Modeling of Thin-Film $Cu(In,Ga)Se_2$ Solar Cells

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Purpose of the work

- To use numerical simulations to investigate the characteristics of thin film CIGS ($Cu(In,Ga)Se_2$) solar cells

- To develop a physics-based compact models

- To investigate the effects of thickness, composition, doping and interface states of the $Zn_{1-x}Mg_xO$ buffer-window layer for Cd-free thin film $Cu(In,Ga)Se_2$ (CIGS) solar cells

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Agenda

- Introduction
- Numerical model
- Compact model
- Cd-free CIGS solar cell
- Conclusions

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- **Introduction**
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- Compact model
- Simulation of damp heat degradation
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Introduction

- Thin-film solar cells can reduce photovoltaic cost and help spreading its use
- CIGS is a promising material able to achieve conversion efficiency as high as 20% (despite its polycrystalline structure)
- The presence of toxic cadmium poses environmental concerns about waste disposal at the end of module life
- $Zn_{1-x}Mg_xO$ is suitable to replace CdS (wide bandgap, i.e. low absorption, and convenient band alignment with the CIGS absorber)

CIGS solar cell structure

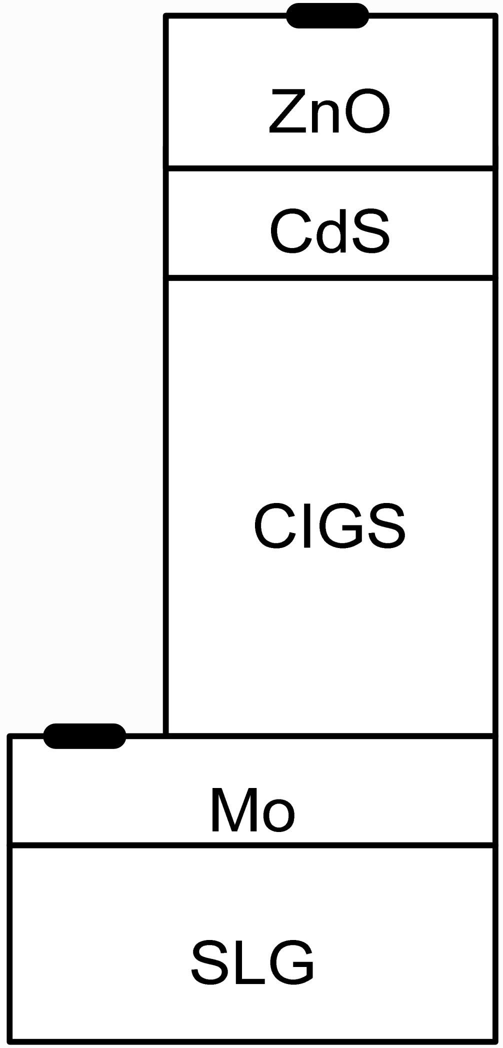
n-doped ZnO window layer

n-doped CdS buffer layer

p-doped CIGS absorber

Molybdenum back-contact

Soda lime glass (SLG)



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Numerical model: electric behavior

- The Poisson, electron and hole continuity and drift-diffusion equations are solved self-consistently

- Fermi-Dirac statistics

- Non-radiantive Shockley-Read-Hall recombination model
- Simulations are performed using Synopsys Sentaurus

Numerical model: optical behavior

- Complex refractive index: $\tilde{n} = n + ik$
- Normal incidence: $Z = \tilde{n}$

$\hat{y} \longrightarrow$

$I_{inc}(\lambda) \longrightarrow$

$a(\lambda) \longrightarrow$ $b(\lambda) \longleftarrow$

$$\begin{bmatrix} \frac{Z_\Sigma(\lambda)}{2Z_m(\lambda)} & \frac{Z_\Delta(\lambda)}{2Z_m(\lambda)} \\ \frac{Z_\Delta(\lambda)}{2Z_m(\lambda)} & \frac{Z_\Sigma(\lambda)}{2Z_m(\lambda)} \end{bmatrix} \qquad \begin{bmatrix} e^{i\frac{2\pi Z_m(\lambda) y}{\lambda}} & 0 \\ 0 & e^{-i\frac{2\pi Z_m(\lambda) y}{\lambda}} \end{bmatrix}$$

m $\qquad$ $m+1$

with:
$$Z_\Sigma(\lambda) = Z_m(\lambda) + Z_{m+1}(\lambda)$$
$$Z_\Delta(\lambda) = Z_m(\lambda) - Z_{m+1}(\lambda)$$

$$I(y,\lambda) = n(\lambda)\,|a(\lambda) + b(\lambda)|^2 I_{inc}(\lambda)$$

$$G^{opt}(y,\lambda) = \frac{4\,\pi\,k(\lambda)\,I(y,\lambda)}{h\,c}$$

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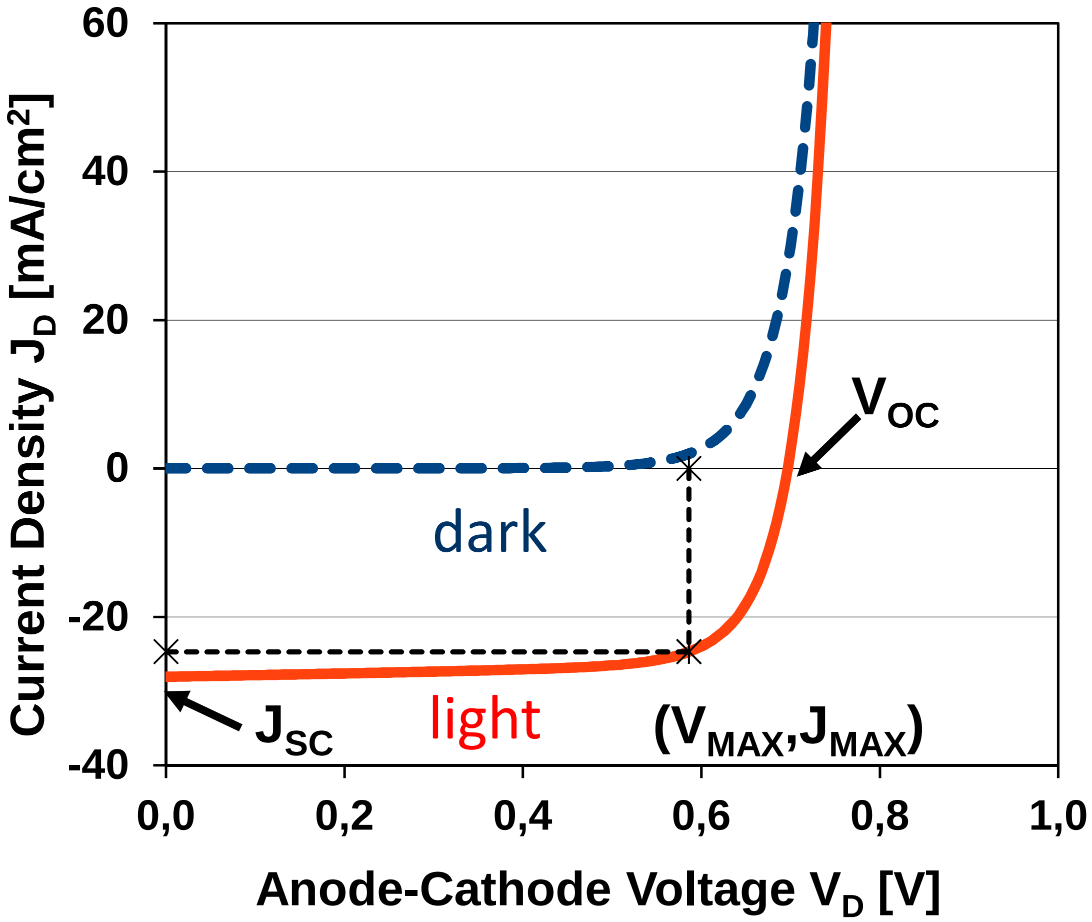
Solar cell electrical parameters



$$FF = \frac{J_{max} \cdot V_{max}}{J_{SC} \cdot V_{OC}}$$

$$\eta = \frac{J_{SC} \cdot V_{OC} \cdot FF}{P_{inc}}$$

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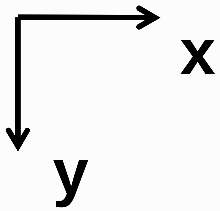
Solar cell structure

