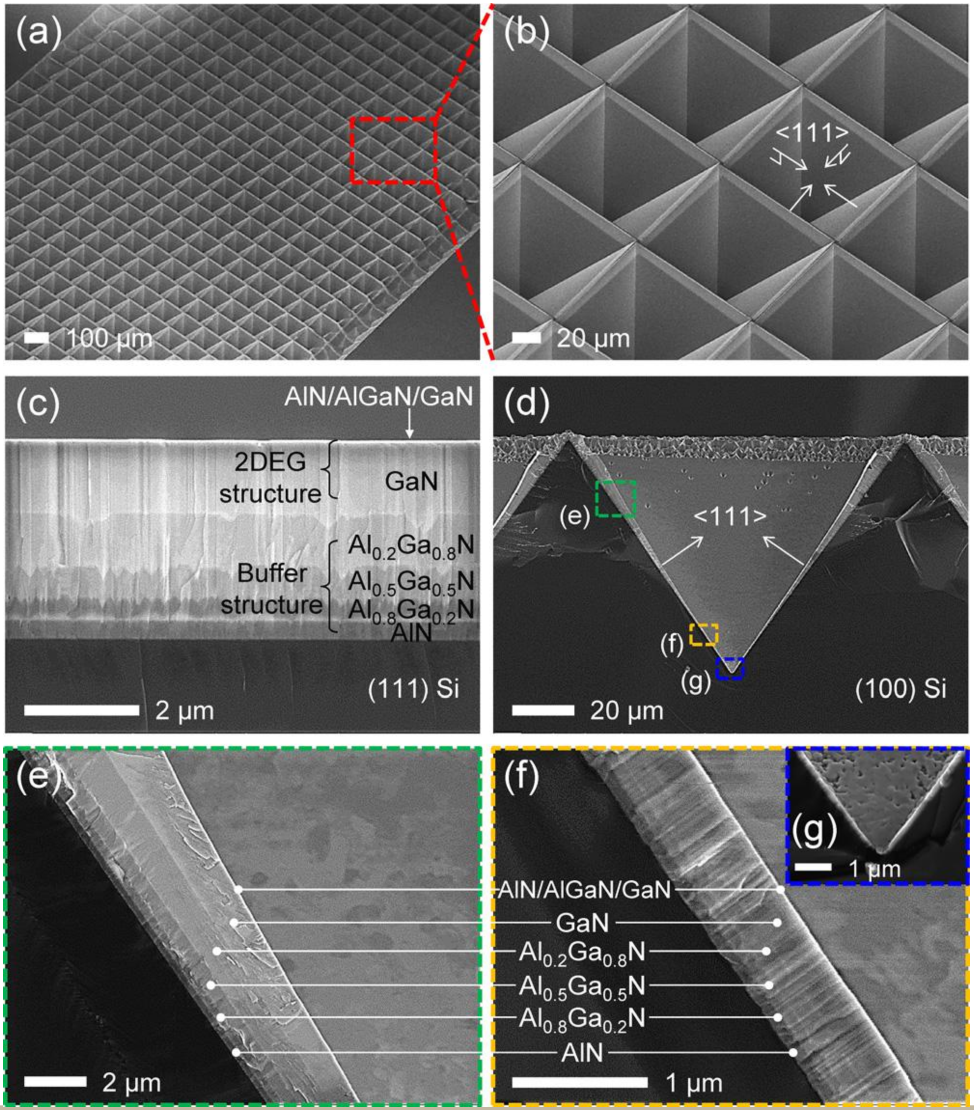


Schematic illustration of the microstructural evolutions of the unpassivated and Al2O3-passivated AlGaN/GaN heterostructures at 600° C in air and in argon.

*Hou, Minmin, Sambhav R. Jain, Hongyun So, Thomas A. Heuser, **Xiaoqing Xu**, et al., Journal of Applied Physics 122, 195102 (2017).*

HEMT Research at Stanford:

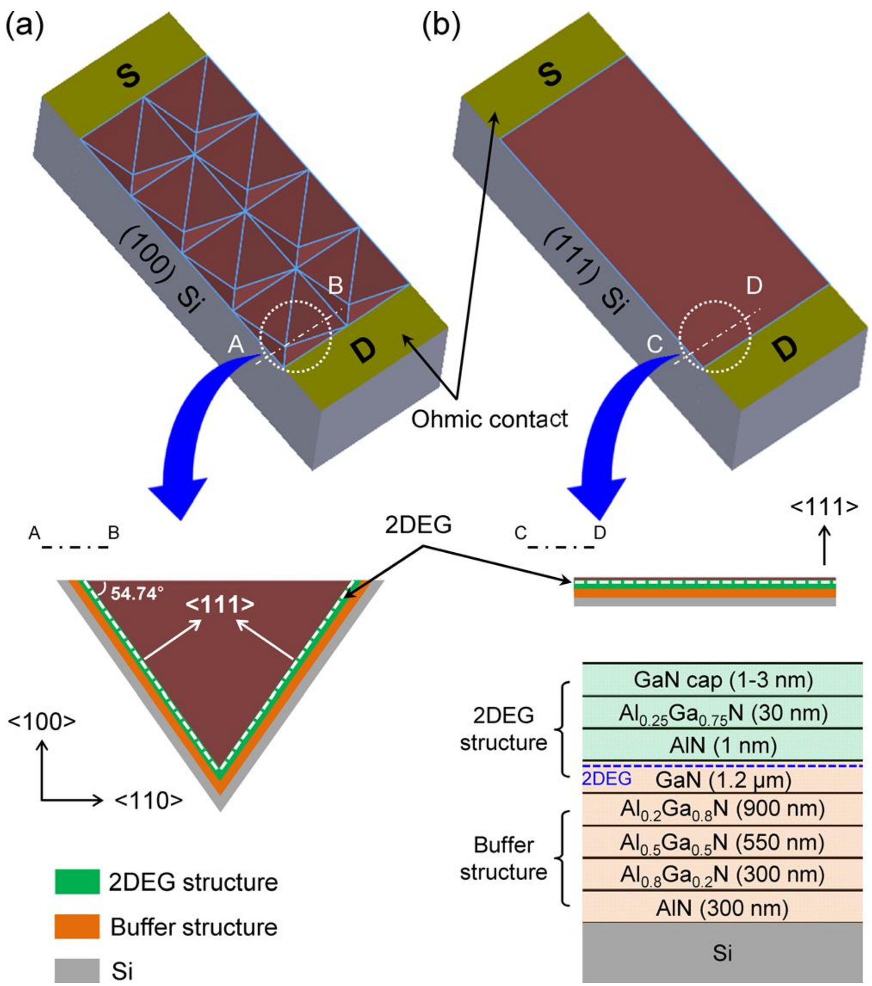
2. 3D inverted pyramidal AlGaN/GaN HEMT

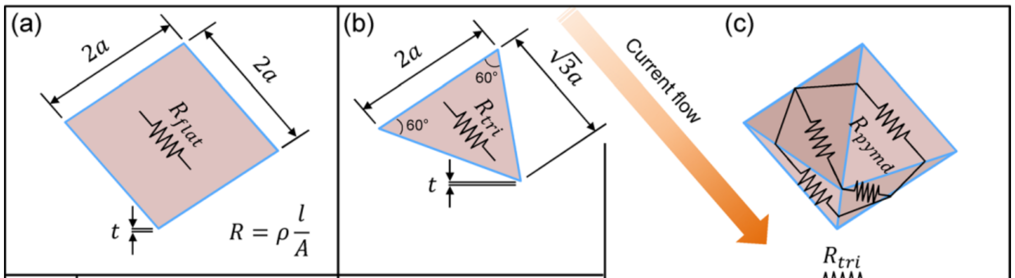


SEM images of the inverted pyramidal silicon surfaces: (a) 40º tilted view and (b) zoomed-in view.
SEM images of group III-nitride multilayers deposited on (c) planar silicon substrate and (d) inverted pyramidal silicon surface with (e)–(g) zoomed-in views at different positions.

Hongyun So, et al.,
Appl. Phys. Lett. 108, 012104 (2016)

Low-resistance gateless HEMT using 3D inverted pyramidal AlGaN/GaN surfaces



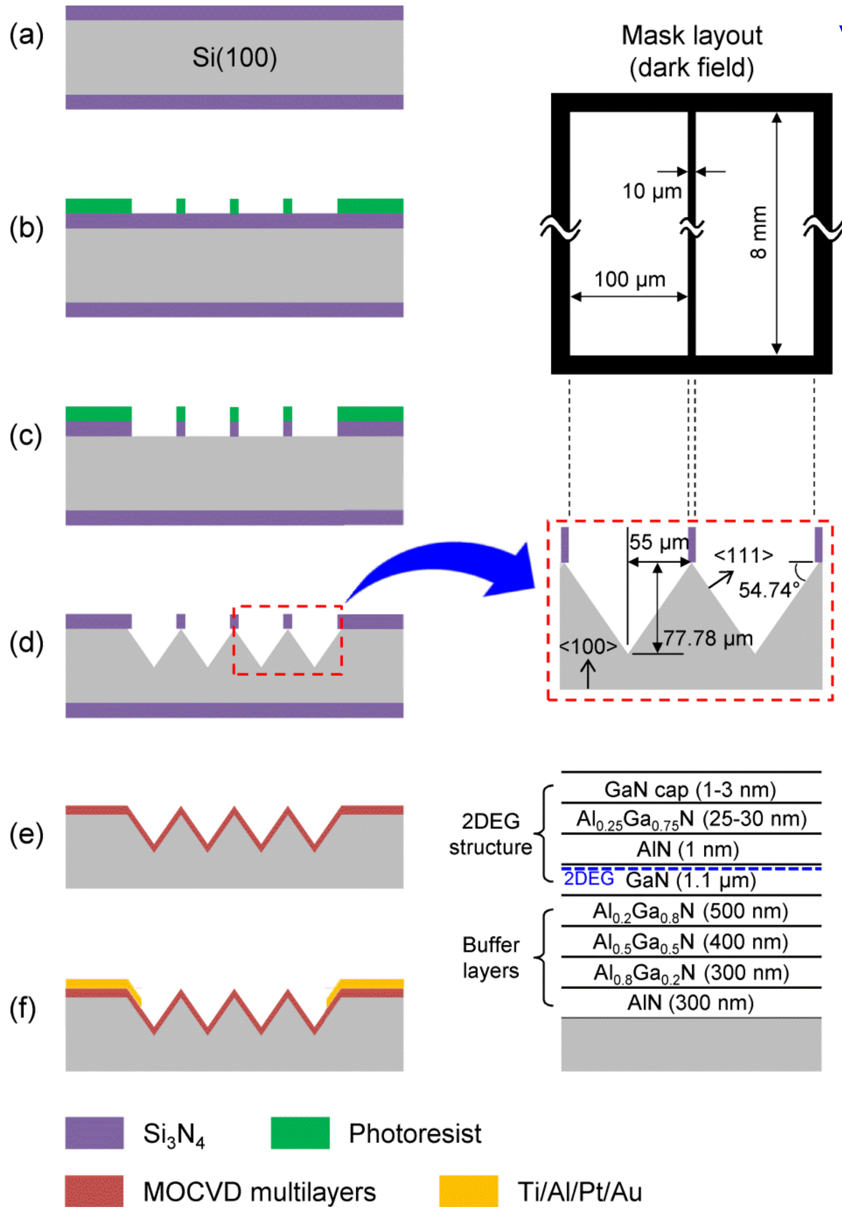


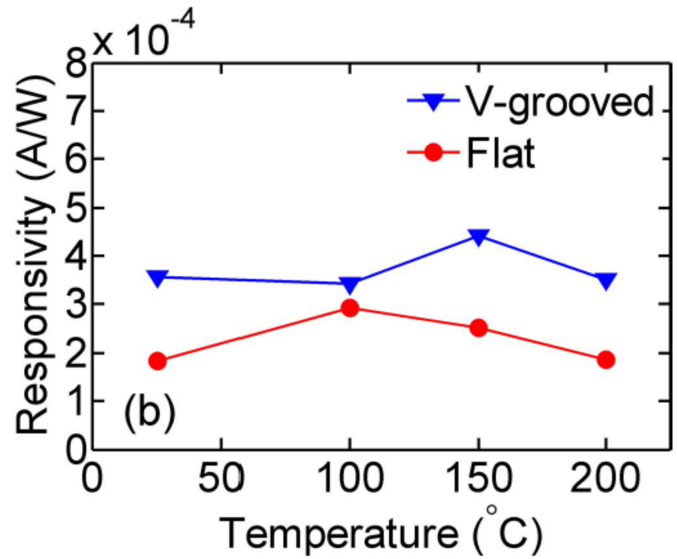
	(a)	(b)	(c)
A	$2at$	$\frac{4}{3}at$	
l	$2a$	$\sqrt{3}a$	
R	$\frac{\rho}{t}(R_{flat})$	$\frac{3\sqrt{3}}{4}\frac{\rho}{t}(R_{tri})$	$R_{Pymd} = \frac{2}{5}R_{tri} = \frac{3\sqrt{3}}{10}\frac{\rho}{t} = 0.52R_{flat}$

Comparison of the electrical resistance of 2DEG channel grown on different surfaces

Hongyun So, et al., Appl. Phys. Lett. 108, 012104 (2016)

V-Grooved AlGaN/GaN Surfaces for High Temperature Ultraviolet Photodetectors





Responsivity as a function of temperature
(ultraviolet intensity of 3 ± 0.1 mW/cm^2 and 1 V bias).

Hongyun So, et al., IEEE SENSORS JOURNAL, VOL. 16, NO. 10, MAY 15, 2016

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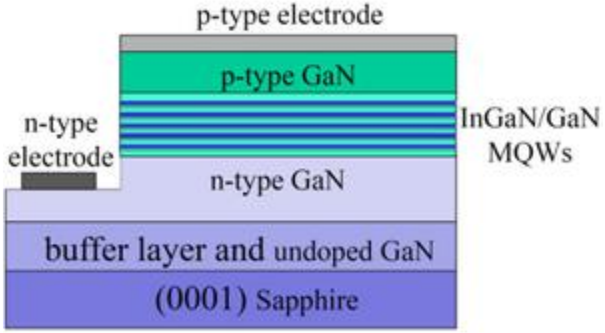
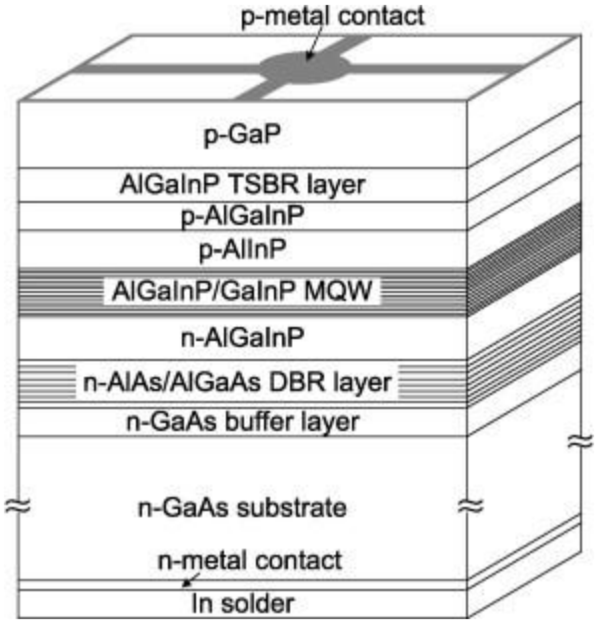
MOCVD hot field-3. Micro LED

InGaN/GaN blue or green LED



Nick Rolston, coursework for PH240, Stanford University, Fall 2014

AlGaInP/GaInP MQW red LED



H.K. Lee, Solid-State Electronics 56 (2011) 79–84

Micro LED

Samsung 75-inch Micro LED display in 2019 SID

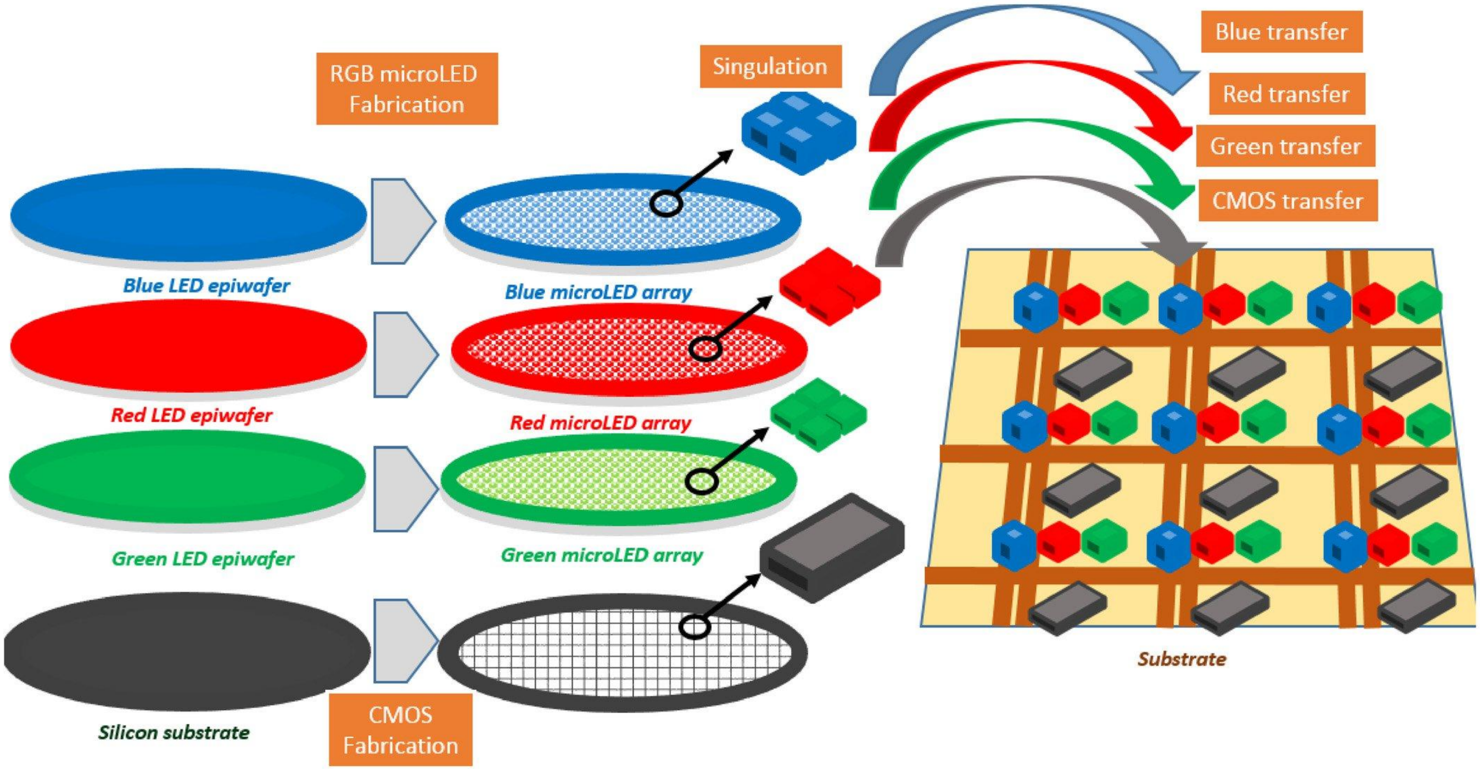
(Image: Samsung)

