OPTICAL BAND GAP DETERMINATION ISSUES FOR AMORPHOUS AND CRYSTALLINE METAL-OXIDE THIN FILMS

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OUTLINE

- Introduction
- Tauc's method
- Unified methodology: sigmoid-Boltzmann function
- Johs-Herzinger generalized critical point model
- Examples

INTRODUCTION

SEMI-CLASSICAL FRAMEWORK

Optical absorption coefficient α (at the photon energy $E = \hbar\omega$) of an electron being excited from the valence (VB) to the conduction (CB) band, is subjected to the transition rate

$$W_{VB\rightarrow CB} = \frac{2\pi}{\hbar}|M|^2 g(E)$$

M - coupling transition matrix element
$g(E)$ - joint electron-hole density of states

$\Rightarrow$ Negligible or no changes in the electron wave-vector $\vec{k}\ (\vec{k_f} \approx \vec{k_i})$

Direct or vertical optical or first-order optical transitions

$\Rightarrow$ Changes in the electron wave-vector $\vec{k}\ (\vec{k_f} \not\approx \vec{k_i})$

Indirect or non-vertical or phonon-assisted optical transitions

DIRECT AND INDIRECT OPTICAL TRANSITIONS IN CRYSTALLINE SEMICONDUCTORS

	Direct	Indirect
	$\alpha_{dir}(E < E_{gap}) = 0$	$\alpha_{ind}(E < E_{gap}) = 0$
	$\alpha_{dir}(E \geq E_{gap}) \propto (E - E_{gap})^{1/2}$	$\alpha_{ind}(E \geq E_{gap}) \propto (E \pm \hbar\Omega - E_{gap})^{2}$
	Determination of E_{gap}: extrapolating the linear least squares fit of α^2 to zero ["α^2 *versus* E" plot].	Determination of E_{gap}: : extrapolating the linear least squares fit of $\alpha^{1/2}$ to zero ["$\alpha^{1/2}$ *versus* E" plot].
Drawbacks	**(a)** No Coulomb attraction is considered which, notably at lower *T*, enhances $\alpha_{dir}(E)$ **(b)** Extrinsic absorption (due to defect states and impurities) may originate $\alpha_{dir}(E < E_{gap}) \neq 0$ **(c)** Parabolic-like $\alpha_{dir}(E \geq E_{gap}) \propto (E - E_{gap})^{1/2}$ shape is valid only at $\vec{k} \approx 0$, that could not be valid in certain band structures and, definitely, is not applicable when $E \gg E_{gap}$	$\hbar\Omega$ denotes the energy of a phonon being emitted ($+\hbar\Omega$) or absorbed ($-\hbar\Omega$): in most cases, the contribution owing to $t\Omega$ can be disregarded

$\alpha_{dir}(E)$ – steep rise profiles
$\alpha_{ind}(E)$ - absorption tails due to higher frequency (or multi-) phonon absorption

Both $\alpha_{dir}(E)$ and $\alpha_{ind}(E)$ – and corresponding Egap values – are affected by the local *T*, the presence of strong electric or magnetic fields, and the physical–chemical characteristics (including doping–alloying effects) of the semiconductor material.

TAUC’S METHOD

RESTRICTIONS TO THE OPTICAL ABSORPTION PROCESSES

1. Absence of $\vec{k}$ conservation

2. Momentum transition matrix element is constant
(for phonon-assisted transitions)

Linear least squares fit of
$(\alpha \cdot E)^{1/2}$ to zero
["$(\alpha \cdot E)^{1/2}$ *versus* E" plot]

Cody approuch $\Rightarrow E_{gap} = E_{Cody}$

3. Density of e^- states close to VB and CB extrema is ~$E^{1/2}$
(similar to crystalline case)

Linear least squares fit of
$(\alpha/E)^{1/2}$ to zero
["$(\alpha/E)^{1/2}$ *versus* E" plot]

Tauc approuch $\Rightarrow E_{gap} = E_{Tauc}$

J. Tauc, R. Grigorovici, & A. Vancu, Optical properties and electronic structure of amorphous germanium. *phys. stat. sol.* **15**:2 (1966) 627, https://doi.org/10.1002/pssb.19660150224
G.D. Cody, B.G. Brooks, & B. Abeles, Optical absorption above the optical gap of amorphous silicon hydride. *Solar Energy Mater* **8**:1-3 (1982) 231, https://doi.org/10.1016/0165-1633(82)90065-X

E_{Tauc} AND E_{Cody} INFLUENCED BY THE α(E) SPECTRUM AND ITS POSTERIOR DATA ANALYSIS

For amorphous semiconductors E_{gap} can be defined by taking E at which the α reaches 10^3 or 10^4 cm^{-1}, rendering the so-called isoabsorption E_{03} or E_{04} bandgaps.

This procedure is useful only when $\alpha(E) \geq 10^3$ cm^{-1} - for samples with thicknesses in the (sub-)μm range.

