Chalcogenide semiconductor research and applications

Tutorial 2: Thin film characterization

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Section 1: Measuring composition
Semiconductor composition analysis

- Optoelectronic properties are determined by intrinsic and extrinsic defects at ppm ($10^{-6}$) levels, and below
- Typical analysis techniques for thin films have precision of ~0.5%, and accuracy of ~10% (and much worse for oxides)

*What do we do?*
Considering the options

**Electron-in, X-ray out**
- Energy-dispersive spectroscopy (EDS)
  - Typically available in electron microscopes
  - Resolution & accuracy <5%
- Wavelength-dispersive spectroscopy (WDS)
  - Require specialized electron microprobe systems
  - Resolution & accuracy <1%

**X-ray in, X-ray out**
- X-ray fluorescence spectroscopy (XRF)
  - Relatively low-cost, accessible
  - Resolution & accuracy <5% (better with standards)

**X-ray in, electron out**
- X-ray photoelectron spectroscopy (XPS)
  - Highly surface-sensitive
  - Resolution & accuracy <5%

**Electron-in, electron-out**
- Auger nanoprobe
  - Resolution & accuracy <5%
  - Excellent spatial resolution

**Ion-in, ion-out**
- Rutheford backscattering (RBS)
  - Resolution & accuracy <5%
  - Uniquely sensitive to oxygen
- Secondary ion mass spectroscopy (SIMS)
  - Resolution & accuracy <ppm
  - Highly technical

*Always consider probe & escape depths!*
Section 2: Measuring optical properties
• Measure transmission ($T$) and reflection ($R$) of a planar material stack

• Quantitative goals:
  – Optical absorption coefficient ($\alpha$)
  – Band gap ($E_g$)

• Unknowns abound
  – Reflection & transmission coefficients at each interface
  – Indices of refraction
  – Thicknesses
Simplifications and assumptions

• Simplification 1: Normal incidence
  – Polarization doesn’t matter
• Simplification 2: Substrate is non-existent
  – \( T_{10} = 1 - R_{10} \)
• Simplification 3: Film is fairly opaque
  – All light absorbed by 2\(^{nd}\) pass through the film
  – \( e^{-\alpha d} << 1, \alpha >> 1/d \)

\[
\alpha = -\frac{1}{d} \ln \left( \frac{T}{(1 - R)^2} \right)
\]
Simplifications and assumptions

- Simplification 4: Effective mass model, parabolic band edges, allowed vertical transitions
  - Tauc equation ($n = 1$ for direct band gap)

\[ \alpha = \frac{A(h\nu - E_g)^n}{h\nu} \]
Implications of the simplifications

- Evaluate assumptions to determine valid regime for Tauc analysis
- Simplification 3
  - $\alpha >> 1/d$
  - Typical film thickness $= 1 \, \mu m \Rightarrow \alpha >> 10^4 \, \text{cm}^{-1}$
- Simplification 4
  - Effective mass model
  - $E_g < h\nu < E_g + 200 \, \text{meV}$ (approximate)
Implications of the simplifications

- Need to discard $\alpha(h\nu)$ data before Tauc analysis
  - Discard data at the low end that doesn’t satisfy $\alpha >> 1/d$
  - Discard data at the high end that doesn’t satisfy effective mass approximation
Section 3: Measuring electrical transport properties
• Drude model relates conductivity ($\sigma$) to free carrier concentration ($n$) and drift mobility ($\mu$)
  – Mobility is determined by generation and dissipation of momentum
  – Carrier mass ($m$) determines velocity for given impulse
  – Momentum relaxation time ($t$) characterizes randomization of carrier motion following given impulse
• Low-field current-voltage measurements – with ohmic contacts and well-defined geometry – determine $\sigma$
• Hall magnetotransport measurements used to disentangle $n$ and $\mu$
  – Hall mobility $\neq$ drift mobility, but we will ignore this

\begin{align*}
  J &= \sigma E \\
  \sigma &= qn\mu \\
  \mu &= q\tau/m
\end{align*}

**Drude model**

**Typical Hall bar measurement geometry**
Details of Hall measurements

- Hall voltage ($V_H$) depends simply on carrier concentration ($n$) for single conduction band
- Realistic samples have lead placement error ($\varepsilon$) that mixes Hall voltage ($V_H$) and longitudinal voltage ($V_L$)

\[
V_L = I_x \frac{1}{\sigma \ v t} = I_x \frac{1}{q n \mu \ v t}
\]
Practical complications

- Signal ($V_H$) tends to vary slowly in time as magnetic field is swept.
- Background ($V_L$) can vary slowly in time due to temperature drift, variable illumination, etc.
- Slowly varying signal and background
  - Need large signal/background ($V_H/V_L$)

**Signal/background:**

$$\frac{V_H}{V_L} = \frac{\frac{I_x B_z}{ntq}}{\frac{1}{n\mu \varepsilon} \frac{\varepsilon}{wt}} = \frac{B_z \mu}{\varepsilon/w}$$

- Geometric factor $x = \varepsilon/w$
Practical limits of Hall measurements for low-mobility samples

- Lead placement error limits sensitivity of Hall measurements for low-mobility samples

- Typical van der Pauw sample, $x \sim 0.1$
  - Challenging to measure $\mu < 10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

- Lithographically-defined Hall bar, $x < 0.01$
  - Possible to measure $\mu < 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$
High-conductivity samples encounter limitations due to small Hall voltage.

Depends on mobility and sample geometry.

Measuring small voltages (<1 μV) possible with lock-in measurements.
Section 4: Measuring minority carrier properties
Doped semiconductors have majority and minority carrier types.

Most electronic transport measurements are insensitive to minority carriers.

Minority carrier processes are critically important for a range of semiconductor technologies:

- Transistors
- Photodetectors
- Lighting
- Solar cells
- Photochemistry
Minority carrier transport in solar cells

- Superposition principle
  - Illumination current
  - + Diode forward current
  - = Total current
- Good solar cell has
  - Large illumination current
  - Large diode turn-on voltage, good rectification
Electron-hole pairs are generated ($G$) as the light is absorbed.

Each electron-hole pair has a probability $P$ of being collected.

$P$ is controlled by the diffusion length $L_{\text{diff}}$.

$L_{\text{diff}}$ is controlled by lifetime $\tau$.

\[
J_{\text{ill}} = \int \, dx \, G \, P
\]

\[
L_{\text{diff}} = \sqrt{D \tau}
\]

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**beware!**
Turn on voltage and $V_{OC}$

- Diode equation
- Saturation current density $J_0$
  - Electron-hole recombination via:
  - Light emission (a light emitting diode)
  - Band-to-band tunneling
  - Auger recombination
  - Defect-assisted recombination (bulk)
  - Defect-assisted recombination (interface)
  - $J_0 = J_{0,1} + J_{0,2} + \ldots$

Effect of recombination currents on $V_{OC}$

$$J_{dark} = J_0 \left( e^{\frac{qV}{kT}} - 1 \right)$$

$$V_{OC} = \frac{kT}{q} \ln \left( \frac{J_{ill}}{J_0} + 1 \right)$$
Turn on voltage and $V_{OC}$

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$R_{\text{radiative}} = Bpn$
$B \sim 10^{-14} - 10^{-10} \text{ cm}^3 \text{ s}^{-1}$

$R_{\text{Auger}} = C(nnp + pnp)$
$C \sim 10^{-30} \text{ cm}^6 \text{ s}^{-1}$

$R_{\text{defect}} = \frac{np}{n\tau_h + p\tau_e}$
$\tau \sim 10^{-12} - 10^{-3} \text{ cm}^3 \text{ s}^{-1}$

$J_{\text{surface}} = nS$
$S \sim 1 - 10^7 \text{ cm s}^{-1}$
Lifetime matters ... a lot

![Plot showing Efficiency vs. \( \tau \) (ns) for various materials.

Jaramillo et al., JAP 119, 035101 (2016)
Lifetime matters ... a lot

![Graph showing lifetime vs efficiency for various materials. The graph is divided into two regions: a red region labeled "NO" for materials with lower efficiency and a green region labeled "YES" for materials with higher efficiency. Different materials are represented by different symbols and colors.](image)

Jaramillo et al., JAP 119, 035101 (2016)
How to measure lifetime

- **Transient**
  - Photoluminescence
  - Photoconductivity

- **Steady state (or quasi steady state)**
  - Photoluminescence
  - Photoconductivity

*Generate minority carriers (typically using light)*

*Measure material response, back out recombination rates through modeling*
Challenges for metrology on thin films

**Want to measure**
- Bulk lifetime ($\tau$)
- Surface recombination velocity ($S$)

**Useful to have**
- Optical absorptivity ($\alpha$), reflectivity ($R$)
- Equilibrium carrier concentration ($\rho$)
- Samples of varying thickness
- Near-total surface passivation
- Minority carrier diffusivity
Instantaneous optical attenuation (Beer-Lambert) leads to exponential excess carrier profile in a uniform material layer.

Excess carriers move through drift & diffusion until reaching symmetrical, half-sine wave profile.

- Diffusion time \( t_{\text{diff}} = d^2/D \)
  - \( D \) = diffusion constant
  - \( d \) = thickness

Evolution of excess carrier concentration through Si wafer following instantaneous illumination at \( t = 0 \)

Does excess carrier profile matter?

**Case I: Diffusion time $\ll$ recombination time**
- Excess carriers reach symmetrical profile
- At long times, free carriers decay with effective lifetime $\tau_{\text{eff}}$
- $\tau_{\text{eff}}$ is a function of both bulk and surface recombination

**Case II: Diffusion time $\gg$ recombination time**
- Excess carriers don’t reach symmetrical profile before recombining
- Carrier profile needs to be explicitly modeled to determine recombination rates
Solving for recombination rates in Case I

- Extract single exponential decay rate $\tau_{\text{eff}}^{-1}$ from long-time tail of experimental signal
- Measure samples with varying $d$ and/or $S$ to determine $\tau$ by regression

$$\frac{1}{\tau_{\text{eff}}} \approx \frac{1}{\tau} + \left( \frac{d^2}{\pi^2 D} + \frac{d}{2S} \right)$$

TRPL measurement of minority carrier recombination in CZTS thin film

Solving for recombination rates in Case II

- Fit data to drift-diffusion model of excess carrier transport

Jaramillo et al., JAP 119, 035101 (2016)
The problem with unknown diffusivity $D$

- Diffusivity ($D$) and surface-recombination velocity ($S$) are strongly correlated
  - $S =$ rate at which minority carriers are consumed at the surface
  - $D =$ rate at which minority carriers are transported to the interface
Other complications (not discussed here)

- Injection-dependence of bulk recombination
- Injection-dependence of surface recombination
- Ambipolar diffusivity and Dember effects

\[ R_{\text{defect}} = \frac{np}{n\tau_h + p\tau_e} \]
Recombination rates & materials processing

Bulk and surface minority carrier recombination in SnS thin films

![Graph showing bulk and surface minority carrier recombination in SnS thin films](image)

$S$ (cm/s) vs. $\tau_0$ (ns)

- **TE1**: TE, not annealed, not oxidized

References:

Jaramillo et al., JAP 119, 035101 (2016)
Measuring composition is not easy, and may not be possible. Straightforward optical property measurements need to be interpreted carefully. Low-mobility semiconductors pose challenges for typical Hall measurements. Minority carriers recombine by different processes; “lifetime” measurements are ambiguous and should consider the application and focus on the relevant mechanisms.