Micro LED advantages

Mini LED and Micro LED		
	Mini LED	Micro LED
Size	100-200μm	Under 100μm
Application	LCD backlight, fine pitch display wall	Self-emitting display wall, micro-projection display wall
Number of LEDs used (in a typical TV)	More than a thousand LEDs (for direct-lit LED backlight)	Millions of LEDs
Schedule of mass production	2018 at the earliest	Probably 2019-2022
Advantages	HDR, notch design, curved design	High luminous efficiency, high brightness, high contrast, high reliability, and short response time
Difference with LCD in prices	20% higher than LCD panel prices	More than 3 times of LCD panel prices in the initial stage of mass production

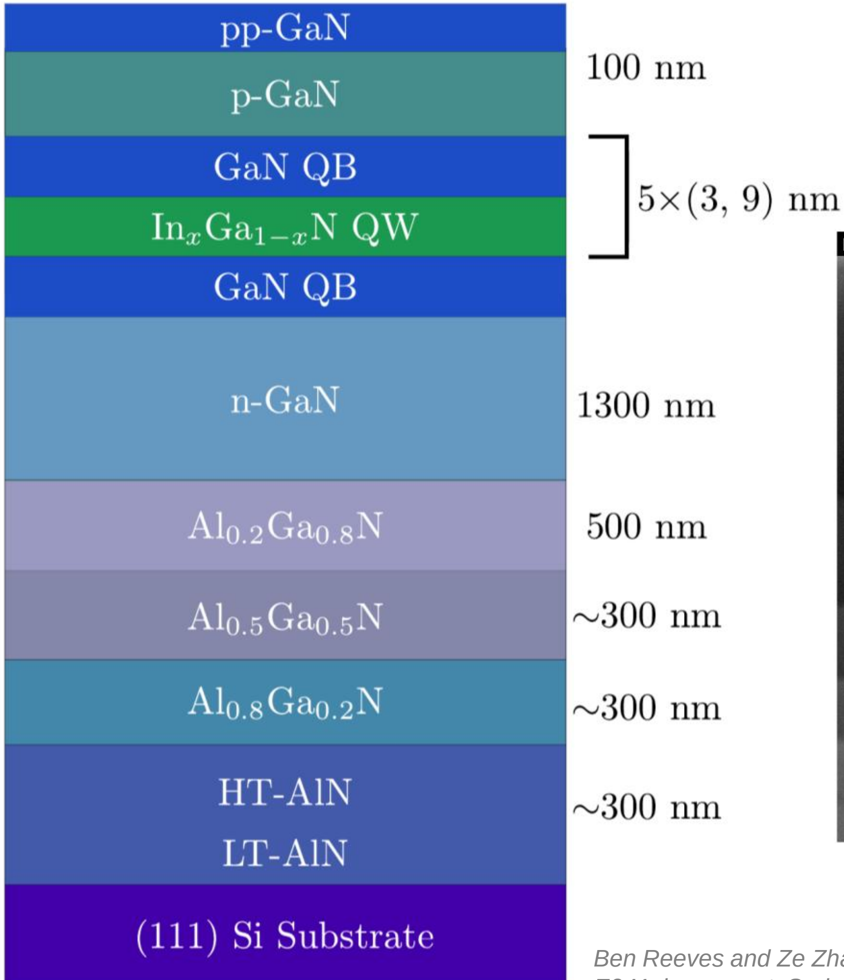
(Source: LEDinside)

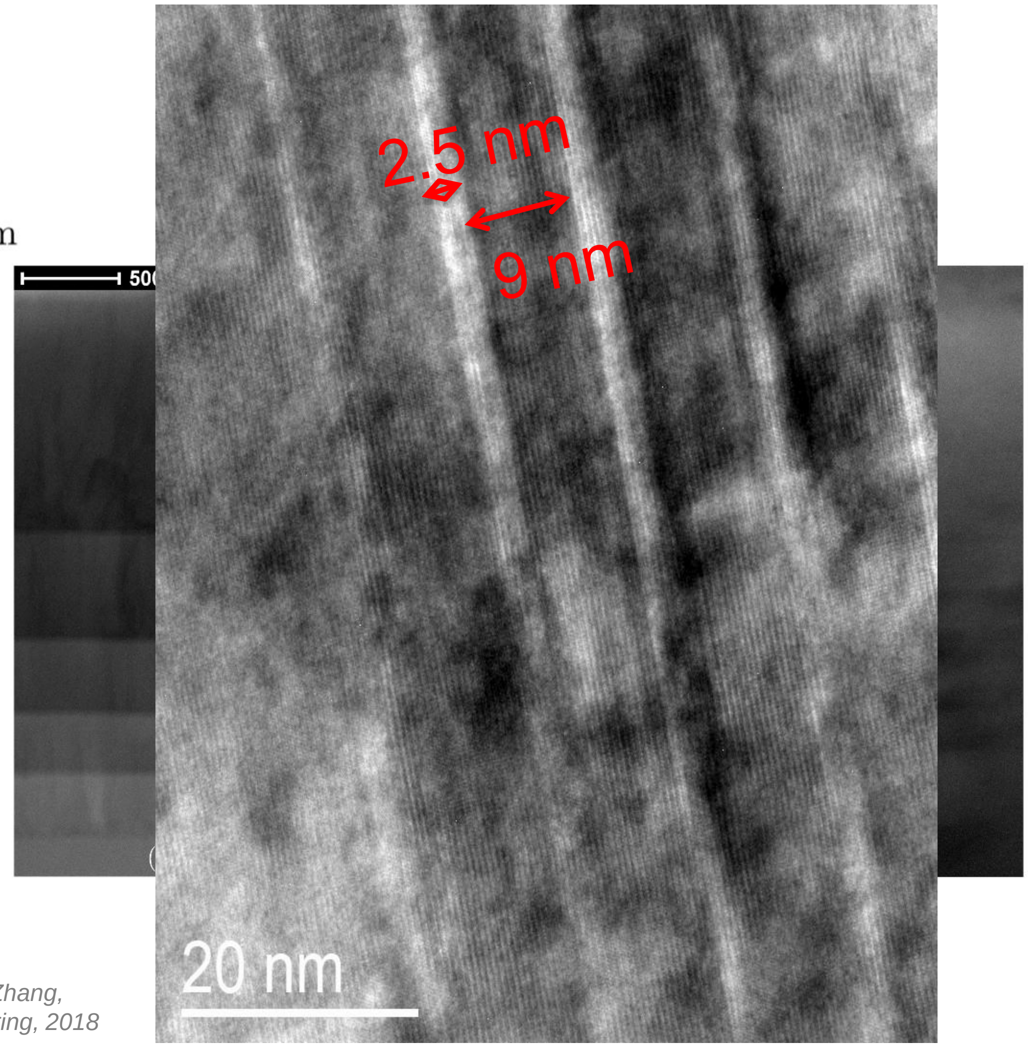
Micro LED process concept



François Templier, Proc. SPIE 10918, Gallium Nitride Materials and Devices XIV, 109181Q (1 March 2019).

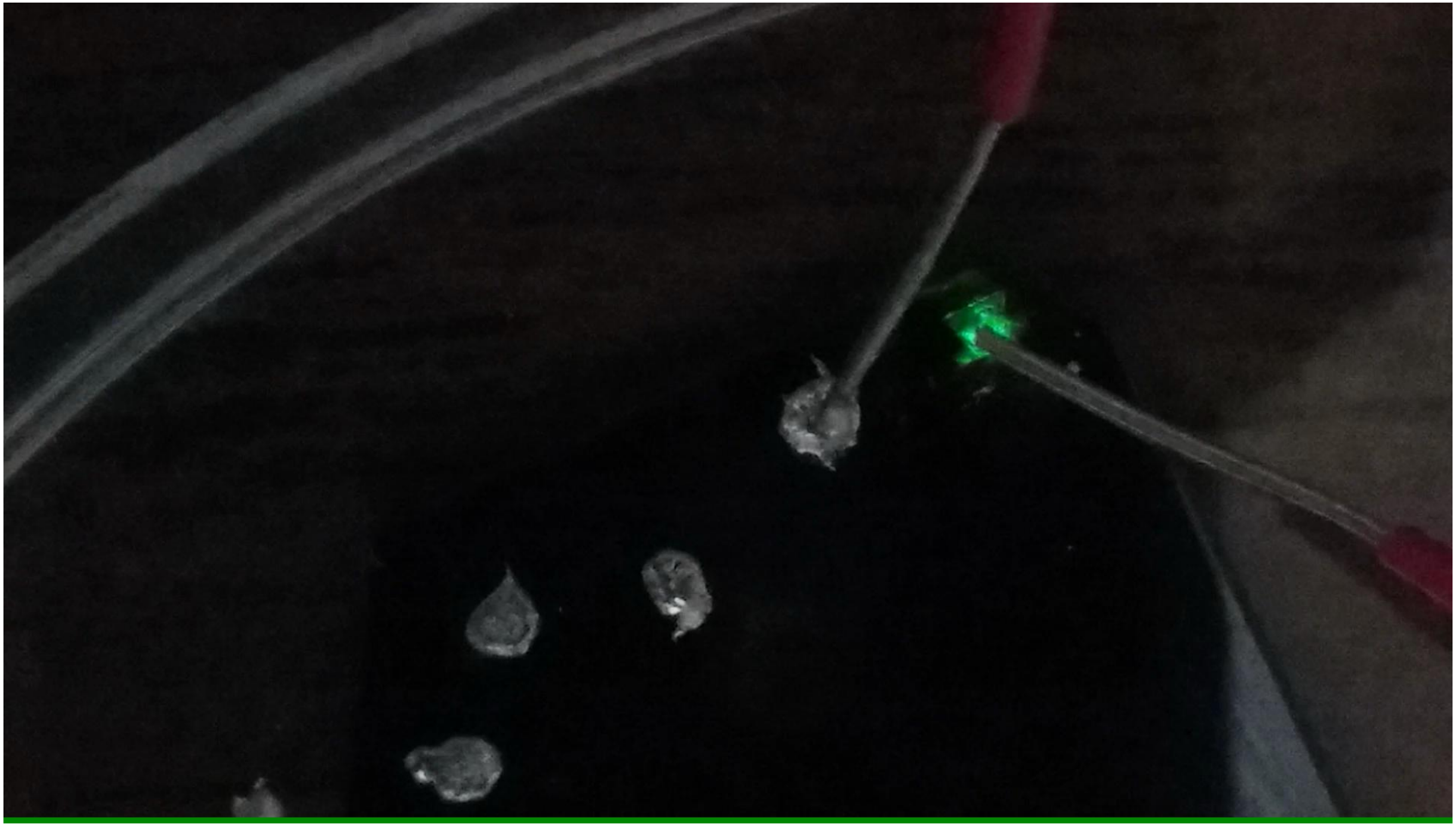
LED Research at Stanford:
InGaN/GaN MQWs for green LED on Si