- CIGS grains: columnar
- Cu-poor GB
  →wider band-gap



- Bulk traps (mid-gap):

$N_b = 10^{12} \leftrightarrow 10^{16}$ [cm^{-3}]

- GB traps (donor):

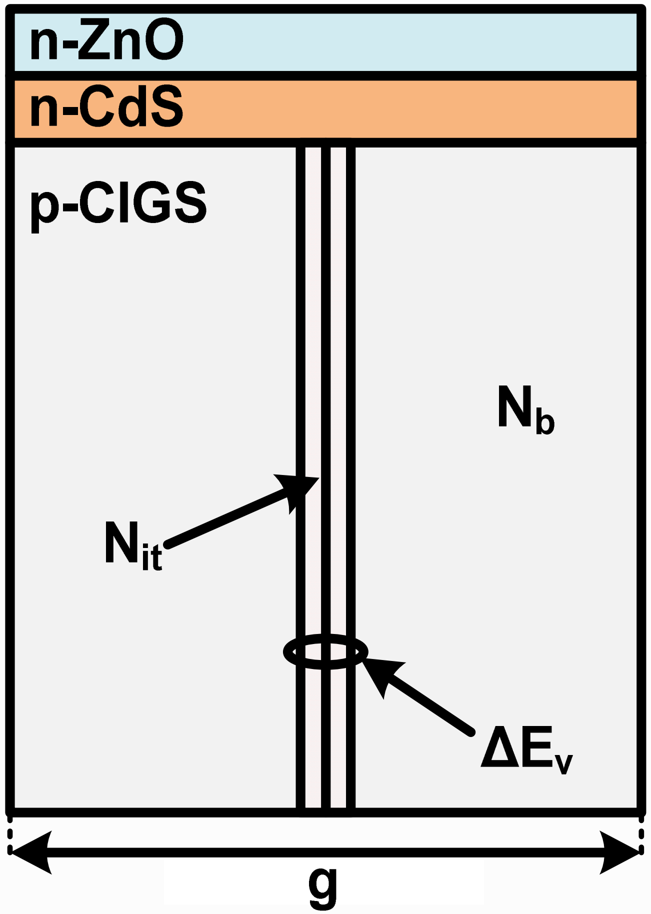
$N_{it} = 2{\cdot}10^{11} \leftrightarrow 4{\cdot}10^{12}$ [cm^{-2}]

- GB valence band discontinuity:

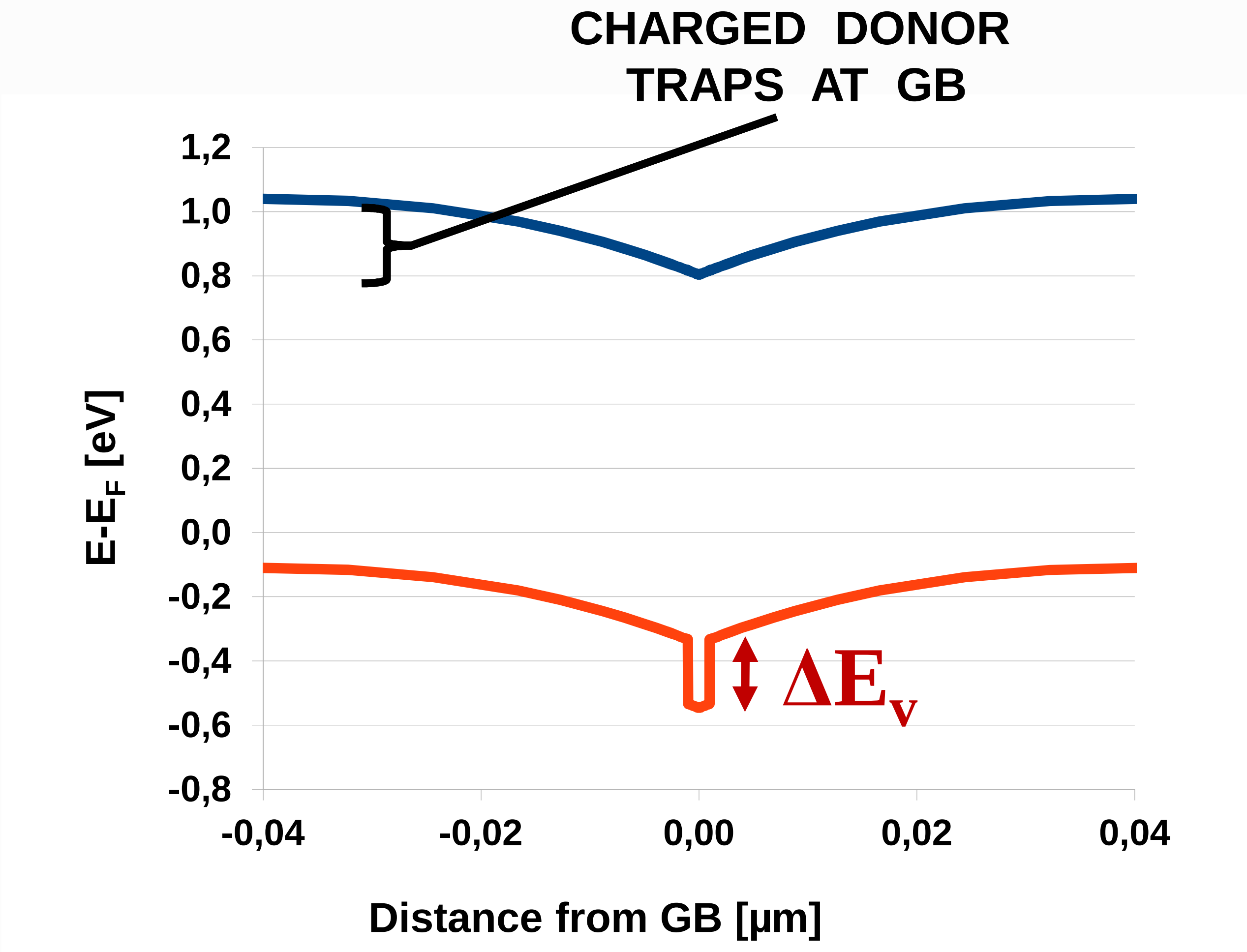
$\Delta E_v = 0 \leftrightarrow 0.4$ [eV]

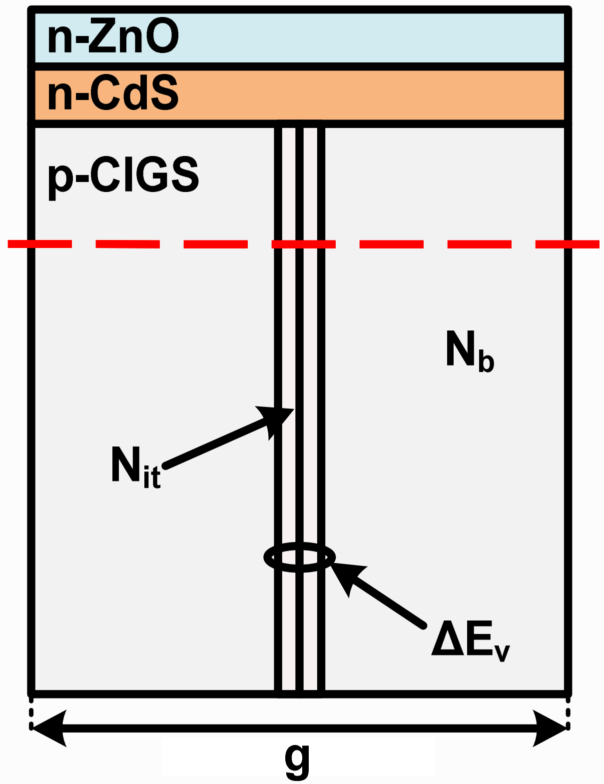
- Grain size:

$g = 0.5 \leftrightarrow 2$ [μm]