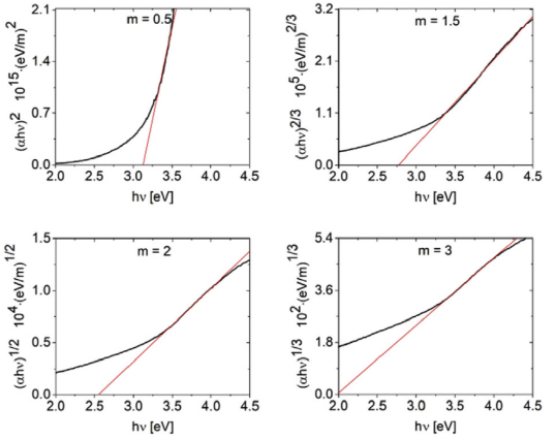
Regardless of the method chosen all of them are influenced by the α(E) spectrum and its posterior data analysis.

- α(E) is susceptible to
  - ⇒ experimental aspects (measurement details, sample thickness etc.)
  - ⇒ mathematical expression chosen to its calculation
    - ✓ E_{gap} values can differ by many meV

Tauc equation

$$\alpha h\nu = a(h\nu - E_g)^m$$

m = {0.5; direct allowed;
1.5; direct forbidden
2; indirect allowed
3} indirect forbidden



E.C. Freeman, & W. Paul, Optical constants of rf sputtered hydrogenated amorphous Si. *Phys. Rev. B* 20:2 (1979) 716, https://doi.org/10.1103/PhysRevB.20.716

OTHER MATHEMATICAL EXPRESSIONS

Mott-Davies approach

direct opt. transitions: $\alpha h\nu = a(h\nu - E_g)^{\frac{d}{n}-1}$

indirect opt. transitions: $\alpha h\nu = a(h\nu - E_g)^{\frac{d_v}{n_v}+\frac{d_c}{n_c}-1}$

α – absorption coefficient
a – constant
$h\nu$ – photon energy
d – effective dimensionality
n – dispersion relation for CB (c) and VB (v)

Inflection-point method from time-dependent perturbation theory

$$\alpha \propto \left(\Delta E_g\right)^{1/2}\left[1-\frac{2}{\pi}\tan^{-1}\left\{\frac{W+\Delta E_g - h\nu}{\Gamma}\right\}\right]$$

W – minimum energy distance between the CB and VB
ΔE_g – the amount of the shifted bandgap energy
Γ – broadening parameter (freq. independent)

The E_g determined by inflection-point method indicates the energy around which the transition from low to high absorption is centered.

Inverse logarithmic derivative method

natural logarithm of Tauc equation yields

$$\ln(\alpha h\nu) = m \ln a + m \ln(h\nu - E_g)$$

by differentiating with respect to $h\nu$ (a does not depend on energy $h\nu$)

$$\frac{d \ln(\alpha h\nu)}{d(h\nu)} = m\frac{1}{h\nu - E_g}$$

inversion of equation yields

$$\frac{1}{\frac{d \ln(\alpha h\nu)}{d(h\nu)}} = \frac{1}{m}(h\nu - E_g)$$

by transforming the left-hand-side, a numerical derivative is obtained

$$\frac{\Delta(h\nu)}{\Delta \ln(\alpha h\nu)} \approx \frac{1}{m}(h\nu - E_g)$$

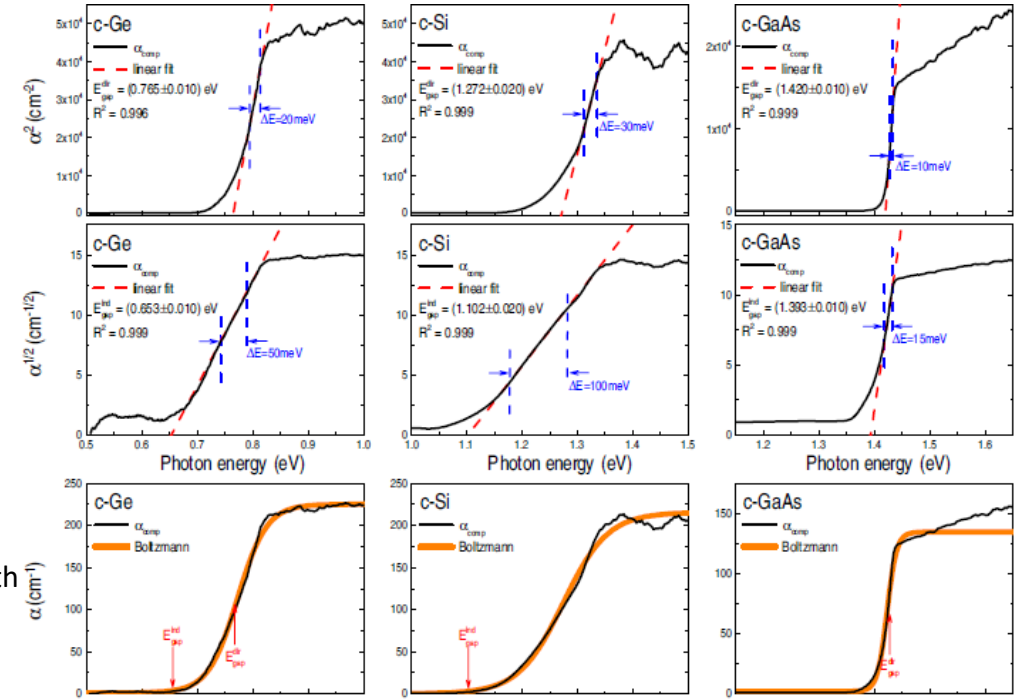
I. Hamberg, C. G. Granqvist, K. -F. Berggren, B. E. Sernelius, and L. Engström, Band-gap widening in heavily Sn-doped In2O3, *Phys. Rev. B* 30 (1984) 3240, https://doi.org/10.1103/PhysRevB.30.3240
The overview of other mathematical expressions taken form the lecture of Ramunas Nedzinskas lectrue, ZnMgO thin films for deep ultraviolet applications: structural and optical approach, 17.02.2021