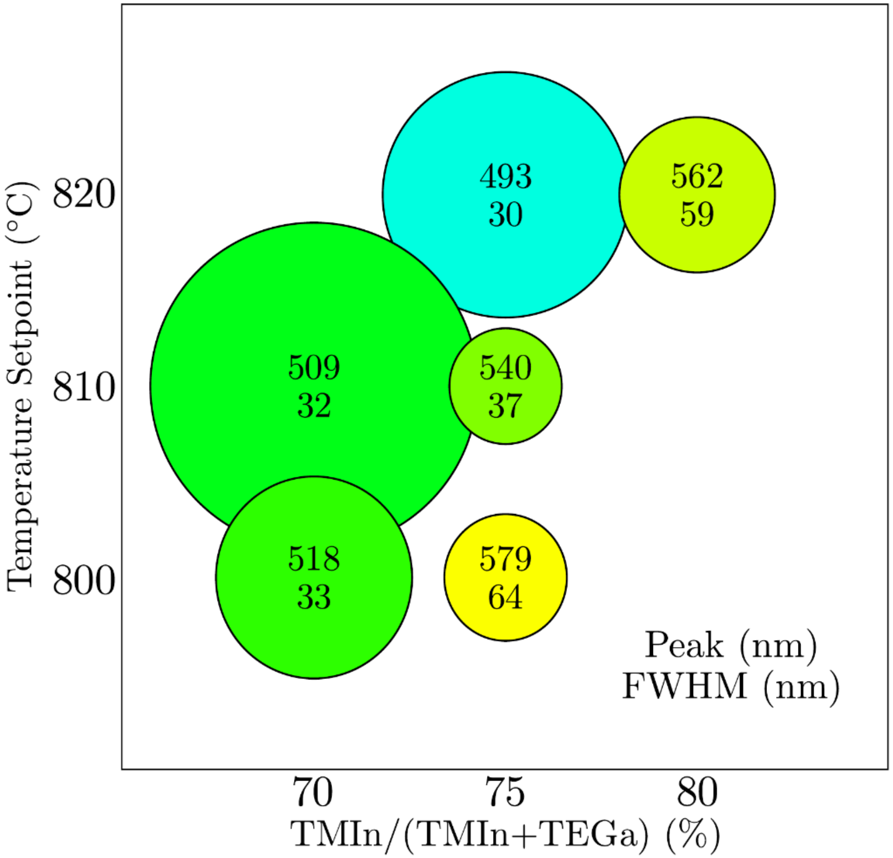
Ben Reeves and Ze Zhang, E241class report, Spring, 2018

Electroluminescence

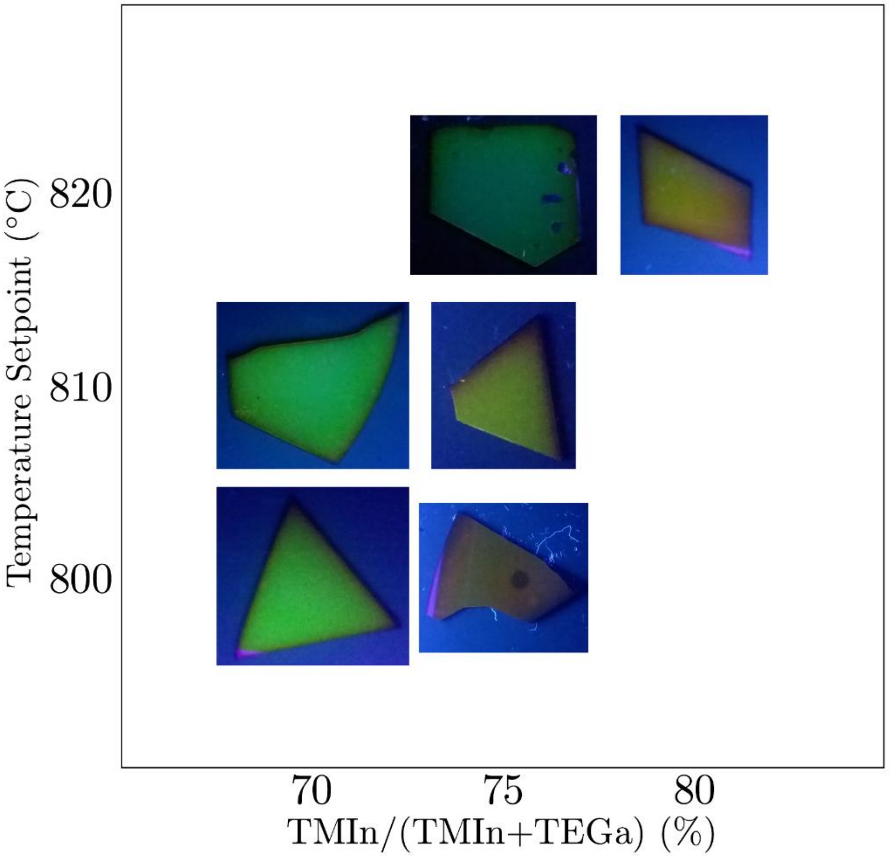


Ben Reeves and Ze Zhang, E241class report, Spring, 2018

Green LED color map



T-TMIn/III vs λ space for MQW LED Structures



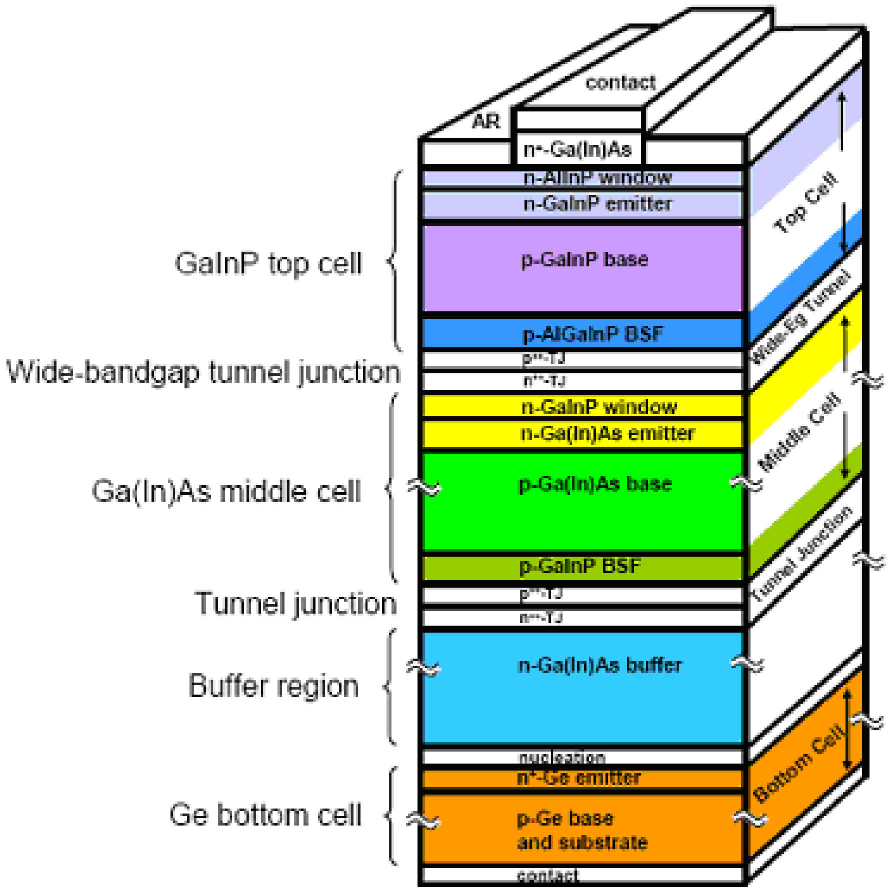
Photoluminescence at 365nm incidence

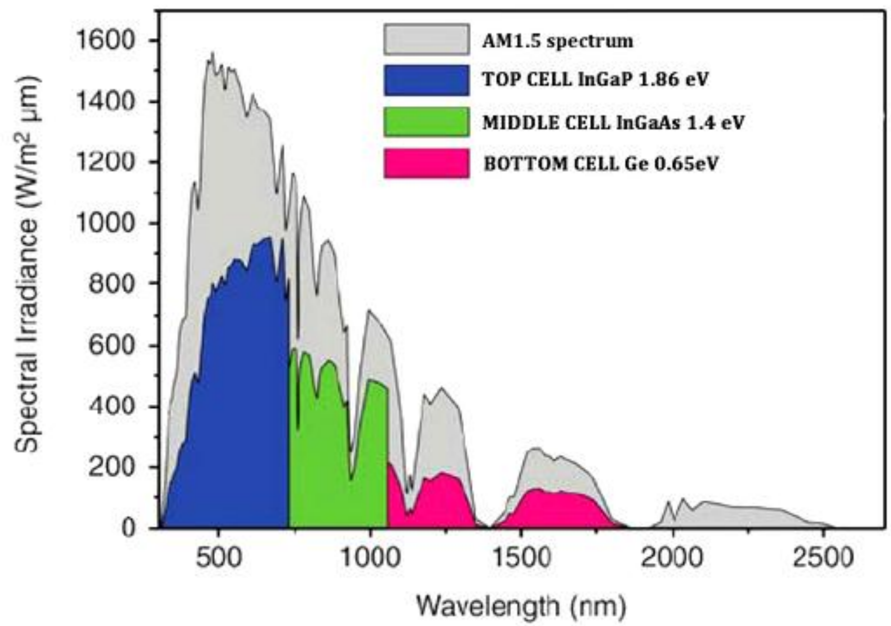
Ben Reeves and Ze Zhang,
E241class report, Spring, 2018

Outline

- **MOCVD introduction**
- **MOCVD enabled applications and related research at Stanford**
  - VCSEL (Vertical-Cavity Surface-Emitting Laser)
  - HEMT (High Electron Mobility Transistor)
  - Micro LED (Light Emitting Diode)
  - Solar energy conversion
- **Emerging substrate techniques**
  - GaN and GaAs substrate challenges
  - Research on re-use substrates

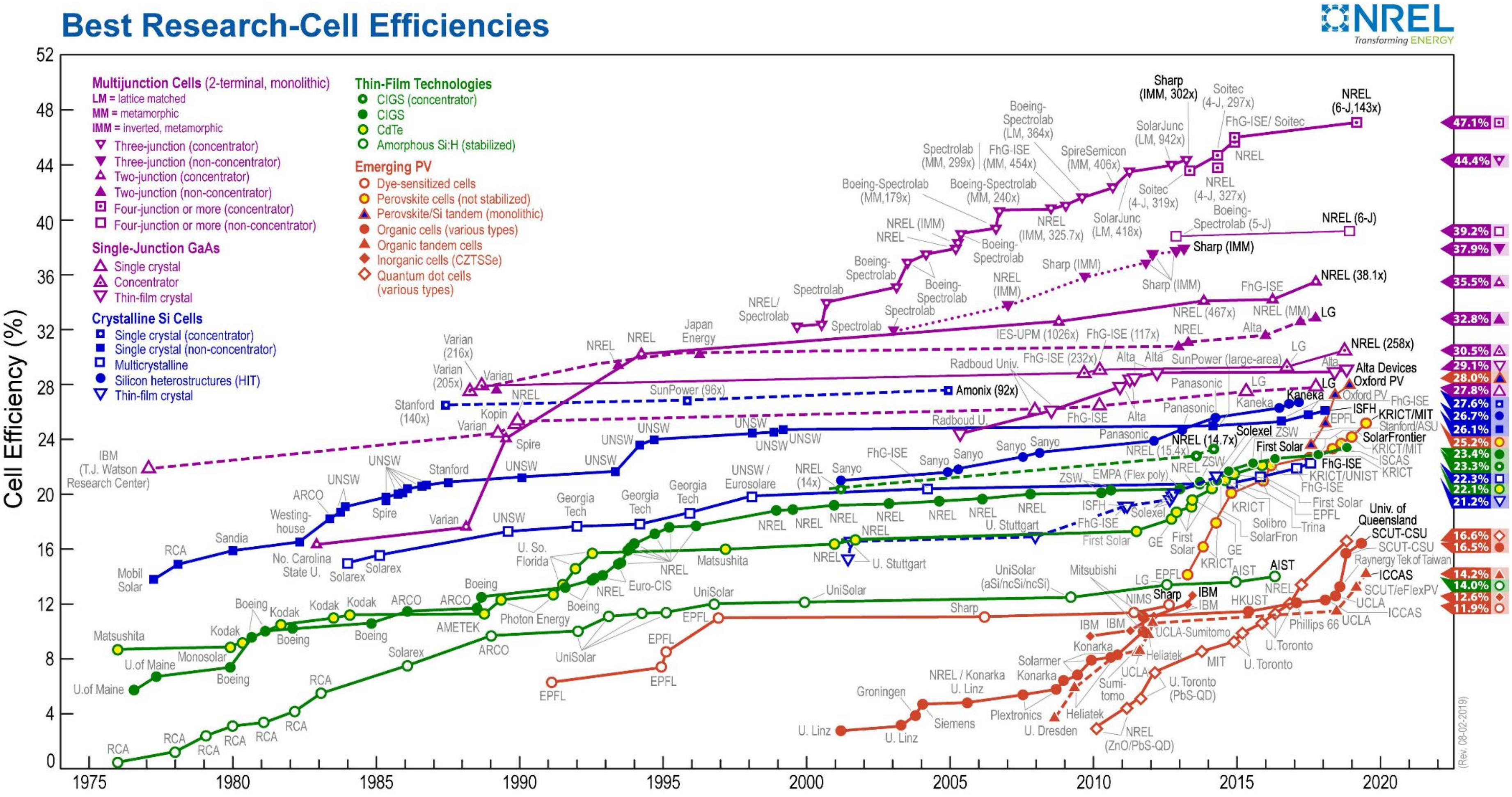
MOCVD hot field-4. Solar energy conversion

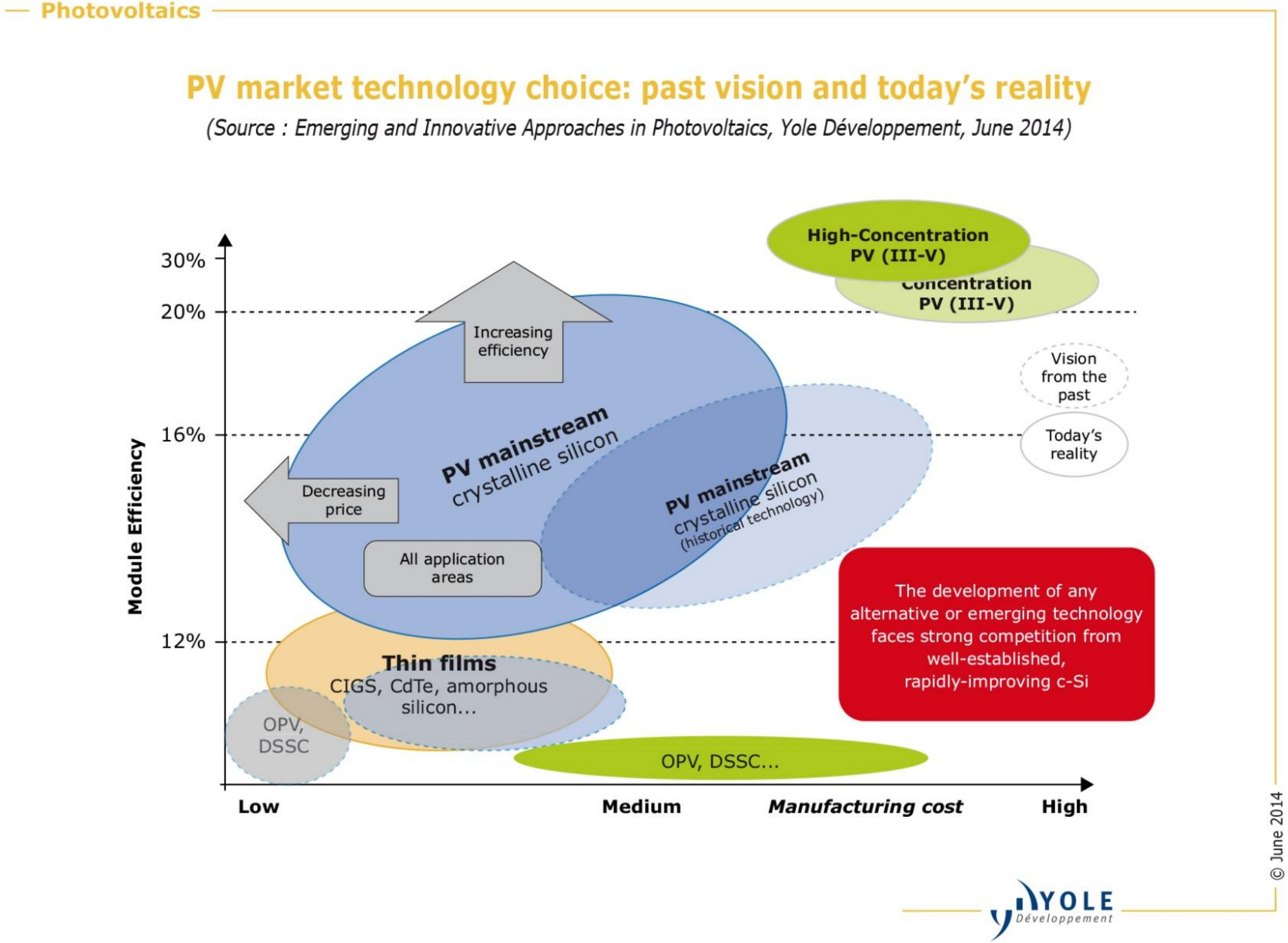




(b)

Natalya V. Yastrebova, Centre for Research in Photonics, University of Ottawa, April 2007, "High-efficiency multi-junction solar cells: Current status and future potential".


Best Research-Cell Efficiencies
NREL
Transforming ENERGY
Cell Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
LM = lattice matched
MM = metamorphic
IMM = inverted, metamorphic
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal (concentrator)
Single crystal (non-concentrator)
Multicrystalline
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
CIGS (concentrator)
CIGS
CdTe
Amorphous Si:H (stabilized)
Emerging PV
Dye-sensitized cells
Perovskite cells (not stabilized)
Perovskite/Si tandem (monolithic)
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells
(various types)
47.1%
44.4%
39.2%
37.9%
35.5%
32.8%
30.5%
29.1%
28.0%
27.8%
27.6%
26.7%
26.1%
25.2%
23.4%
23.3%
22.3%
22.1%
21.2%
16.6%
16.5%
14.2%
14.0%
12.6%
11.9%
1975
1980
1985
1990
1995
2000
2005
2010
2015
2020
(Rev. 08-02-2019)


Photovoltaics
PV market technology choice: past vision and today's reality
(Source : Emerging and Innovative Approaches in Photovoltaics, Yole Développement, June 2014)
High-Concentration PV (III-V)
Concentration PV (III-V)
30%
20%
16%
12%
Module Efficiency
Increasing efficiency
Decreasing price
PV mainstream crystalline silicon
All application areas
PV mainstream crystalline silicon (historical technology)
Vision from the past
Today's reality
The development of any alternative or emerging technology faces strong competition from well-established, rapidly-improving c-Si
Thin films CIGS, CdTe, amorphous silicon...
OPV, DSSC
OPV, DSSC...
Low
Medium
Manufacturing cost
High
© June 2014
YOLE Développement

Solar energy conversion research at Stanford:

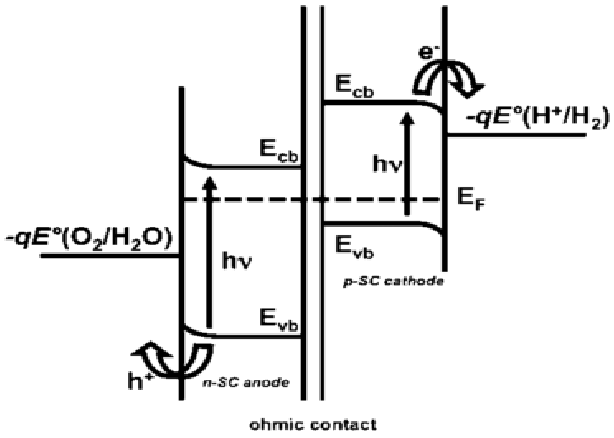
GaAs NW Array for Photoelectrochemical Water Oxidation

Photoelectrochemical (PEC) cells

- Sunlight in, fuel out → energy conversion & storage

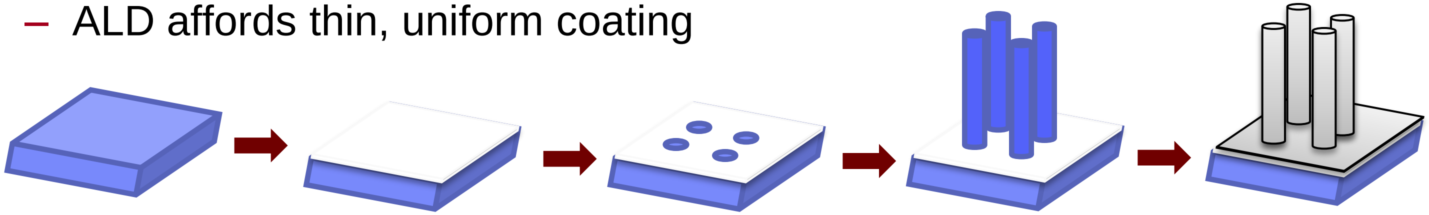
GaAs nanowires protected with ALD nickel oxide

- GaAs: high efficiency photovoltaic material
- Nanowires: large surface area and efficient light absorption
- Nickel oxide: electrocatalytically active protection layer
  - Ni-Fe oxides have some of the lowest reported overpotentials for OER
  - Low resistance and reflectivity
  - ALD affords thin, uniform coating

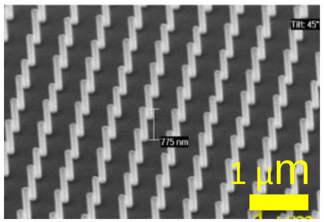


p/n-PEC (photoanode/cathode cell)

Adapted from Lewis et al., Chem Reviews 2010



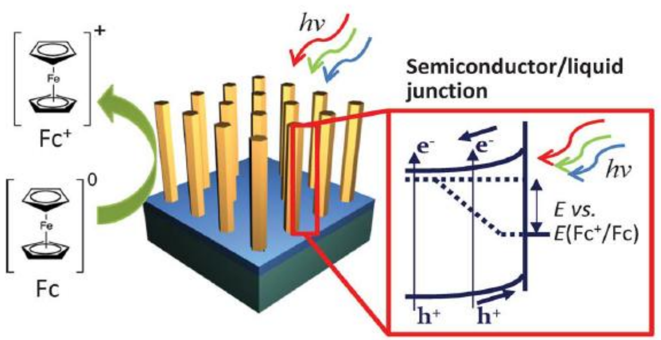
GaAs Substrate — SiO_2 Mask — Holes via E-beam lithography — GaAs NW via MOCVD — NiO Coating via ALD

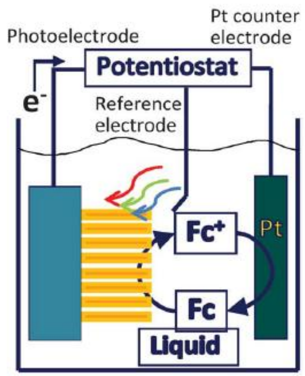


SEM image of GaAs NW

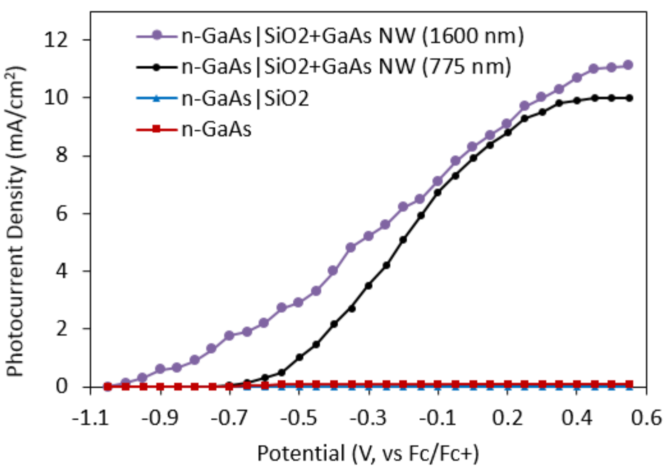
Non-aqueous measurement setup (no NiO coating)

- Non-corrosive environment and kinetically facile redox couple
- Current is generated when photon-induced minority charge carriers perform redox reactions at electrode surface





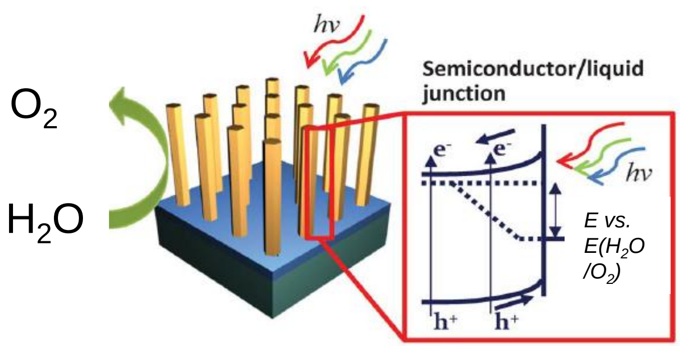
Adapted from Hu et al., Energy Environ. Sci. 2013



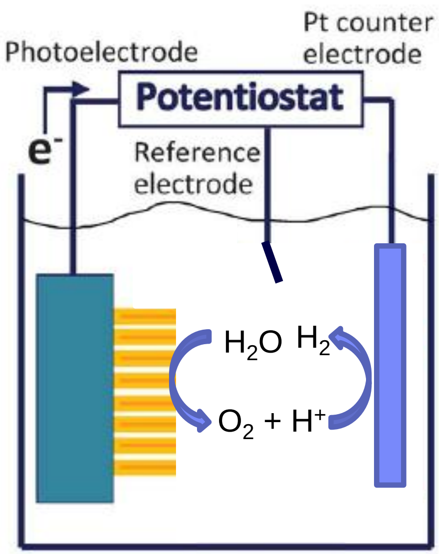
Joy Zeng*, Xiaoqing Xu* ,Vijay Parameshwaran*,
59th Electronic Materials Conference, June 2017, South Bend, Indiana

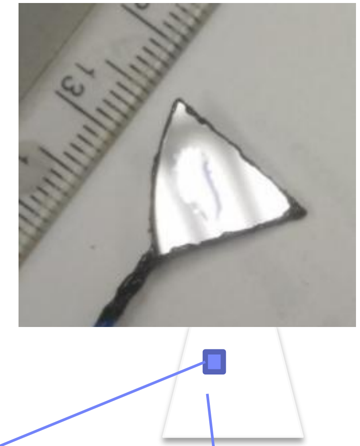
Aqueous (OER) measurement (36nm NiO coating)

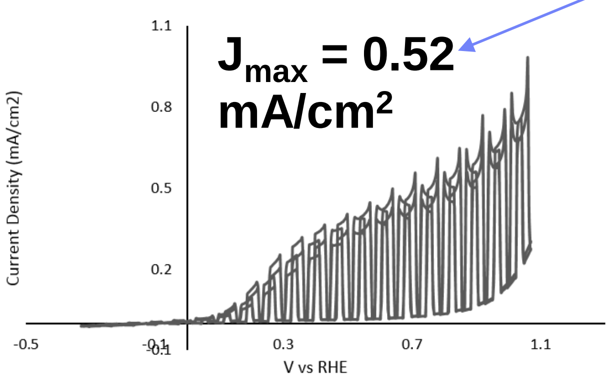
- Aqueous conditions - redox species are H_2O, H_2, and O_2

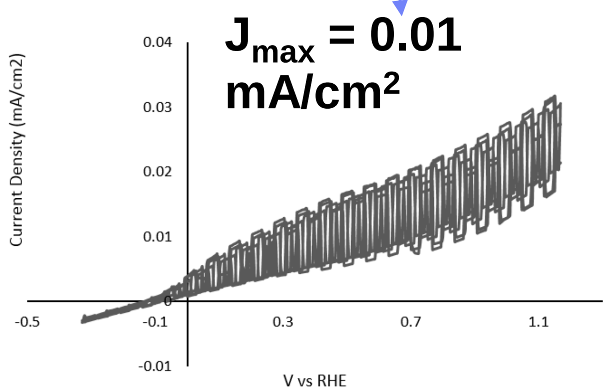


Adapted from Hu et al., Energy Environ. Sci. 2013









Joy Zeng*, Xiaoqing Xu* ,Vijay Parameshwaran*, 59th Electronic Materials Conference, June 2017, South Bend, Indiana

Yeah, these are great applications!

Bu….t, cost???

Substrate, epilayer growth, fabrication, package and testing…

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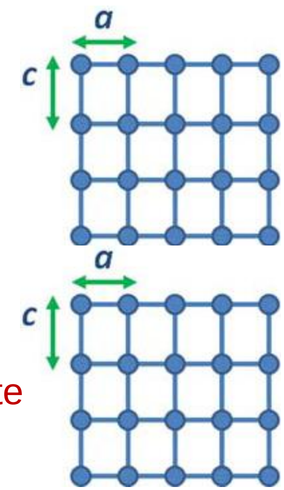
MOCVD/MOVP-*Epitaxy* Schematic

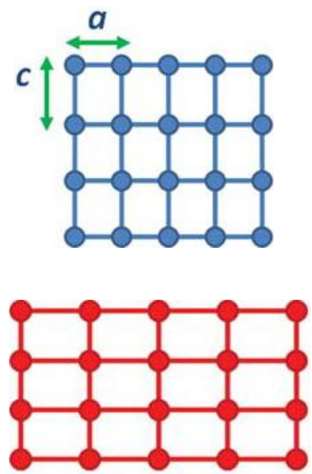
Homoepitaxy

Heteroepitaxy

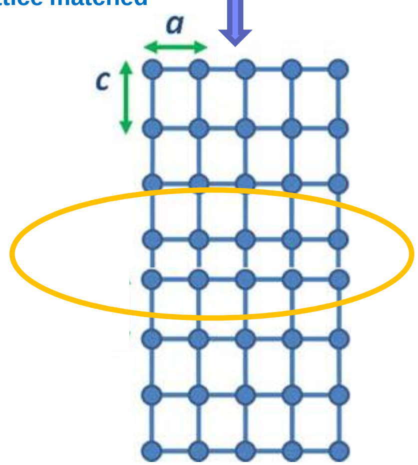
Epi-film

Substrate

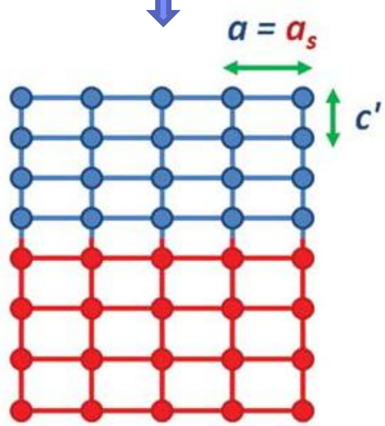




Lattice matched



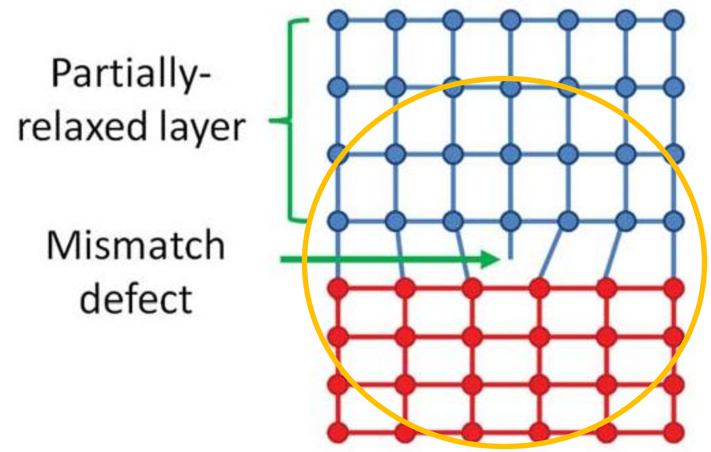
Strained



GaN on GaN

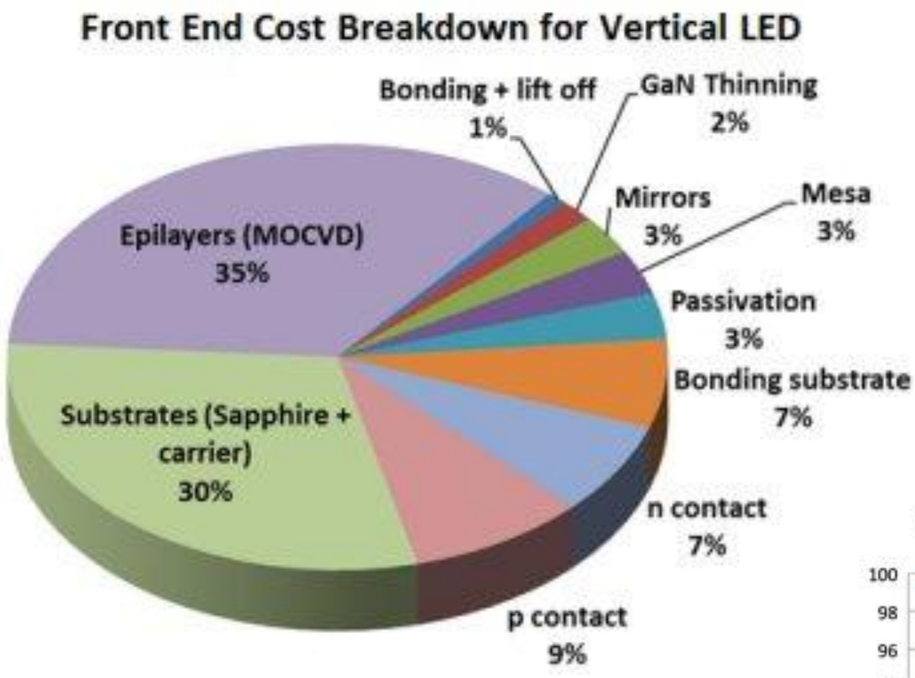
GaN on Sapphire

Defect (dislocation) form to relieve the strain

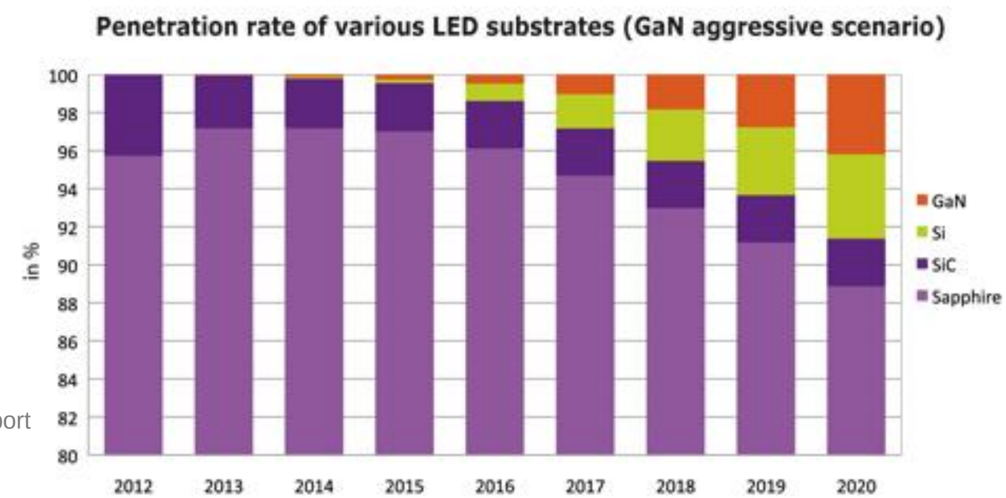


Adapted and modified from Muhammad Iqbal Bakti Utama, Nanoscale. 2013 May 7;5(9):3570-88

