Sources of Shockley-Read-Hall recombination in III-nitrides

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GaN, InN, AlN are key materials for light emitting diodes (LEDs)

UCSB SSLEC, 2012

Cree.com

hardware-360.com
III-nitrides in power electronics to reduce conversion loss
III-nitrides in power electronics to reduce conversion loss

www.transphorm.com
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GaN power electronics
Motivation: improve the efficiency of light emitters
Carriers recombine across the band gap to emit light in LEDs
Shockley-Read-Hall: Recombine at a defect, no light emitted
Goal: Use first-principles calculations to determine the microscopic mechanisms responsible for Shockley-Read-Hall
Outline

• **Shockley Read Hall from first principles**
  – Calculation of defect levels
  – Carrier capture mechanisms and rates

• **SRH in InGaN alloys**
  – What is the mechanism?
  – Green and yellow alloys
  – Blue and violet alloys
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What is the nature of these defect levels and how do we calculate them?
Consider a point defect:
Consider a donor-type defect:
Carrier capture changes charge state of defect
Formation energy

\[ E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}} \]

Formation energy

\[ E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}} \]

- Calculations: \( E_{\text{tot}} \), electrostatic correction
- Variables: \( E_F, \mu_i \)

Computational details

- Density functional theory
- HSE hybrid functional
  
  
  - Band gaps
  - Localized defect states
- PAW pseudopotentials in VASP
  

- Norm-conserving pseudopotentials in CPMD
  
Formation energy depends on Fermi level

\[ E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}} \]
Formation energy depends on Fermi level

\[ E_f^X = E_{\text{tot}}^X - E_{\text{tot}}^\text{bulk} - \sum_i n_i \mu_i + qE_F + E_{\text{corr}} \]
Formation energy depends on Fermi level

\[ E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}} \]
Charge-state transition levels correspond to "defect levels"

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Carrier capture rate depends on capture coefficients.

\[ R_n = C_n N^+ n \]  
\[ R_p = C_p N^0 p \]
Carrier capture rate depends on capture coefficients

\begin{align}
(1) \quad R_n &= C_n N^+ n \\
(2) \quad R_p &= C_p N^0 p
\end{align}

Units: \([R_n/p] = \text{cm}^{-3}\text{s}^{-1}\)
Carrier capture rate depends on capture coefficients.

(1) $R_n = C_n N^+ n$

Units: $[C_{n/p}] = \text{cm}^3 \text{s}^{-1}$

(2) $R_p = C_p N^0 p$
Recombination rate depends on slower capture process

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

W. Shockley and W. T. Read, Phys. Rev. 87, 835 (1952)
R. N. Hall, Phys. Rev. 87, 387 (1952)
Capture can occur radiatively or nonradiatively.
Nonradiative processes are relevant for SRH.

Radiative capture is slow.
Atomic structure included using configuration coordinate diagram
Atomic structure included using configuration coordinate diagram
“Vibronic” wavefunctions obtained from CC diagram
Adding electron hole pair increases energy by $E_g$
Different charge state of defect has different equilibrium $Q$. 

The diagram illustrates the energy levels for different charge states of a defect. The energy levels are labeled as $D^{0}+h^{+}$, $D^{+1}+e^{-}+h^{+}$, and $D^{+1}$. The change in energy between these states is denoted by $\Delta E$. The diagram also shows the conduction band maximum (CBM) and the valence band maximum (VBM) with $E_{g}$ representing the bandgap.
Nonradiative capture at a defect occurs by multiphonon emission

Nonradiative capture coefficient from Fermi's golden rule

\[ C_n = \frac{2\pi \Omega}{\hbar} g \sum_m w_m \sum_n |\Delta H_{i,m;f,n}^{e-ph}|^2 \delta(E_{i,m} - E_{f,n}) \]
Linear coupling approximation

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

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

\( W_{if} \), Electron-phonon coupling

Overlap between vibronic states

1D approximation

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

\[ \Delta H_{im; fn}^{e-ph} \approx \sum_k \langle \psi_i | \partial \hat{H} / \partial Q | \psi_f \rangle \langle \chi_{im} | Q - Q_0 | \chi_{fn} \rangle \]
1D approximation