EXAMPLE

(1) limited energy ranges (ΔE ≤ 100 meV) provids good linear fits
(2) Both direct and indirect E_{gap} values can be achieved from the α^2 and $\alpha^{1/2}$ *versus* E plots.

Whole process (including graphical representation, fitting range, and *goodness-of-fit*) is susceptible to the operator's intervention.

Sigmoid-Boltzmann function is simple and consistent with the optical processes regarding the experimental determination of E_{gap}.

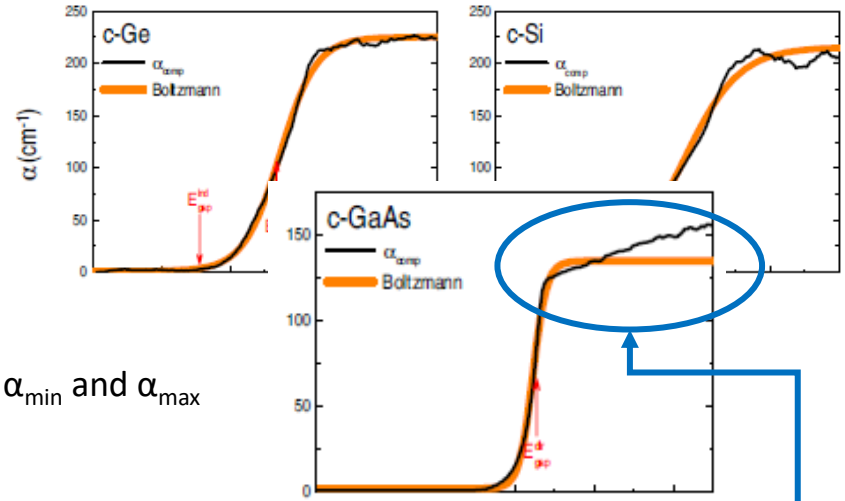


A. R. Zanatta, Revisiting the optical bandgap of semiconductors and the proposal of a unified methodology to its determination, Scientific Reports | (2019) 9:11225 | https://doi.org/10.1038/s41598-019-47670-y

UNIFIED METHODOLOGY: SIGMOID-BOLTZMANN FUNCTION

SIGMOID-BOLTZMANN FUNCTION: SBF

$$\alpha(E) = \alpha_{max} + \frac{\alpha_{min} - \alpha_{max}}{1 + \exp\left(\frac{E - E_0^{Boltz}}{\delta E}\right)}$$