LED substrate cost

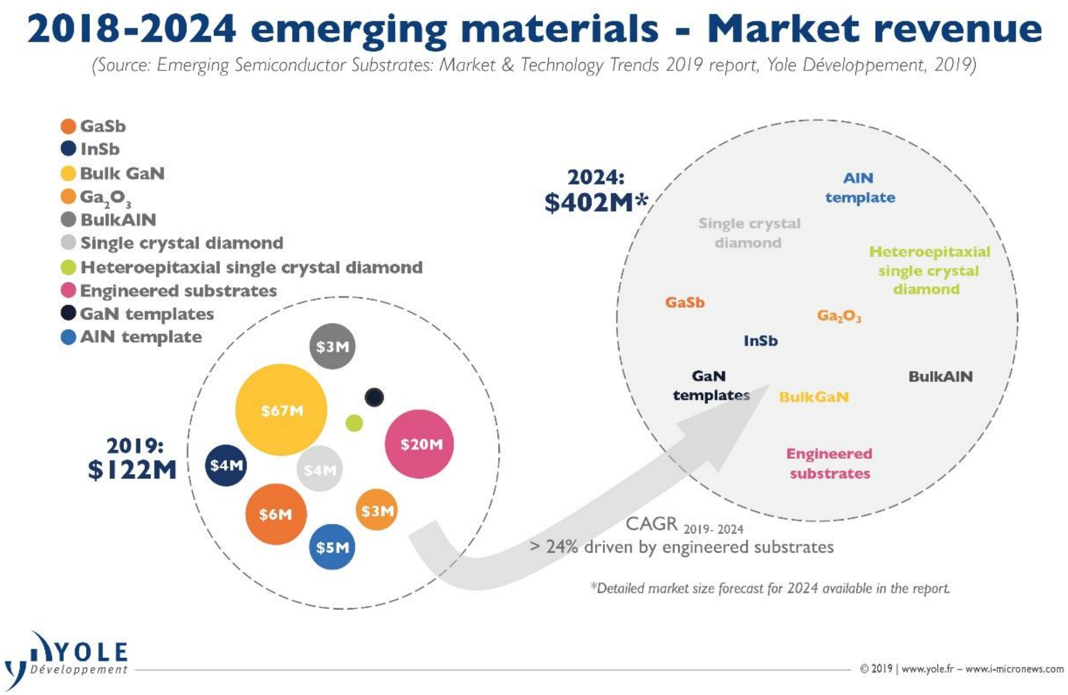


http://www.semiconductor-today.com/news_items/2012/JULY/YOLELEDFRONTEND_040712.html



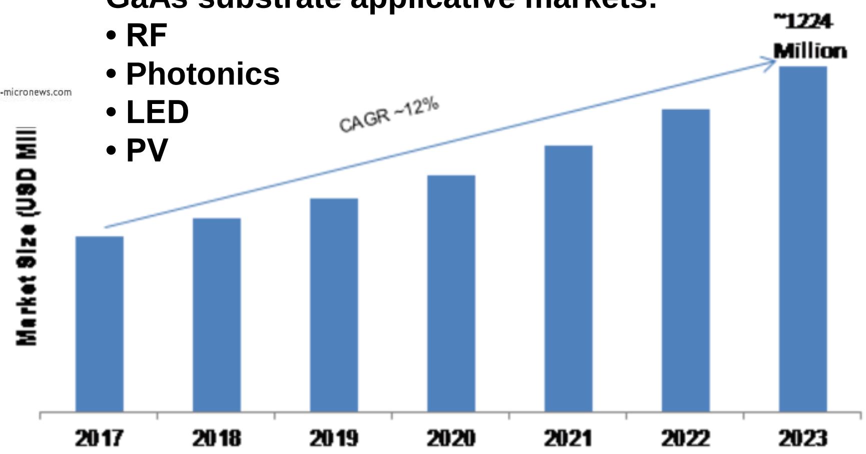
Yole_Bulk GaN_Penetration_rate_November_2013_Report

GaN and GaAs substrate in demand



GaAs substrate applicative markets:

- **RF**
- **Photonics**
- **LED**
- **PV**



Source: MRFR Analysis

Problems and possible directions

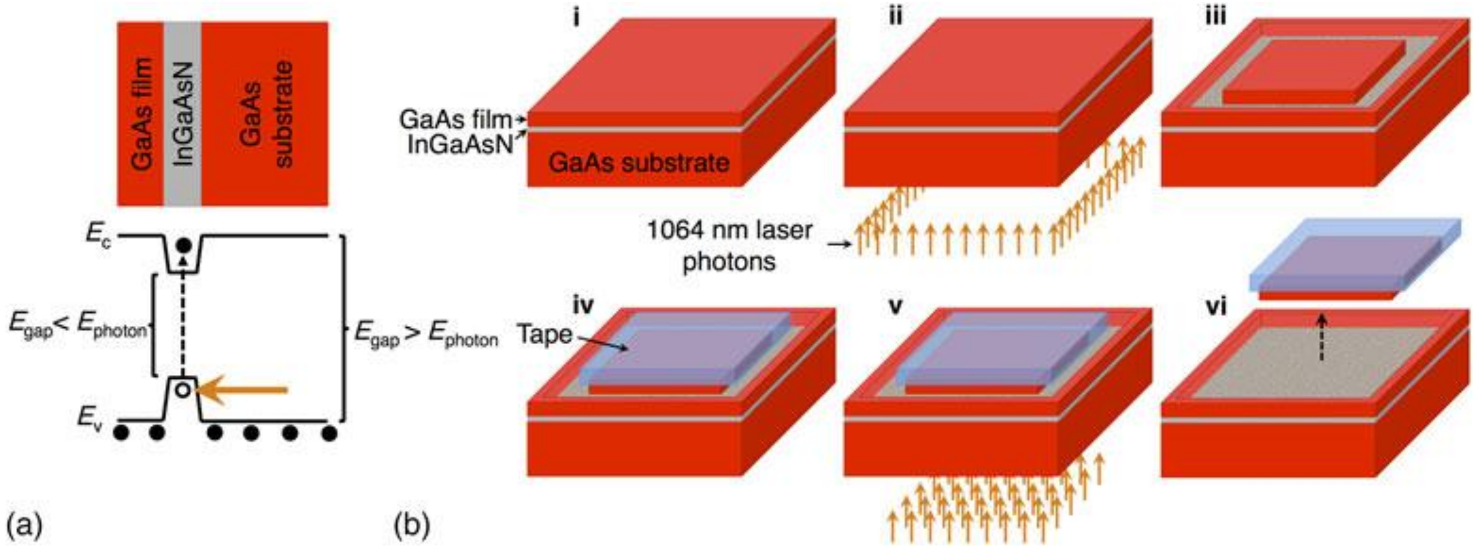
■**Homoepitaxy:** **Most bulk GaN techniques are immature and far from practical application; HVPE GaN is still too expensive; Bulk GaAs is also expensive, especially for low profit products like solar cell**

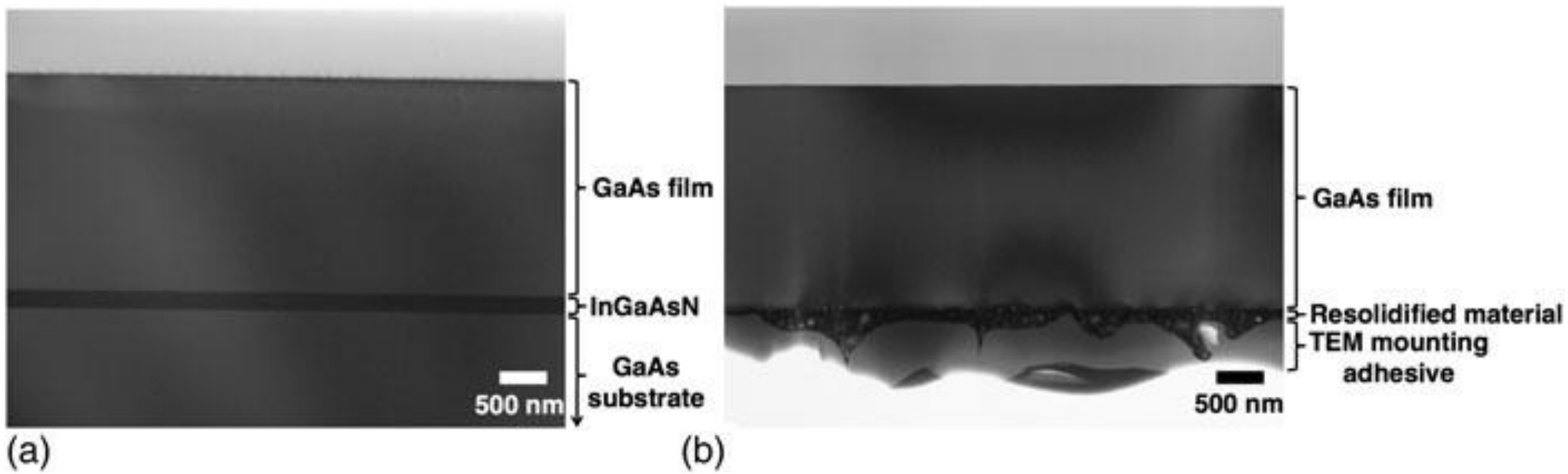
■**Heteroepitaxy:** **cheaper but sacrifice growth quality; still need scale up to reduce cost**

Possible directions

1. **Reuse GaN/GaAs substrates->Laser lift off, or remote epitaxy?**
Need suitable laser and low defect large scale bulk substrates
2. **Growth on cheaper substrate-> GaN/GaAs growth on Si?**
Need scale up, 8" and above
Need to improve growth quality on Si
3. **Breakthrough in bulk GaN technique-> Ammonothermal growth?**
Need larger diameter, 6" and above

Stanford substrate research: Laser liftoff of gallium arsenide thin films





Both as-grown and post-liftoff GaAs films are free of dislocations!

Garrett J. Hayes and Bruce M. Clemens, MRS Communications (2015), 5, 1–5

End of Talk

Thank you!

Questions?