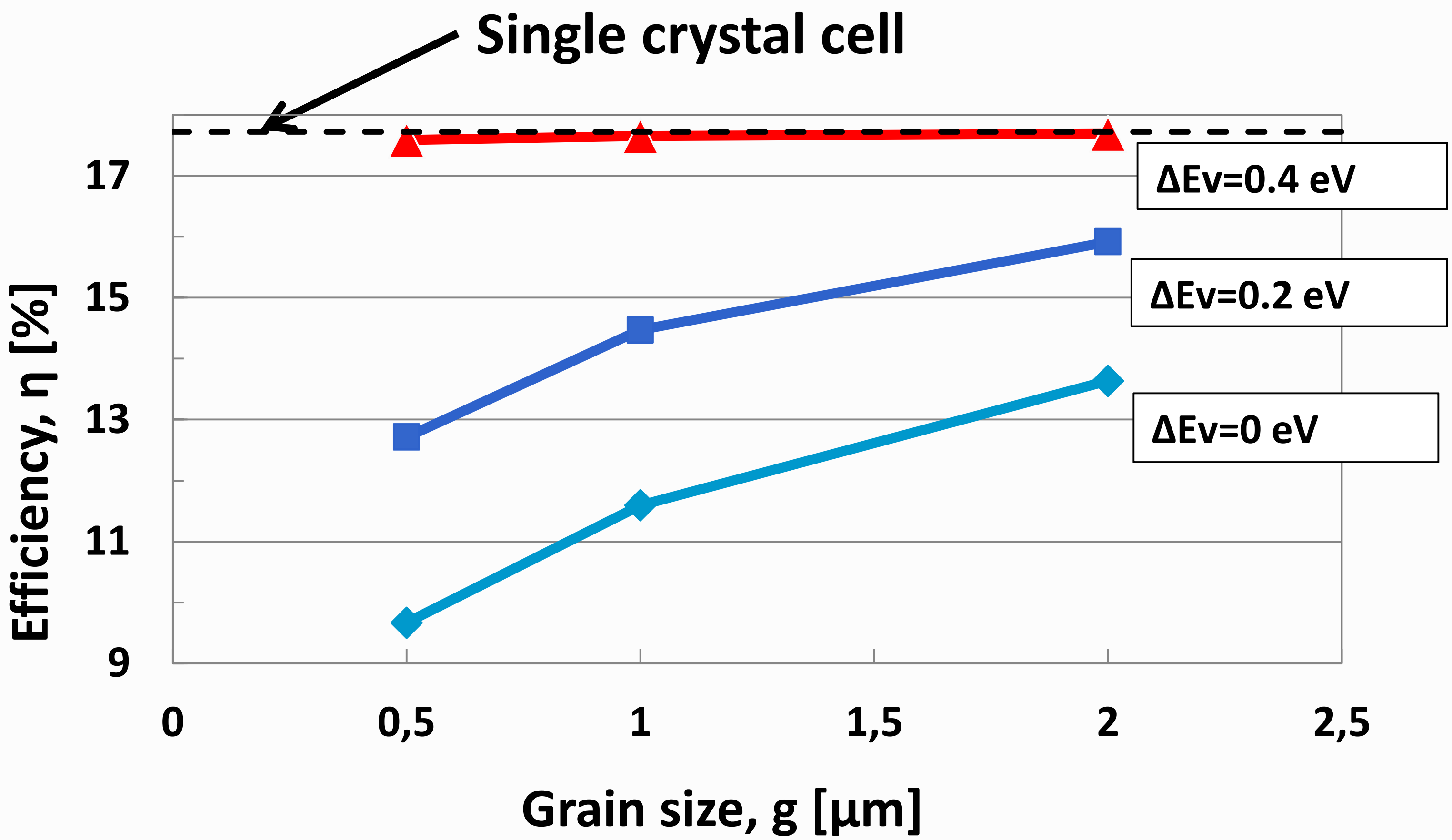


Solar cell structure





Efficiency versus grain size



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