Optoelectronic Materials: Transparent Conductors, Light Emitters

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with

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Density Functional Theory and Beyond

Berlin, July 21, 2015
Transparent conducting oxides

Transparent conducting oxides (TCOs) have many applications:
- Contacts in solar cells
- Electrodes in LCD screens
- Touchscreens
- Smart windows

Possible because materials combine:
- Transparency
- Conductivity
Absorption processes

Direct valence- to conduction-band transition
→ band gap is 3.6 eV (344 nm)
→ no absorption in visible range (even into the UV)

Example: SnO$_2$
Absorption processes

Direct transition between conduction bands:
→ first to second conduction band: 4.7 eV (262 nm)
→ also not in visible range
Absorption processes

Indirect transition:
conduction band to conduction band

SnO$_2$
Absorption processes

Indirect transition:
→ requires additional momentum: e.g., from phonons

Often described by Drude model → phenomenological
Theoretical description

Absorption coefficient $\rightarrow$ Fermi’s golden rule

$$\alpha^{el-ph}(\omega) = \frac{C}{\omega} \frac{1}{V_{cell}} \frac{1}{N_k N_q} \sum_{\nu ij k q} |\hat{e} \cdot (S_1 + S_2)|^2 \times P \delta(\varepsilon_{j,k+q} - \varepsilon_{ik} - \hbar \omega \pm \hbar \omega_{\nu q})$$

\[\hat{e}\] light polarization

$$S_1 = \sum_m \frac{\mathbf{p}_{im}(\mathbf{k}) g_{mij,\nu}^{el-ph}(\mathbf{k}, q)}{\varepsilon_{mk} - \varepsilon_{ik} - \hbar \omega}$$

$$S_2 = \sum_m \frac{g_{im,\nu}^{el-ph}(\mathbf{k}, q) \mathbf{p}_{mj}(\mathbf{k} + q)}{\varepsilon_{m,k+q} - \varepsilon_{ik} \pm \hbar \omega_{\nu q}}$$

$$P = \left( n_{\nu q} + \frac{1}{2} \pm \frac{1}{2} \right) (f_{ik} - f_{j,k+q})$$

Delta function: conservation of energy

The + signs indicates phonon emission, the – sign phonon absorption.

No fitting parameters! $\rightarrow$ predictive!
Computational details: \( \text{SnO}_2 \)

- Norm-conserving pseudopotentials
- Plane-wave basis
- Local Density Approximation (LDA)
- Density functional perturbation theory (DFPT) to obtain phonons
- Absorption calculated at 300K

**Focus on \( \text{SnO}_2 \) (techniques are general)**

\( \text{SnO}_2 \): - rutile structure
- 6 atoms/unit cell
  - \( c \) direction important
Absorption spectrum

Linear on log-log scale

Over large range of wavelengths: power law!

Deviation for wavelengths < 450 nm
Absorption < 450 nm

\[ \alpha_{\text{el-ph}}(\omega) = \frac{C}{\omega} \frac{1}{V_{\text{cell}}} \frac{1}{N_k N_q} \sum_{\nu i j k q} |\tilde{e} \cdot (S_1 + S_2)|^2 \times P\delta(\epsilon_{j,k+q} - \epsilon_{ik} - \hbar \omega \pm \hbar \omega_{\nu q}) \]

\[ \rightarrow \text{absorption due to states near the band edges} \]
Contributions to absorption @ 300K

Emission of phonons is biggest contribution
→ possible even at low temperatures

⇒ Fundamental limit!
Fröhlich versus first principles

Similar power law for large wavelengths, but completely misses increase < 450 nm
→ Fröhlich only captures intraband transitions
Importance of LO modes

For large wavelengths: LO mode is dominant
Small wavelengths: other modes become important
→ defines region Fröhlich model can be used
Device implications

Using our numbers and $I = I_0 e^{-\alpha x}$

For $5 \times 10^{20}$ cm$^{-3}$ carriers:

- Visible absorption: 2.5%
- Ultraviolet absorption: 12%
- Infrared absorption: 39% (telecom wavelength 1.5 μm)

Numbers for only one absorption process (due to phonons)
Since emission of phonons is always possible $\rightarrow$ fundamental limit

LEDs for solid-state lighting

UCSB SSLEC, 2012

Cree.com
“ABC model” for internal quantum efficiency of LEDs

\[ R = An \]

\[ R = Bn^2 \]

\[ R = Cn^3 \]

\[ \eta = \frac{Bn^2}{An + Bn^2 + Cn^3} \]
Auger: loss mechanism

\[ R = C n^3 \]
Direct & Indirect Auger recombination

Direct Auger

Indirect Auger

Carrier scattering by:

Electron-phonon

Alloy scattering

Charged defects

Bulashevich & Karpov, pssc (2008)
Indirect Auger recombination

\[ R = 2 \frac{2\pi}{\hbar} \sum_{1234q\nu} f_1 f_2 (1 - f_3)(1 - f_4) |\tilde{M}_{1234}|^2 \]

\[ \times \delta_{k_1 + k_2 + q, k_3 + k_4} \times \delta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4 \mp \hbar\omega_{q\nu}) \]

\[ \tilde{M}_{1234} = \sum_m \frac{\langle 1 | \Delta V | m \rangle \langle m 2 | W | 34 \rangle}{\epsilon_m \pm \hbar\omega_{q\nu} - \epsilon_1} + \ldots \]

Atomic-scale calculations from first principles, explicitly study microscopic scattering mechanisms

- **Electrons**: local density approximation + scissors operator
- **Phonons**: density functional perturbation theory
- **Dielectric function**: G. Cappellini *et al.*, PRB 1993
Calculating the Auger coefficient

\[ R = 2 \frac{2\pi}{\hbar} \sum_{1234} f_1 f_2 (1 - f_3) (1 - f_4) |M_{1234}|^2 \]

\[ \times \delta_{k_1+k_2, k_3+k_4} \times \delta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4) \]

- Conserve momentum, eliminate \( k_4 \)-sum ⇒ 9D integral
- \( \delta \rightarrow \) Gaussian, vary band gap
- Sampling of \( k_1, k_2, k_3 \) on grid
- Generate all \( k_4 = k_1 + k_2 - k_3 \), pre-calculate wave functions
- \#\( k_1, k_2, k_3 \) ≈ 10-100, \#\( k_4 \) ≈ 1,000-5,000
- Parallel Auger code, biggest run ~3,000 CPUs for 4h
Auger Recombination in GaN and InGaN

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,*
Short-range scattering

Need to model **short-range scattering** and **bands at edge of BZ**: First-principles theory
Shockley-Read Hall (SRH) and Auger are loss mechanisms.
Microscopic mechanisms of Shockley-Read Hall recombination unknown

- What are the mechanisms?
- What defects/impurities are responsible?
- What are the rates?
Why study defects?

• “Defects”
  – Extended defects
    • dislocations
  – Point defects:
    • Native defects
    • Impurities

• Defects often determine the properties of materials
  – Doping and its limitations
  – Device degradation
  – Diffusion
  – Radiative and nonradiative recombination
Formalism

- $E_{\text{form}}$: formation energy

Concentration of defects or impurities:

\[ C = N_{\text{sites}} \exp \left( - \frac{E_{\text{form}}}{kT} \right) \]

- Example: gallium vacancy in GaN

\[ E_{\text{form}}(V_{\text{Ga}}^{3-}) = E_{\text{tot}}(V_{\text{Ga}}^{3-})^{3} - E_{\text{tot}}(\text{bulk}) + \mu_{\text{Ga}} - 3 \ E_{\text{F}} \]

$\mu_{O}$: energy of oxygen in reservoir, i.e., oxygen chemical potential

$E_{\text{F}}$: energy of electron in its reservoir, i.e., the Fermi level

- **General expression**

\[ E_{\text{form}}(D^{q}) = E_{\text{tot}}(D^{q}) - E_{\text{tot}}(\text{bulk}) + n_{i} \mu_{i} + qE_{\text{F}} \]

$n_{i}$: number of atoms being exchanged to form the defect
Point defects in GaN

- Comprehensive study of point defects in GaN, using state-of-the-art methods
- Density functional theory, charge-state corrections
- Methodology:

Impurities in GaN: Carbon

- Carbon: common unintentional impurity
- Carbon on a nitrogen site: defect level ~1 eV above the valence band

First-principles approach for studying loss mechanisms

• Density functional theory (DFT)
• Hybrid functional provides accurate description of
  – Band gaps
  – Localized states
  – Vibronic properties of defects
J. Heyd, G. E. Scuseria, M. Ernzerhof,
• Supercell approach for studying defects
J. L. Lyons, A. Janotti, and C. G. Van de Walle,
Shockley-Read Hall (SRH) based on 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
General form of nonradiative capture coefficient

Describes transition from initial electronic state \((i)\) and vibronic state \((m)\) to final electronic state \((f)\) and vibronic state \((n)\)

\[
C_p = \frac{2\pi V}{\hbar} g \sum_m \omega_m \sum_n |\Delta H_{im;fn}^{\text{e-ph}}|^2 \delta(E_{im} - E_{fn})
\]

- Volume
- Thermal occupation of phonons
- Electron-phonon coupling
- Energy conservation
First order in the electron-phonon coupling

Describes transition from initial electronic state \((i)\) and vibronic state \((m)\) to final electronic state \((f)\) and vibronic state \((n)\)

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

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

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

Overlap between vibronic states
Electron-phonon coupling: One-dimensional approximation

- Consider one special phonon mode that couples most strongly to distortion caused by carrier capture
- Good approximation for system with strong electron-phonon coupling
  - Gives accurate phonon broadening of lineshapes

Determine vibronic states for special mode

- To obtain $\Delta Q$, $\chi_i$, $\chi_f$:
  - generate “configuration coordinate diagram”
- *e.g.*, for hole capture at $C_N$ in GaN:
Electron-phonon coupling for special mode

\[ W_{if} = \langle \Psi_i \mid \frac{\partial \hat{H}}{\partial Q} \mid \Psi_f \rangle \approx \langle \psi_i \mid \frac{\partial \hat{h}}{\partial Q} \mid \psi_f \rangle = (\epsilon_f - \epsilon_i) \langle \psi_i \mid \frac{\partial \psi_f}{\partial Q} \rangle \]

Approximate many-body quantities by single-particle counterparts

- DFT calculations yield
  - single-particle wavefunctions \((\psi_{i/f})\)
  - eigenvalues \((\epsilon_{i/f})\)
  - response to displacement \(Q\)

see also:
Results: Hole capture at $C_N$ in GaN

A. Alkauskas, Q. Yan, and C. G. Van de Walle, PRB 90, 075202 (2014).

In progress: Hole capture at $V_{Ga}$ complexes

- Complexes with $V_{Ga}$ have midgap levels, may be important as recombination centers
  - $V_{Ga}$-O$_N$-H: $C_p \approx 8 \times 10^{-11}$ cm$^3$s$^{-1}$
  - $V_{Ga}$-2H: $C_p \approx 2 \times 10^{-10}$ cm$^3$s$^{-1}$
Summary

• First-principles approach for nonradiative capture rates

• Luminescence lineshapes for cases of strong and intermediate electron-phonon coupling

• Origin of SRH recombination in nitrides