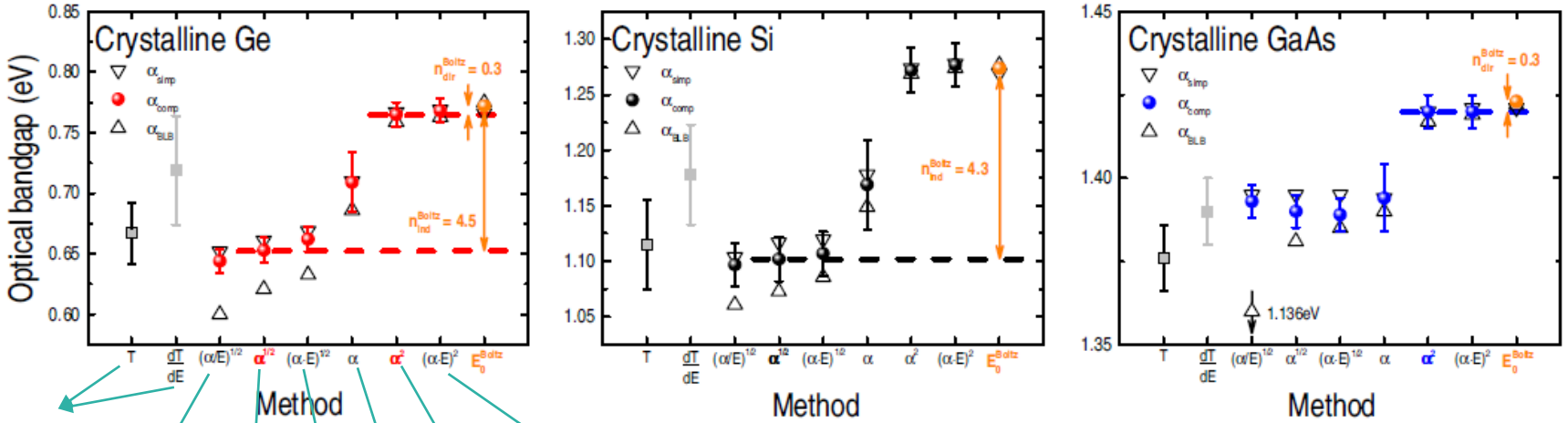


α_{min} (α_{max}) - minimum (maximum) absorption coefficient
E_0^{Boltz} - energy coordinate at which α is halfway between α_{min} and α_{max}
δE - associated with the slope of the sigmoid curve

Advantages:
- Simple
- Comprise ~500 meV energy range (instead of only ~100 meV in case of linear fits)

Disadvantages: provides good fit as long as
- Reproduced a high portion of the α(E) spectrum
- variables $\alpha_{min,max}$, E_0^{Boltz}, and δE have little uncertainty
  ⇒some deviations at high photon energies

COMPARISON OF DIFFERENT METHODS



Extrapolation (*energy derivative*) of the transmittance curve T (*dT/dE*)

Cody's bandgap

Indirect Egap

Tauc's bandgap

Extrapolation of α(E)

Direct Egap

Inappropriate (but extensively applied) version of the Tauc's bandgap

- Cody's indirect, and Tauc's optical bandgaps are almost the same
- $\alpha_{BLB}(E)$ data yields underestimated E_{gap}'s
- E_0^{Boltz} values provided by the $\alpha_{BLB}(E)$, $\alpha_{simp}(E)$, and $\alpha_{comp}(E)$ spectra are identical

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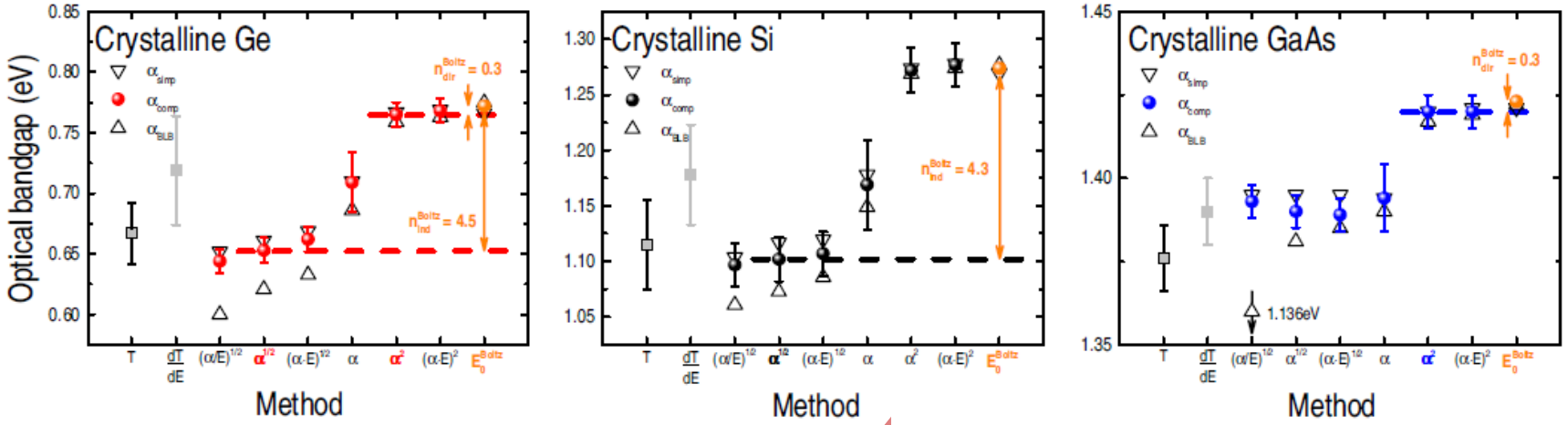

Due to the (1) second-order (phonon-assisted) nature of the optical transitions and (2) of the omission of the light reflection contributions,

E_0^{Boltz} values show good emphasizes and suitability in determining the E_{gap} of crystalline semiconductirors.

- Cody's indirect, and Tauc's optical bandgaps are almost the same
- $\alpha_{BLB}(E)$ data yields underestimated E_{gap}'s
- E_0^{Boltz} values provided by the $\alpha_{BLB}(E)$, $\alpha_{simp}(E)$, and $\alpha_{comp}(E)$ spectra are identical

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SIGMOID-BOLTZMANN FUNCTION

Numerous experimental results suggests existance of

- Central energy E_0^{Boltz} around which most of the optical transitions take place
- Its corresponding distribution δE ownes the differences in the nature of the bandgaps, presence of disorder etc.

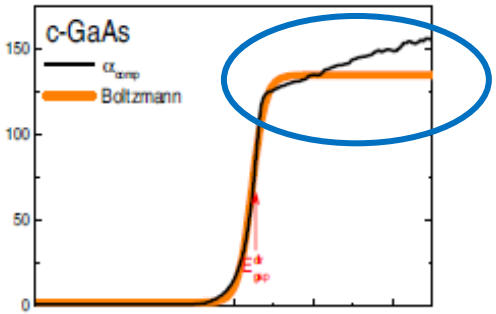
$$\mathrm{E}_{\mathrm{gap}}^{\mathrm{Boltz}} = \mathrm{E}_0^{\mathrm{Boltz}} - \mathrm{n}_{\mathrm{dir-ind}}^{\mathrm{Boltz}} \times \delta E$$

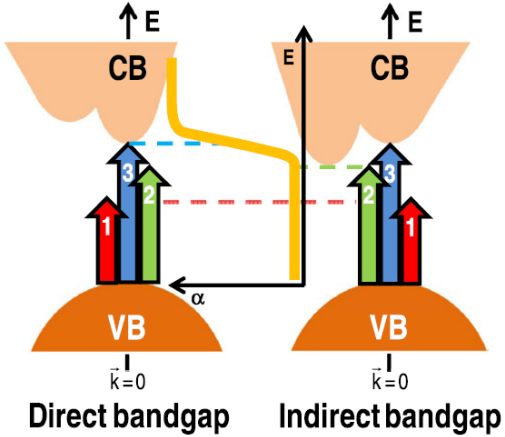
Onsets:

$n_{dir}^{Boltz} \sim 0.3 \quad n_{amorp}^{Boltz} \sim 3.6$

$n_{indir}^{Boltz} \sim 4.3$

E_{gap}'s with an accuracy (absolute error) below 10 meV





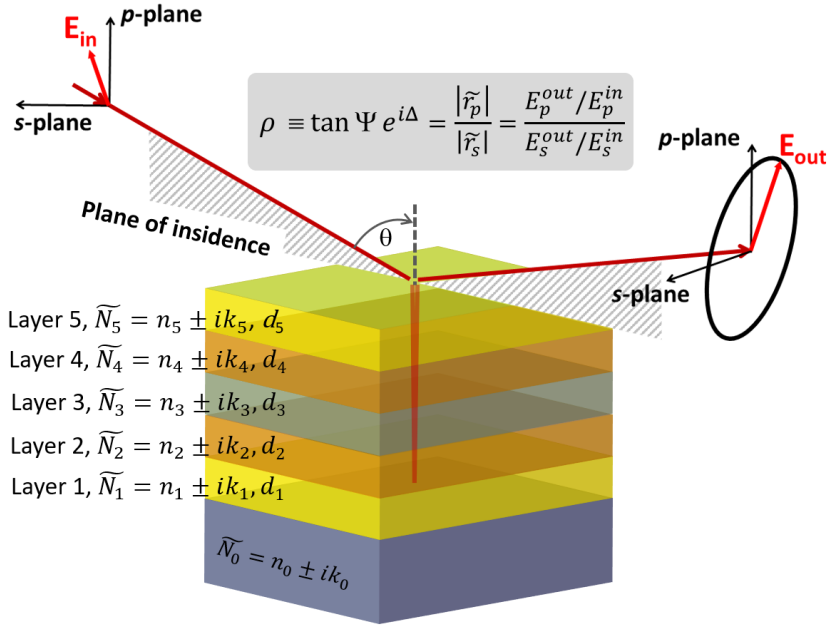
1 - below bandgap (no absorption)
2 - absorption onset (due to defects and/or phonon-assisted processes)
3 - high absorption edge (maximum of the optical absorption rate)

A. R. Zanatta, Scientific Reports 9 (2019) 11225, https://doi.org/10.1038/s41598-019-47670-y

M. Zubkins, J. Gabrusenoks, G. Chikvaidze, I. Aulika, J. Butikova, R. Kalendarev, L. Bikse, "Amorphous ultra-wide bandgap ZnO_x thin films deposited at cryogenic temperatures", J. of Applied Physics 128 (2020) 215303, https://doi.org/10.1063/5.0028901

DIRECT FIT OF COMPLEX DIELECTRIC FUNCTION

REFLECTION, TRANSMISSION AND MAIN ELLIPSOMETRIC ANGLE FITTING



$$\tan\Psi e^{i\Delta} = \rho(\widehat{N_0}, \widehat{N_1}, \widehat{N_2}, \widehat{N_3}, \widehat{N_4}, \widehat{N_5}, d_1, d_2, d_3, d_4, d_5, \lambda, \theta, t, V, T)$$

Fresnel reflection and transmission coefficients

$$r_s = \frac{\sin(\varphi_2 - \varphi_1)}{\sin(\varphi_2 + \varphi_1)} = \frac{N_1 \cos\varphi_1 - \sqrt{N_2^2 - N_1^2 \sin^2\varphi_1}}{N_1 \cos\varphi_1 + \sqrt{N_2^2 - N_1^2 \sin^2\varphi_1}} \equiv \tan\psi_s \exp(i\Delta_s)$$

$$r_p = \frac{\tan(\varphi_2 - \varphi_1)}{\tan(\varphi_2 + \varphi_1)} = \frac{N_1/\cos\varphi_1 - N_2/\sqrt{1 - (N_1/N_2)^2 \sin^2\varphi_1}}{N_1/\cos\varphi_1 + N_2/\sqrt{1 - (N_1/N_2)^2 \sin^2\varphi_1}} \equiv \tan\psi_p \exp(i\Delta_p),$$

$$t_s = \frac{2\sin\varphi_2 \cos\varphi_1}{\sin(\varphi_2 + \varphi_1)} \qquad t_p = \frac{2\sin\varphi_2 \cos\varphi_1}{\sin(\varphi_2 + \varphi_1)\cos(\varphi_2 - \varphi_1)}$$

$$\varepsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$

$$\varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega'$$

H. G. Tompiks and E. A. Irene, Handbook of ellipsometry, William Andrew publishing, Springer (2005) ISBN 0-8155-1499-9

TAUC-LORENTZ & CODY-LORENTZ OSC

$$\varepsilon_{T-L}(E) = \varepsilon_{n1} + i\varepsilon_{n2} \qquad \text{where}$$

$$\varepsilon_{n2} = \left[\frac{Amp_n Eo_n Br_n (E - Eg_n)^2}{\left(E^2 - Eo_n{}^2\right)^2 + Br_n{}^2 E^2} \cdot \frac{1}{E}\right] \qquad E > Eg_n$$

$$\varepsilon_{n2} = 0 \qquad E \le Eg_n$$

$$\varepsilon_{n1} = \frac{2}{\pi} P \int_{Eg_n}^{\infty} \frac{\xi \varepsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi \qquad \text{[a], [b]}$$

$\varepsilon_{n\_C\text{-}L} = \varepsilon_{n1} + i\varepsilon_{n2}$, where

$$\varepsilon_2(E) = \begin{cases} \frac{E_1}{E} \exp\left(\frac{(E - E_{gn} - E_{tn})}{E_{un}}\right); & 0 < E \le (E_{gn} + E_{tn}) \\ G(E)L(E) = \frac{(E - E_{gn})^2}{(E - E_{gn})^2 + E_{pn}{}^2} \cdot \frac{A_n E_{on} \Gamma_n E}{\left[(E^2 - E_{on}^2)^2 + \Gamma_n{}^2 E^2\right]}; & E > (E_{gn} + E_{tn}) \end{cases}$$

$$E_1 = (E_{gn} + E_{tn}) G(E_{gn} + E_{tn}) L(E_{gn} + E_{tn})$$

G(E)≡near-bandgap function L(E)≡Lorentz oscillator function

$$\varepsilon_{n1} = \frac{2}{\pi} P \int_0^{\infty} \frac{\xi \varepsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi$$ (This is an integral in two parts*)

n ≡ *oscillator #*

Fit parameters (units):

- *Amp**n** (eV),*
- *Eo**n** (eV),*
- *Br**n** (eV)*
- *Eg**n** (eV)*

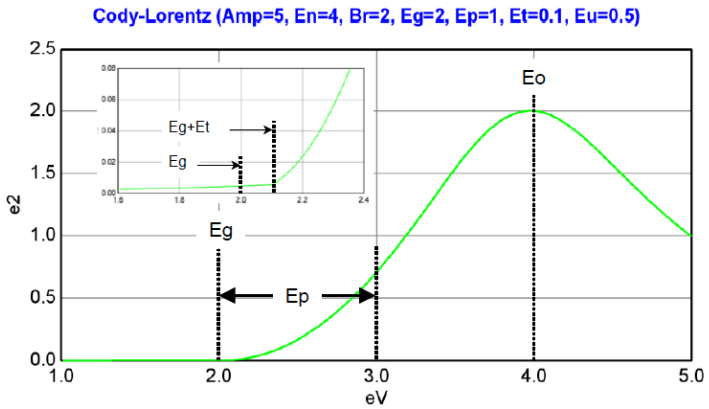
Tauc Absorption Formula: $\varepsilon_2(E) \propto [(E - Eg)^2/E^2]$

Cody Absorption Formula: $\varepsilon_2(E) \propto (E - Eg)^2$

n ≡ *oscillator #*

Fit parameters:

