Materials Design for Long-Wavelength LEDs

Chris G. Van de Walle
Materials Department, University of California, Santa Barbara

Acknowledgments:
Cyrus Dreyer (Stony Brook University)
Darshana Wickramaratne,
John Lyons (Naval Research Laboratory)
Jimmy-Xuan Shen (Lawrence Berkeley National Lab.)
Anderson Janotti (University of Delaware)
Audrius Alkauskas (Ctr. f. Phys. Sci. &Tech., Lithuania)
Qimin Yan (Temple University)
Nicholas Adamski, Jim Speck (UCSB)

DOE, NSF, ARO, AFOSR
The work was supported by the grant DE-SC0010689 funded by the U.S. Department of Energy, Office of Science.

2019 SSL R&D Workshop
Dallas/Fort Worth, Texas
January 29, 2019
Nitride semiconductors for solid-state lighting

Efficiency
Nonradiative: Auger

Nonradiative: Defect-assisted

Radiative
“ABC model” for internal quantum efficiency of LEDs

Defect-assisted: \( R = An \)
Radiative: \( R = Bn^2 \)
Auger: \( R = Cn^3 \)

“Shockley-Read-Hall”

\[ \eta = \frac{Bn^2}{An + Bn^2 + Cn^3} \]
Internal quantum efficiency: IQE

\[ \text{IQE} = \frac{Bn^2}{An + Bn^2 + Cn^3} \]

David and Grundmann, APL 96, 103504 (2010).
Outline

• Identifying loss mechanisms
  – Theory, computations, experiment
• Examples: nitrides (blue and green)
• Longer wavelengths
  – Existing materials
  – New materials
Loss mechanisms: high carrier density, $\sim n^3$

Auger recombination

$$R = Cn^3$$
Direct & Indirect Auger recombination

Carrier scattering by:

- Electron-phonon
- Alloy scattering
- Charged defects

Bulashevich & Karpov, pssc (2008)
Auger Recombination in GaN and InGaN

Auger Recombination in GaN and InGaN

First-principles calculations
- Density-functional theory
- Hybrid functional for correct electronic structure
- Full treatment of phonons and electron-phonon interactions

The Smoking Gun:
Direct observation of Auger electrons


Justin Iveland,1 Lucio Martinelli,2 Jacques Peretti,2 James S. Speck,1 and Claude Weisbuch1,2,*
Droop vs. device band gap

Internal quantum efficiency

\[ \eta = \frac{Bn^2}{An + Bn^2 + Cn^3} \]

Carrier density (cm\(^{-3}\))
Auger recombination

Extend first-principles treatment of Auger recombination to lower-gap semiconductors

Build deeper understanding of the mechanisms that govern Auger recombination by investigating other materials.

GaN, GaAs, InAs.

K. A. Bulashevich and S. Y. Karpov, 
phys. stat. sol. (c) 5, 2066 (2008).
Calculated Auger rate coefficients in GaAs-based alloys

Experiment 3-11 \times 10^{-30} \text{cm}^6\text{s}^{-1} \ [\text{Strauss et al., APL 62, 55 (1993)}]

Auger recombination in InAs

- Spin-orbit splitting enhances Auger

- experimental values: $10^{-27} - 10^{-26} \text{ cm}^6\text{s}^{-1}$

General theory of Auger recombination

- GaN: indirect Auger dominates
- GaAs: phonon-assisted and direct Auger recombination of similar strength
- InAs: direct Auger dominates

Auger recombination in red LEDs

- Auger recombination is as strong in red light emitters as it is in green
- But easily addressed in devices: increase the volume of the active layer!
  - More QWs
  - Wider QWs
- Lower carrier density → less impact of Auger

Shockley-Read-Hall (SRH), Auger

\[ R = An \]

\[ R = Cn^3 \]

Loss: max IQE

Loss: “Droop”
Shockley-Read-Hall recombination: Microscopic mechanisms largely unknown

- What are the mechanisms?
- What defects/impurities are responsible?
- What are the rates?
Radiative and nonradiative capture
Shockley-Read-Hall: nonradiative capture of carriers by defects

- First step to understand SRH: Calculate rate of nonradiative capture at defects
- Given by:
  - Defect density $N_D$, $N_A$
  - Carrier density $n, p$
  - Capture coefficient $C_p$, $C_n$
- Capture coefficient gives rate of capture of one carrier at one defect in a volume $V$: $C_{n/p} = V r$
- Capture due to change in electronic state due to electron-phonon coupling
Results: Hole capture at $C_N$ in GaN

For efficient Shockley-Read-Hall recombination need both fast electron \textit{and} hole capture.
Shockley-Read-Hall

- Need both
  - fast capture of electrons
  - fast capture of holes


- Gallium vacancies
  - Introduce midgap levels
  - But: high formation energy
  - Complexes with
    » Oxygen
    » Hydrogen

$V_{Ga-O_N-2H}$ complex
$V_{Ga-O_N-2H}$ complex

**In GaN:**
- $(+/0)$ defect level at $\sim 1.0$ eV above the valence band
  - fast hole capture
  - slow electron capture

**In InGaN:**
- Smaller gap
- Defect level closer to the conduction band
  - Increases rate of electron capture
$V_{Ga-O_N-2H}$ complex

- **SRH coefficient $A$:**
  
  \[ A \approx N C_n \]
  
  - Assume $N=10^{16}$ cm$^{-3}$
  - $n=10^{18}$ cm$^{-3}$

- **Radiative versus nonradiative recombination:**
  
  - Defect-assisted recombination rate becomes of same magnitude as radiative recombination rate if $A=10^7$ s$^{-1}$
  - 2.4 eV (green) or below: significant defect-assisted nonradiative recombination
High levels of calcium in MBE InGaN

Likely source: calcium contamination due to substrate wafer polishing
- Also observed in GaInNAs

Examined various configurations
- Ca_Ga most favorable in n-type material
Calcium is detrimental to green and yellow LEDs
Shockley-Read-Hall in InGaN

• SRH rate is governed by slower of electron or hole capture process
  – Electron capture coefficient $C_n$ decreases exponentially with distance from the conduction band.
  – Hole capture coefficient $C_p$ decreases exponentially with distance from the valence band.