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

\[ \Delta H_{im;fn}^{e-ph} \approx \sum_k \langle \psi_i | \partial \hat{H} / \partial Q | \psi_f \rangle \langle \chi_{im} | Q - Q_0 | \chi_{fn} \rangle \]

Special 1D configuration coordinate

- Linear interpolation between equilibrium geometries of charge states of defect
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GaN, InN, AlN are key materials for light emitting diodes (LEDs)
Goal: Predict defects responsible for SRH recombination in green LEDs
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SRH rate from experiment: ABC model

\[ R = A n \]

\[ R = B n^2 \]

\[ R = C n^3 \]

\[ \eta = \frac{B n^2}{A n + B n^2 + C n^3} \]
ABC model fits internal quantum efficiency

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

David and Grundmann, APL 96, 103504 (2010).
ABC model fits internal quantum efficiency

\[ \eta = \frac{B n^2}{A n + B n^2 + C n^3} \]

\( A \sim 10^{6} - 10^{8} \text{ s}^{-1} \)

\( A n \sim 10^{24} - 10^{26} \text{ s}^{-1} \text{ cm}^{-3} \)
Defects responsible for SRH in GaN must capture carriers nonradiatively.
Capture coefficients depend exponentially on classical “barriers”

\[ C_{\{n,p\}} \approx C_0 + C_1 e^{\frac{-\Delta E_b}{k_B T}} \]
Capture coefficients depend exponentially on classical “barriers”

\[
C_{\{n,p\}} \approx C_0 + C_1 e^{-\frac{\Delta E_b}{k_B T}}
\]
Mid gap level: Both “barriers” low
Level near the CBM:
Hole capture slow

\[ R_{SRH} = nN \frac{C_n C_p}{C_n + C_p} \approx nN C_p \]
Level near VBM: Electron capture slow

\[ R_{\text{SRH}} = nN \frac{C_n C_p}{C_n + C_p} \]
\[ \simeq nN C_n \]
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Common defects and impurities in GaN
Gallium vacancies complexed with O and/or H have mid-gap states in GaN.
$V_{Ga}^{-3H}$ and $V_{Ga}^{-O_N^{-2H}}$ have lowest formation energy.
Electron capture is the rate limiting process.

\[ R_{SRH} = nN \frac{C_n C_p}{C_n + C_p} \approx nN C_n \]
Defect level moves closer to the conduction band in InGaN alloys

Defect density: $N = 10^{16} \text{ cm}^{-3}$
Carrier density: $n = 10^{18} \text{ cm}^{-3}$
Temperature: $120^\circ \text{C}$

$R_{\text{rad}} \approx 4 \times 10^{25} \text{ cm}^{-3}\text{s}^{-1}$


Defect density: $N = 10^{16} \text{ cm}^{-3}$

~20% reduction in efficiency for green devices

Radiative recombination suppressed for yellow wavelengths

Defect density: $N = 10^{16} \text{ cm}^{-3}$

No light emitted for yellow devices

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What about complexes with several defect levels?
Maybe we haven't found the right defect yet?
Maybe we haven't found the right defect yet?

We cannot explain SRH in wide band gap InGaN alloys with typical mechanisms.
Electronic structure of -1 charge state allows for excited states

$V_{Ga-O_N}$
Electronic structure of -1 charge state allows for excited states

\[ V_{Ga-O_N} \]

\[ q = -1 \]
\[ S = 1/2 \]

A. Alkauskas, C. E. Dreyer, J. L. Lyons, and C. G. Van de Walle PRB 93, 201304(R) (2016)
Excited state is additional curve on formation energy plot

$V_{Ga-O_N}$

$q = -1$
$S = 1/2$

A. Alkauskas, C. E. Dreyer, J. L. Lyons, and C. G. Van de Walle PRB 93, 201304(R) (2016)
Neutral charge state also has excited states

$V_{\text{Ga-ON}}$

$q = 0$
$S = 1$

A. Alkauskas, C. E. Dreyer, J. L. Lyons, and C. G. Van de Walle PRB 93, 201304(R) (2016)
Excited state provide additional levels for capture
Capture into excited state enhances hole capture in the -2 charge state
Capture into excited state enhances electron capture in the +1 charge state.
Excited state mechanism gives rates for $V_{Ga}-O_N$ consistent with experiment
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Conclusions

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PRB 93, 201304(R) (2016)
APL 108, 141101 (2016)