- *Amp**n** (eV)*
- *Br**n** (eV)*
- *Eo**n** (eV)*
- *Eg**n** (eV)*
- *Ep**n** (eV)*
- *Et**n** (eV)*
- *Eu**n** (eV)*



H. G. Tompiks and E. A. Irene, Handbook of ellipsometry, William Andrew publishing, Springer (2005) ISBN 0-8155-1499-9

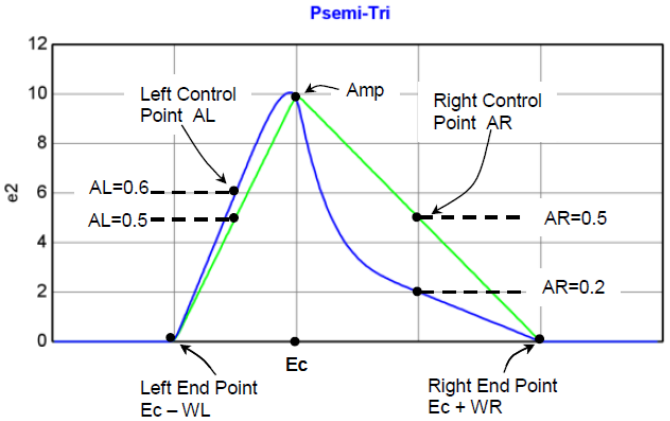
JOHS-HERZINGER GENERALIZED CRITICAL POINT MODEL

JOHS-HERZINGER GENERALIZED CRITICAL POINT MODEL - JHGCPM

This is oscillator model combines highly flexible function shape with Kramer-Kronig consistent properties.

$$\varepsilon(E) = 1 + i\sum_{j=1}^{m}\int_{E_{\min}}^{E_{\max}} W_j(E')\Phi_j(E, E', \sigma_j)dE' + i\sum_{j=m+1}^{j=m+P} A_j\int_0^{\infty}\delta(E' - E_j)\Phi_j(E, E', \sigma_j)dE'$$

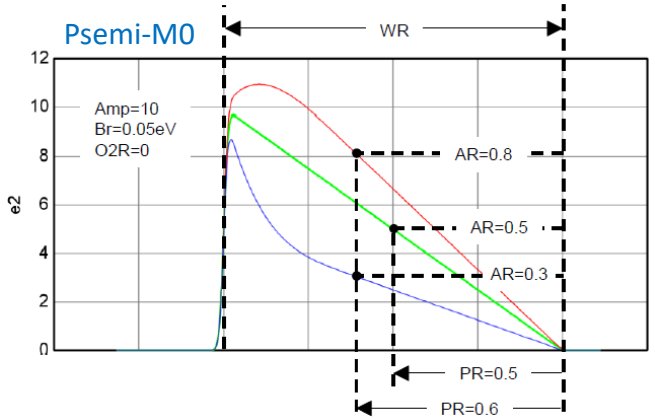
The ε_2 part consists of four polynomials splines connected end-to-end. Each spline connects smoothly with the adjacent spline, forming a single, continues function:



n ≡ oscillator #

Fit parameters (units):

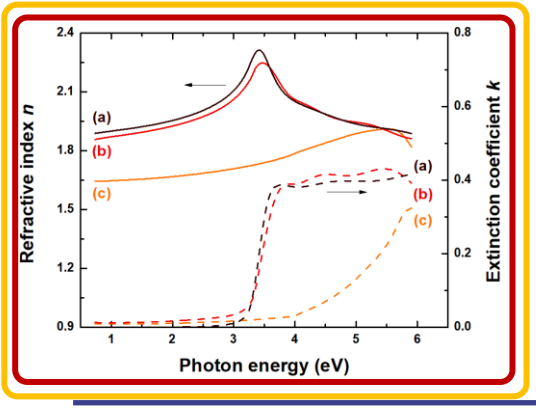
- *Amp**n** (no units),*
- *Br**n** (eV),*
- *Ec**n** (eV),*
- *WL**n** (eV)*
- *WR**n** (eV)*
- *AL**n** (no units)*
- *AR**n** (no units)*

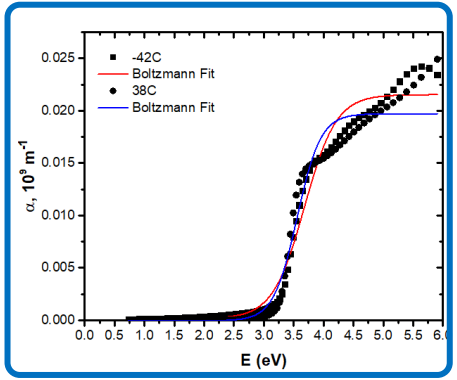


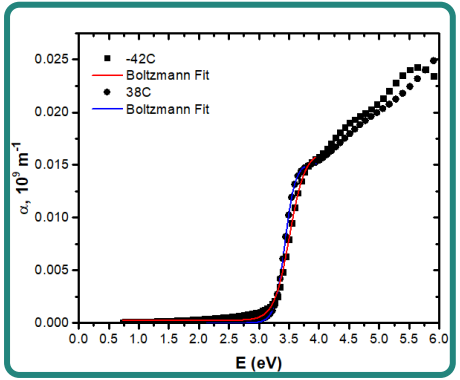
C. M. Herzinger, B. D. Johs, patent "Dielectric functionparametric model, and method of use", 1998, US005796983A
P. Petrik, Parameterization of the dielectric function of semiconductor nanocrystals, Physica. B, Condensed Matter 46:46 (2014) 2, https://doi.org/10.1016/j.physb.2014.03.065

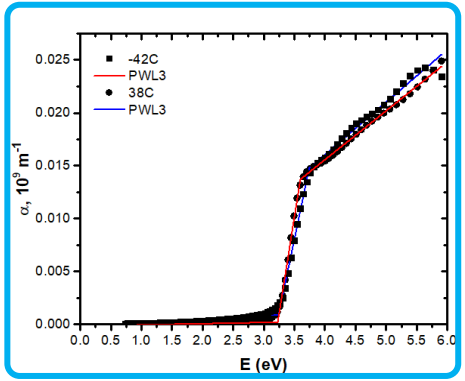
EXAMPLE: ZnO_2 FABRICATED AT CRYOGENIC *T*

Depos. T (°C)	Transmission data	Ellipsometry data				
	E_g (eV)	E_{Cody} (eV)	E_{gap} (eV) applying JHGCPM	E_{gap} (eV) applying SBF to whole α(E)	E_{gap} (eV) applying SBF to selected α(E)	E_{gap} (eV) applying PWL3 to α(E)
+38	~ 3.43	3.117 ± 0.002	3.49 ± 0.06	3.50 ± 0.20	3.41 ± 0.09	3.41 ± 0.02
-42	~ 3.41	3.191 ± 0.022	3.39 ± 0.02	2.73 ± 0.27	3.05 ± 0.13	3.38 ± 0.01
-103	~ 4.97	4.65 ± 0.40	4.76 ± 0.24	-	-	4.92 ± 0.01









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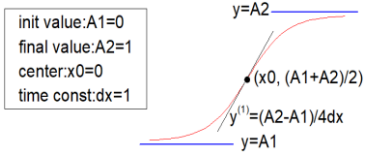
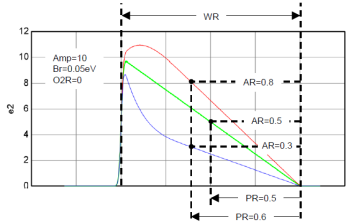
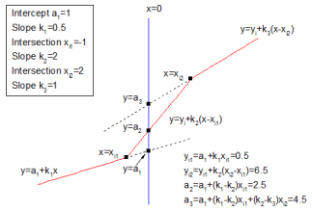
CONCLUSION







Boltzmann functions provides good fits as long as:

- they are reproduced at high portion of the α(E) spectrum, and
- they presented the variables $\alpha_{min,max}$, E_0^{Boltz}, and δE with little uncertainty

Drawbacks: some deviations at high photon energies may appear for materials, which absorption coefficient increases with increase of $E > E_0^{Boltz}$.

Johs-Herzinger generalized critical point model provides good fits as long as

- they are reproduced at high portion of the α(E) spectrum

Drawbacks: complex dielectric function, software of certain complexity are needed

Alternatives:

- Boltzmann function: in case the absorption coefficient increases with increase of $E > E_0^{Boltz}$, narrower spectral region should be analysed avoiding the «critical» regions of absorption.
- Piecewise linear three point method can be considered a relatively good comprise, too.

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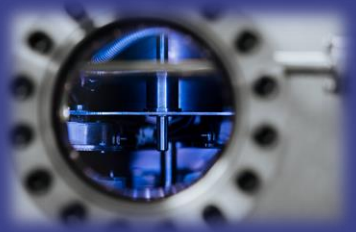
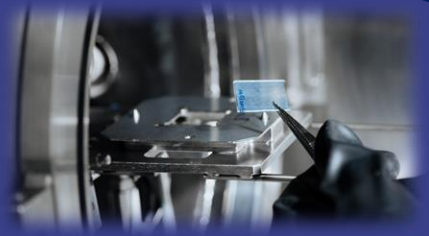
CAMART²

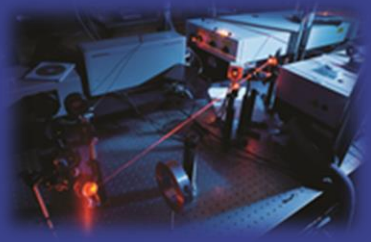
FLPP
FUNDAMENTAL AND APPLIED RESEARCH PROJECTS

Latvian Council of Science





Thin Films Laboratory



Laboratory of Spectroscopy

Thank you for your attention & welcome to collaborate!

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