• Most efficient centers: level near midgap.

\[ R_{SRH} = nN \frac{C_n C_p}{C_n + C_p} \]

$n$: carrier density, $N$: defect density
Transition-metal impurities

- In conventional semiconductors: recognized as “killer centers”
- Have received scant attention in nitrides
  - Fe level is 0.5 eV below CBM
  - Far from midgap → assumed not to lead to SRH recombination
- But experimental evidence of rapid recombination for both electrons and holes!

- DLTS [A. Polyakov et al., J. Appl. Phys. 93, 5388 (2003)]
- Calculations [D. Wickramaratne et al., Appl. Phys. Lett. 109, 162107 (2016).]
Iron impurities in GaN

Fe-doped GaN buffer in nitride HEMTS

Stainless steel HVPE reactors

Fe is introduced intentionally and unintentionally during the growth of GaN devices.

How to explain high recombination rates?

Take excited states into account!

Al₂O₃ components of reactors

Fe₂O₃ is a contaminant in Al₂O₃; reduction of Fe₂O₃ can occur in presence of Ga during growth

Excited states

<table>
<thead>
<tr>
<th></th>
<th>Calculated (cm³s⁻¹)</th>
<th>Experiment (cm³s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron capture</td>
<td>1.1x10⁻⁸</td>
<td>5.5x10⁻⁸</td>
</tr>
<tr>
<td>Hole capture</td>
<td>7.1x10⁻⁸</td>
<td>1.8x10⁻⁸</td>
</tr>
</tbody>
</table>

T=300K

So what about long wavelength?

“Green gap”

Efficiency decreases
– going to longer $\lambda$ with nitrides
– going to shorter $\lambda$ with phosphides

So what about long wavelength?

“Green gap”

Efficiency decreases
- going to longer $\lambda$ with nitrides
- going to shorter $\lambda$ with phosphides

On the nitrides side:
- Higher In content
  $\rightarrow$ lattice mismatch
  $\rightarrow$ strain
  $\rightarrow$ phase separation, point-defect formation

- Address:
  » Virtual substrates
  » Novel substrates?
  » New materials

Band gaps of ZnGeN\(_2\) and ZnSnN\(_2\) span visible spectrum; lattice mismatch less than 7% (lower than 12% mismatch between GaN & InN)

The replacement of one group-III element (Ga) with \textit{two} group-IV elements (e.g., Zn and Ge) opens up a whole new design space.

Group-II elements could be Zn, Cd, Be, Mg. Group-IV elements could be Si, Ge, Sn.
Zn-IV-Nitrides

- Potential for band-gap engineering and polarization engineering
- But... growth is challenging
  - Tendency for antisite disorder
  - Doping control difficult
  - Would benefit from more systematic experimental studies


Prior work:
So what about long wavelength?

“Green gap”

Efficiency decreases
- going to longer $\lambda$ with nitrides
- going to shorter $\lambda$ with phosphides

On the phosphides side:
- AlGaInP
- Internal quantum efficiency has been studied in less detail than in nitrides
- Efficiency of red not a pressing issue for traditional applications; but crucial for (micro)displays and for RGB solid-state lighting

Phosphides

- **Green gap**
  - Carrier confinement becomes problematic for AlGaInP at higher energies (max direct gap is 2.33 eV)

![Diagram showing bandgap energy and corresponding wavelength versus lattice constant of (Al\(_x\)Ga\(_{1-x}\))\(_y\)In\(_{1-y}\)P at 300 K. The dashed vertical line shows (Al\(_x\)Ga\(_{1-x}\))\(_y\)In\(_{1-y}\)P lattice matched to GaAs (adopted from Chen et al., 1997).](image-url)
Quantum efficiency decreases at lower currents
Regime where Shockley-Read-Hall more important
A coefficient increases towards green
» Shockley-Read-Hall or other effects?

Defect-assisted recombination mechanisms

Multi-phonon emission

Impurity Auger
New materials?

- **II-IV-phosphides, II-IV arsenides**
  - Review:
    A. D. Martinez, A. N. Fioretti, Eric S. Toberer, and A. C. Tamboli,
Scandium

Periodic Table of the Elements

Atomic masses in parentheses are those of the most stable or common isotope.
New materials?...

• **II-IV-phosphides, II-IV arsenides**
  
  – Review:

• **Incorporate scandium?**
  
  – Scandium: the “other” group-III element, at the start of the transition metals
  – Recent work on ScAlN
  – ScP: rocksalt structure. But low-Sc alloys with GaP or AlP would be zincblende.
Summary

• First-principles calculations:
  – Quantitative results
  – + insights in physics
• Progress in methodology
• Recombination mechanisms
• Re-examine current materials
• Explore new materials

References: