MOCVD enables cutting-age applications

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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)

AIXTRON 200/4 III-V MOCVD
Temperature up to 800°C

AIXTRON CCS III-N MOCVD
Temperature up to 1300°C

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

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

Close Coupled Showerhead: The Concept
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.

Material capability of MOCVD
MOCVD/MOVPE Growth Mechanisms

GaN for example:

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

atomic step  surface diffusion and reaction  incorporation and growth

horizontal gas flow

boundary layer
mass transport to the surface by diffusion
precursor decomposition
adsorption
wafer surface

gas phase
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-\textit{Epitaxy} Schematic

Defect (dislocation) form to relieve the strain

Adapted and modified 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)

New sensor systems for extreme harsh environments
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MOCVD hot field-1 VCSEL

Structure diagram of VSCEL

Structure of DBR

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

Adam W. Bushmaker, IEEE Photonics Journal, 1504011, Vol. 11, No. 5, October 2019
VCSEL for mobile phone

VCSELs vs. LEDs, Edge Emitters

LED
- Incoherent
- Lambertian emission from all facets

VCSEL
- Coherent
- Symmetrical
- Low divergence optical beam
- No astigmatism
- Mirrors formed vertically during epi growth

EEL
- Coherent
- Elliptical, astigmatic optical emission
- Mirrors formed by cleaving and coating

All sources are grown by either MOCVD or MBE
VCSEL for Lidar

VCSEL Research at Stanford: GaAs based long wavelength VCSELS

Li Zhao, PhD thesis, Stanford University, 2019
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EPC’s GaN Power Transistor Structure

Scanning electron micrograph cross section of an eGaN FET

MOCVD hot field-2. HEMT
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 $\text{Al}_x\text{Ga}_{1-x}\text{N}$ barrier and (d) the thickness mapping of the full HEMT structure.
Wafer scale high uniformity

<table>
<thead>
<tr>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>Average (cm²/Vs)</th>
<th>Stdev%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_1 ) (cm²/Vs)</td>
<td>1205.7</td>
<td>1218.1</td>
<td>1217.8</td>
<td>1206.4</td>
<td>1230.6</td>
<td>--</td>
</tr>
<tr>
<td>( \mu_2 ) (cm²/Vs)</td>
<td>1210.5</td>
<td>1207.7</td>
<td>1206.6</td>
<td>1206.4</td>
<td>1226.2</td>
<td>--</td>
</tr>
<tr>
<td>( \mu ) (cm²/Vs)</td>
<td>1208.1</td>
<td>1212.9</td>
<td>1212.2</td>
<td>1206.4</td>
<td>1228.4</td>
<td>1213.6</td>
</tr>
</tbody>
</table>

Xiaoqing Xu et al., AIP Advances 6, 115016 (2016)
Degradation of 2DEG transport properties after 600 °C annealing

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.

HEMT Research at Stanford:

2. 3D inverted pyramidal AlGaN/GaN HEMT

SEM images of the inverted pyramidal silicon surfaces: (a) 40° 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.

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

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

Responsivity as a function of temperature (ultraviolet intensity of $3 \pm 0.1 \text{ mW/cm}^2$ and 1 V bias).

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MOCVD hot field-3. Micro LED

InGaN/GaN blue or green LED

AlGaInP/GaInP MQW red LED

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

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

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

(Source: LEDinside)
Micro LED process concept

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

### Layers and Thicknesses

<table>
<thead>
<tr>
<th>Layer Description</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>pp-GaN</td>
<td>100 nm</td>
</tr>
<tr>
<td>p-GaN</td>
<td></td>
</tr>
<tr>
<td>GaN QB</td>
<td></td>
</tr>
<tr>
<td>In$<em>x$Ga$</em>{1-x}$N QW</td>
<td>5×(3, 9) nm</td>
</tr>
<tr>
<td>GaN QB</td>
<td></td>
</tr>
<tr>
<td>n-GaN</td>
<td>1300 nm</td>
</tr>
<tr>
<td>Al$<em>{0.2}$Ga$</em>{0.8}$N</td>
<td>500 nm</td>
</tr>
<tr>
<td>Al$<em>{0.5}$Ga$</em>{0.5}$N</td>
<td>~300 nm</td>
</tr>
<tr>
<td>Al$<em>{0.8}$Ga$</em>{0.2}$N</td>
<td>~300 nm</td>
</tr>
<tr>
<td>HT-AlN</td>
<td>~300 nm</td>
</tr>
<tr>
<td>LT-AlN</td>
<td>~300 nm</td>
</tr>
<tr>
<td>(111) Si Substrate</td>
<td>20 nm</td>
</tr>
</tbody>
</table>

*Image details:*

- 2.5 nm feature
- 9 nm feature

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*Ben Reeves and Ze Zhang, E241 class report, Spring, 2018*
Electroluminescence
Green LED color map

T-TMIn/III vs $\lambda$ space for MQW LED Structures

Photoluminescence at 365nm incidence

Ben Reeves and Ze Zhang,
E241 class report, Spring, 2018
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MOCVD hot field-4. Solar energy conversion

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

- Multijunction Cells (2-terminal, monolithic)
  - LM = lattice matched
  - IM = inverted, metamorphic
  - Three-junction (non-concentrator)
  - Two-junction (concentrator)
  - Two-junction (non-concentrator)
  - Four-junction or more (concentrator)
  - Four-junction or more (non-concentrator)

- 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)

- 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

- Cell Efficiency (%)
PV market technology choice: past vision and today’s reality

(Source: Emerging and Innovative Approaches in Photovoltaics, Yole Développement, June 2014)
Solar energy conversion research at Stanford: GaAs NW Array for Photoelectrochemical Water Oxidation

Photoelectrochemical (PEC) cells

- Sunlight in, fuel out $\rightarrow$ 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

Adapted from Lewis et al., Chem Reviews 2010
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

Aqueous (OER) measurement (36nm NiO coating)

- Aqueous conditions - redox species are H₂O, H₂, and O₂


Adapted from Hu et al., Energy Environ. Sci. 2013
Yeah, these are great applications!
But... cost???
Substrate, epilayer growth, fabrication, package and testing...
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MOCVD/MOVP- *Epitaxy* Schematic

Homoepitaxy

Heteroepitaxy

Defect (dislocation) form to relieve the strain

GaN on GaN

GaN on Sapphire

- Lattice matched
- Strained
- Partially-relaxed layer
- Mismatch defect

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


Yole_Bulk_GaN_Penetration_rate_November_2013_Report
GaN and GaAs substrate in demand

2018-2024 emerging materials - Market revenue

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!
End of Talk

Thank you!

Questions?