First-principles studies of recombination mechanisms in light emitters

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“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: Experimental

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

Will illustrate with GaN, but concepts and methodologies are general
Loss mechanisms: Auger

\[ R = C n^3 \]

“Droop”
Auger Recombination in GaN and InGaN

Theory ($T=300$ K, 2.5 eV):

$C \approx 10^{-30}$ cm$^6$s$^{-1}$

Experiment:

$3.5 \times 10^{-31} - 2.0 \times 10^{-30}$ cm$^6$s$^{-1}$


Shockley-Read-Hall (SRH), Auger

Loss: max IQE

\[ R = An \]

Loss: “Droop”

\[ R = Cn^3 \]
Shockley-Read-Hall recombination: Microscopic mechanisms still unknown

- What are the mechanisms?
- What defects/impurities are responsible?
- What are the rates?
Computational Methods

- Density functional theory (DFT), VASP
- Traditional functionals (LDA, GGA): “Band-gap problem”
  - makes quantitative predictions difficult
- Hybrid functional (HSE)
  - Includes a fraction of screened Hartree-Fock exchange
  - Accurate structural parameters, band gaps
  - Accurate prediction of defects
    - formation energies
    - transition levels

Configuration Coordinate diagram

Charge state $D^0$ has different atomic configuration from $D^{+1}$.
Configuration Coordinate diagram

Electron capture

$D^{+1} + e^- + h^+$

$D^0 + h^+$

$D^{+1}$

$\Delta E$

Energy

Generalized coordinate $Q$

CBM

(+1/0)

VBM

$E_g$
Configuration Coordinate diagram

Energy

Generalized coordinate $Q$

$D^0 + h^+$

$D^+ + e^- + h^+$

$D^+ - 1$

$\Delta E$

Hole capture

CBM

(+1/0)

VBM

$E_g$

Configuration Coordinate diagram from first principles

C. E Dreyer et al., APL 108, 141101 (2016).
Configuration Coordinate diagram from first principles

Transition from +1 to 0 charge state: combination of QM tunneling and thermal (phonon-assisted) transition

C. E Dreyer et al., APL 108, 141101 (2016).
Nonradiative capture coefficient from Fermi's golden rule

\[ C_n = \frac{2\pi\Omega}{\hbar} g \sum_m w_m \sum_n \left| \Delta H_{im;fn}^{e-ph} \right|^2 \delta(E_{im} - E_{fn}) \]

\[ \Delta H_{im;fn}^{e-ph} = \sum_k \langle \psi_i | \partial \hat{H} / \partial Q_k | \psi_f \rangle \langle \chi_{im} | Q_k - Q_{0;k} | \chi_{fn} \rangle \]

\( W_{ij} \) Electron-phonon coupling

Overlap between vibronic states

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.

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

\( r \): carrier density, \( N \): defect density
Shockley-Read-Hall in InGaN

• Identify plausible recombination centers
  – Point defects
  – Impurities

• 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
• SRH coefficient $A$
  Assume $N=10^{16}$ cm$^{-3}$, $n=10^{18}$ cm$^{-3}$, $T=120^\circ$C
• Radiative versus nonradiative recombination:
  – SRH 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
• Impurities can also cause SRH!

C. E. Dreyer et al., APL 108, 141101 (2016).
Summary

• First-principles calculations:
  – Quantitative results + insights in physics
• Progress in methodology
• Nonradiative recombination

References: