Electrical and optical properties II

Amorphous semiconductors and insulators
Outline

• Semiconductors $E_g < 4 \text{ eV}$
• Insulators $E_g > 4 \text{ eV}$
• Conduction mechanisms
• Excitations of electrons from localized states at the Fermi level to the conduction band (or holes to the valence band)
• Trapping in empty gap states
• Hopping between localized states at the Fermi level
• Optical properties: Polaron absorption, Urbach tails
Band conduction

- Donors to conduction band
- Multiple trapping
Hopping conductivity

• Hopping at the Fermi level – "R-hopping"

• R-E hopping
Conductivity: Semiconductors

- Semiconductors: $\sigma = n e \mu_e + p e \mu_h$
- Generally:
  $$\sigma = e \int D(E) \mu(E) f(E)(1 - f(E)) dE$$
- $f(E)$ – Fermi-Dirac distribution function
- $D(E)$ – density of states
- $\mu(E)$ – mobility
- Amorphous material with mobility edge at $E_c$
- $\mu(E) \sim 0$ for localized states in the band gap.
- $f(E)(1-f(E)) \sim \exp[-(E-E_F)/k_B T]$, if $E-E_F >> k_B T$
Amorphous semiconductors/insulators

- Case of electron conduction
- Excitation of electrons from $E_F$ to the conduction band. The main contribution comes from $E \approx E_c$.

$$
\sigma \approx eD(E_c) \mu e k_B T \exp[-(E_c - E_F) / k_B T]
$$

- Similar equation is obtained for hole conduction
- Prefactor: Mott suggested $\sigma_0 \sim e^2 / \hbar L_i$
- Of the order of the "minimum metallic conductivity", and $L_i$ is an inelastic scattering length
Meyer-Neldel rule

- $\Delta E = E_c - E_F$ depends on temperature
- Fermi level sinks towards mid-gap as $T$ increases.
- Mobility edge changes due to thermal expansion and electron-phonon coupling
- Approx: $\Delta E(T) = \Delta E(0) - \gamma T$

$$\sigma = \sigma_0 \exp(\gamma / k_B) \exp[-\Delta E(0) / k_B T]$$

- Exp. a-Si:H (vary doping)

$$\sigma' = \sigma_0 \exp(\gamma / k_B) = \sigma_0 \exp(G \Delta E(0))$$

Source: Elliott, Physics of amorphous materials
Hopping conductivity - 1

- Phonon-assisted tunneling between localized states at the Fermi level

- Competition between energy needed for the hop and the influence of spatial separation on the probability for a hop

- Wave function:
  \[ \psi(r) \sim \exp(-\alpha r) \]

- Tunneling probability from state i to j
  \[ \sim \exp(-2ar_{ij}) \]

- Possibility to gain energy from a phonon
  \[ \sim \exp\left(-\frac{\Delta E}{k_B T}\right) \]

- Balance between these terms depends on temperature and spatial separation
Hopping conductivity - 2

- Mobility $\mu = eD/k_B T = e\gamma r^2/6k_B T$, where $D$ is the diffusion coefficient and $\gamma$ is the hopping rate.
- Conductivity prefactor:
  \[ \sigma_0 \approx \gamma_0 e^2 r_{ij}^2 D(E_F) / 6 \]
- Conductivity:
  \[ \sigma_{ij} = \sigma_0 \exp(-\Delta E / k_B T) \exp(-2\alpha r_{ij}) \]
- Consider that an electron can hop to sites within radius $r$ and energy $\Delta E$.
- The optimal hop occurs when only one site can be reached.
Variable range hopping - 1

- An electron can reach $N$ sites where
  \[ N = 4\pi r^3 D(E_F) \Delta E / 3 \]
- $N=1 \Rightarrow \Delta E = 3/4\pi r^3 D(E_F)$
- Maximise the conductivity by minimising the exponent, $x$, in the $e^{-x}$ function:
  \[
  \frac{d}{dR} \left( 2\alpha r + 3/4\pi r^3 D(E_F) k_B T \right) = 0
  \]
  \[
  \Rightarrow r_m = \left( \frac{9}{8\pi \alpha D(E_F) k_B T} \right)^{1/4}
  \]
Variable range hopping - 2

• Finally we obtain (Mott’s law)

\[
\sigma = \sigma_0 \exp\left(-\left(\frac{T_o}{T}\right)^{1/4}\right)
\]

\[
T_0 = \frac{512\alpha^3}{9\pi D(E_F)k_B}
\]

• Typically $1/\alpha \approx 10 \text{ Å}$, $r_m$ depends on localized DOS, but may be of the order of 1-10 nm

• For localized states in the band gap

$D(E_F) \sim 10^{18} - 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$
Percolation treatment

- We only considered a single hop
- In reality we have a complicated resistor network with a wide (exponential) spread of conductances
- A percolation treatment gives Mott’s law, except for a numerical constant in $T_0$.

$$\sum_{j \neq i} \sigma_{ij} (V_i - V_j) = 0$$

The percolation path appears:

\[ \sigma \sim \sigma(\text{critical}) \]

Source: Overhof, Festkörperprobleme
Hopping vs. band conduction

- The exponent in Mott’s law becomes different in case of two dimensions and if $D(E_F)$ varies rapidly around $E_F$
- Variable range hopping is favored by low temperature and a large localized DOS
- Band conduction is favored by high temperature and a low localized DOS
- Crossover: Compare terms $\sim \exp(-2\alpha r_{ij})$ and $\sim \exp(-(E_c - E_F)/k_B T)$
Ex: amorphous Ge

- Conductivity plotted in two different ways

Source: Overhof, Festkörperprobleme 16 (1976)
Multiple trapping - 1

- Trapping of electrons from the conduction band, or generally from "transport states"
- $p(r,t)$ – probability that a transport state is occupied
- $p_i(r,t)$ – probability that trap state "i" is occupied
- $w_i$ – capture rate
- $r_i$ – release rate

- Trapping equations

\[ P(r,t) = p(r,t) + \sum_{i} p_i(r,t) \]
\[ \frac{\partial p_i(r,t)}{\partial t} = w_i p(r,t) - r_i p_i(r,t) \]
\[ \frac{\partial P(r,t)}{\partial t} = g(r,t) - \mu E \nabla p(r,t) \]

- Here $g$ is the rate of excitation of carriers to the transport states
Multiple trapping - 2

- These equations form the basis for the transient photoconductivity method for measuring localized band gap states
- In an insulator material, charge carriers will be generated in the transport states by thermal excitation from the Fermi level
- Maybe excitation to the conduction band
- Trap-controlled hopping: Excitation to a maximum of the localized DOS; the lower lying empty states act as traps
- Conductivity proportional to the average release rate
- Power-law distribution of release rates (for example exponential band tails) – very long time-dependent transients – DC conductivity may be difficult to observe
- Conductivity related to the cutoff of the power-law distribution
High field conduction

- Apply a high voltage, $V$, i.e. a high electric field, $F$, to the sample
- Energy depends on position: $E = E(0) - eFr$
- Band conduction: Excitation from donors, space charge limited conduction with traps
- Hopping conduction

- Electron energies vary with position – "tilted energy bands"
Donors: Band conduction

- Poole-Frenkel effect
- Coulomb potential
- The electron has to climb an energy barrier to the conduction band
- Current density
  \[ J = J(0) \exp(\beta F^{1/2} / kT) \]
  \[ \beta = e^3 / \pi \varepsilon_0 \varepsilon \]
- Exp: $\beta$ differs from this value

- Donor state

- $E = E_0 - e^2/4\pi \varepsilon_0 \varepsilon r - eF r$

\[ \frac{dE}{dr} = 0 \Rightarrow r_m = (e / 4\pi \varepsilon_0 \varepsilon F)^{1/2} \]
Space charge limited currents

- At high applied voltages, charge may be injected from the contact into a close so called space charge region in the conduction band of an insulator.
- Space charge limited currents: $J \sim V^2$
- Single trap level decreases the current but does not modify the voltage dependence.
- Broad distribution of trap levels.
- Exponential DOS: $D(E) = N_0 \exp\left(-E / kT_0\right)$
- Current becomes: $J \sim V^{1+T_0/T}$
High field hopping

- Low fields, ohmic region: Variable range hopping, Mott’s law
- Moderate fields $eFr<k_BT$ treated by percolation theory
  $$\sigma(F) = \sigma(0) \exp\left(-CeFr_p / kT\right)$$
- Other exponential dependences also possible
- Very high fields: $eFr>>k_BT$
- Electrons ”hop down” in high E-field
- Accessible states: $N=4\pi r^3 eFrD(E_F)/3$
- Mott argument, $N=1$
  $$\sigma = \sigma_0^{hf} \exp\left(-\left(F_o / F\right)^{1/4}\right)$$
  $$F_o = \frac{64\alpha^4}{e\pi D(E_F)}$$
How to distinguish these phenomena?

- See which eqn. gives the best fit to exp?
- But there may be crossovers between different mechanisms
- Examine the derivative of the current is very useful
  \[ \Delta = \frac{d(\ln \sigma)}{d(1/F)} \approx nAF^{1-n} \]
- We can determine the exponent \( n \)!
- We can write in the form:
  \[ J \sim F^m \exp(-A/F^n) \]

**Table I. Values of the parameters \( m \) and \( n \) for different high-field conduction mechanisms.**

<table>
<thead>
<tr>
<th>Conduction mechanisms</th>
<th>( n ) ( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic percolation, moderate fields</td>
<td>-2</td>
</tr>
<tr>
<td>Directed percolation, moderate fields</td>
<td>-1</td>
</tr>
<tr>
<td>Poole's law</td>
<td>-1</td>
</tr>
<tr>
<td>Poole-Frenkel conduction</td>
<td>-0.5</td>
</tr>
<tr>
<td>Space-charge-limited conduction</td>
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</tr>
<tr>
<td>High-field percolation theory</td>
<td>0.25</td>
</tr>
<tr>
<td>(hopping or tunneling)</td>
<td>0.33</td>
</tr>
<tr>
<td>Particle-particle tunneling</td>
<td>1</td>
</tr>
<tr>
<td>Field ionization</td>
<td>1</td>
</tr>
</tbody>
</table>

- Analogous method for the temperature dependence
Ex: Amorphous $\text{Ta}_x\text{Nb}_y\text{O}_5$ films

- Ta2O5:
  - Space charge limited conduction

- Other films:
  - Poole-Frenkel conduction

- a-SiO$_2$ (not shown) $n=-1$, i.e. high field hopping

Source: Strömme et al.
Ex: Metal-insulator composites

- Au-Al$_2$O$_3$: $n=-1$
- Points to high field hopping at moderate fields
- Co-Al$_2$O$_3$: $n=0$, then much higher $-n$
- Detailed mechanism unknown
- $n=0$ may point to the importance of trap states in this material
Polarons - 1

- A charge carrier in a material always distorts the surroundings - even in crystal
- Lower energy state
- Strong electron-phonon interaction – the carrier may become self-trapped
- Large polaron: Extends over several atomic distances
- Small polaron: atomic distance

Source: Elliott, Physics of amorphous materials
Electron-phonon interaction

- Fröhlich model: Interactions with longitudinal optical phonons
- Coupling constant
  \[ \alpha = \frac{e^2}{4\pi\varepsilon_0\hbar} \sqrt{\frac{m}{2\hbar \omega_{LO}}} (\varepsilon^{-1}_\infty - \varepsilon(0)^{-1}) \]
- Weak coupling: \( \alpha \ll 1 \)
- Strong coupling: \( \alpha \gg 1 \)
- Measurable parameters
- Energy as a function of "configuration", q
Polarons - 2

- Polaron binding energy
  \[ W_H = \alpha^2 \hbar \omega_{LO} / 3\pi \]

- Polaron radius, \( \beta^{-1} \)
  \[ \beta = \frac{e^2 m}{12\pi \varepsilon_0 \hbar^2 \sqrt{\pi}} \left( \varepsilon^{-1}_\infty - \varepsilon(0)^{-1} \right) \]

- The polaron sits in a potential well and can be transported by hopping between these wells.

- Polarons in conduction band: The charge carrier concentration, \( n \) can be high and constant, if \( E_F \) is in the band, while the mobility is small and thermally activated.

- Excitation of carriers into the band: Both \( n \) and \( \mu \) are thermally activated.
Polaron hopping - 1

• An occupied site has a lower energy than an unoccupied site
• Energy from phonons make the transition possible
• An atomic distortion momentarily brings the energy level of an occupied site into coincidence with a neighboring unoccupied site, in order for the charge transfer to take place
• Adiabatic regime: Electron transfer faster than vibrational motion → several forward-backward hops
• Nonadiabatic regime: Small probability of electron transfer during a lattice vibration. Gives similar results to VRH, but there we considered only an electron gaining energy from a single phonon.
• At all but the lowest temperatures, multiphonon processes are important.
Polaron hopping - 2

- Polaron hopping energy $W_H$
- Disorder energy, $W_D$
- Activation energy:
  $W = W_H + W_D/2$
  (if $W_D$ small)

\[ \sigma = \sigma_0 \exp\left[-\frac{(\Delta E + W)}{k_B T}\right] \]

- Thermopower does not depend on $W$!
- Hall effect also activated.

- Hopping process:

- In addition disorder may cause the bottom of the two wells to be at different energies
VRH of polarons

- Polaron sites on a lattice: Thermally activated conduction
- Disorder in positions of sites: Variable range hopping

\[ \sigma = \sigma_0 \exp\left(-\left(\frac{T_o}{T}\right)^{1/4}\right) \]

- Important in transition metal oxides and glasses with transition metal ions
- Ex: V$_2$O$_5$-P$_2$O$_5$ glass
- Conductivity and Hall mobility

Source: Elliott, Physics of amorphous materials
Polarons or electrons?

• Jonker plot: $S$ vs. $\ln \sigma$ for samples with varying stoichiometry or doping

• Example:

Some optical effects

• Strong absorption for energies higher than the band gap, $E_g$.
• The shape of the interband absorption is modified (broadened) because of the breakdown of the $k$-selection rule
• At lower energies various absorption phenomena may be present:
  • Polaron absorption in the near infrared or thermal infrared
  • Absorption involving exponential band tails (Urbach tails)
  • Weak absorption from defect and impurity states
Polaron absorption

- Optical transition: Two-site model
- Absorption centered around energy $4W_H$
- Optical conductivity:

$$\sigma_1(\omega) \sim \exp\left[\frac{-(\hbar\omega - 4W_H)^2}{16W_H k_B T}\right]$$

if $k_B T > E_{LO}$
- Low T: Phonon broadening

Source: Elliott, Physics of amorphous materials
Polaron absorption: Exp

- Most studied in TiO$_2$ and WO$_3$
- Ex: WO$_{2.72}$ and V-doped material
- Absorption peak centered at $\sim$1 eV
- Present in crystals
- Amorphous WO$_3$ doped with protons or Li$^+$: Electrochromism due to polaron absorption

Defects: O vacancies

Similar peak by intercalation of H$^+$, Li$^+$

Source: Salje et al.
Ex: WO$_3$

- Fröhlich model, but intermediate polaron
- Phonon broadening

- Experiment on Li-doped WO$_3$ films
- Polaron radius 6-7 Å

Source: Bo Sernelius, LiU
The optical band gap

- Assume that the DOS in the valence and conduction bands vary as power laws of energy with indices \( p \) and \( q \), respectively.
- Good approximation close to band edges (mobility edges)
  \[
  \omega \alpha(\omega) \sim \omega^2 \varepsilon_2(\omega) \sim (\hbar \omega - E_g)^{p+q+1}
  \]
- Parabolic bands
  \[
  \omega \alpha(\omega) \sim (\hbar \omega - E_g)^2
  \]
- Extrapolation gives "Tauc gap"
- Is it the "true" band gap?

Source: Elliott, Physics of amorphous materials
Urbach (band) tail

- At lower energies we see an Urbach tail
- Extended to localized state transitions
- Exponential DOS
  \[ \alpha(\omega) \sim \exp[-A(T)(E_U - \hbar \omega)] \]
- Structural disorder
- Defect bands have lower optical absorption strength and are difficult to observe

Source: Elliott, Physics of amorphous materials
Ex: TiO$_2$ thin films

- Polycrystalline films by sputtering
- More sub-stoichiometric as Ar/O$_2$ ratio in the sputter gas decreases
- Oxygen vacancies
- Urbach tail seen for all samples (oscillations are not real!)
- Polaron absorption at low oxygen content