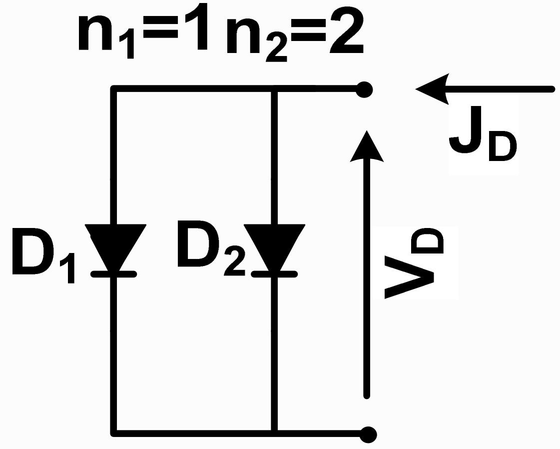
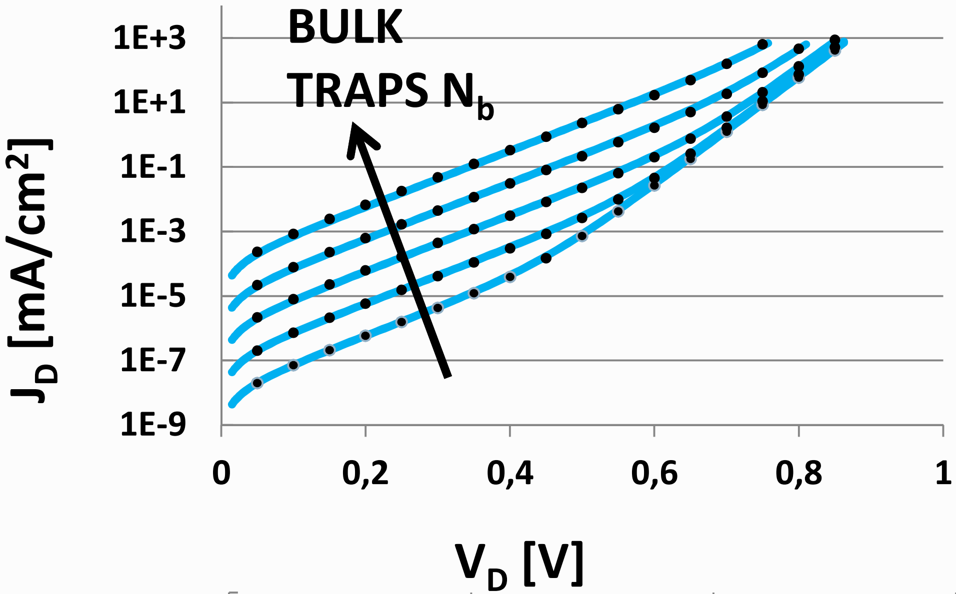
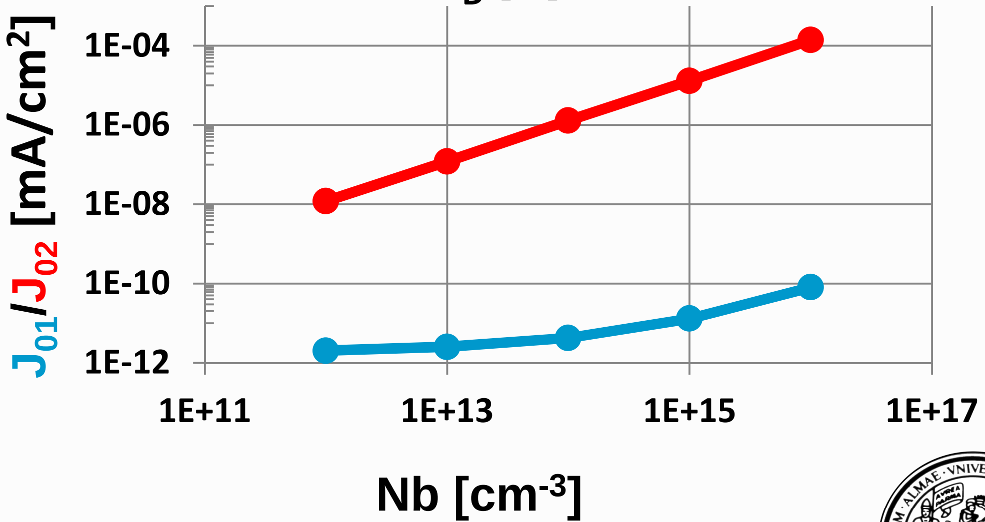
Compact model: single crystal cell



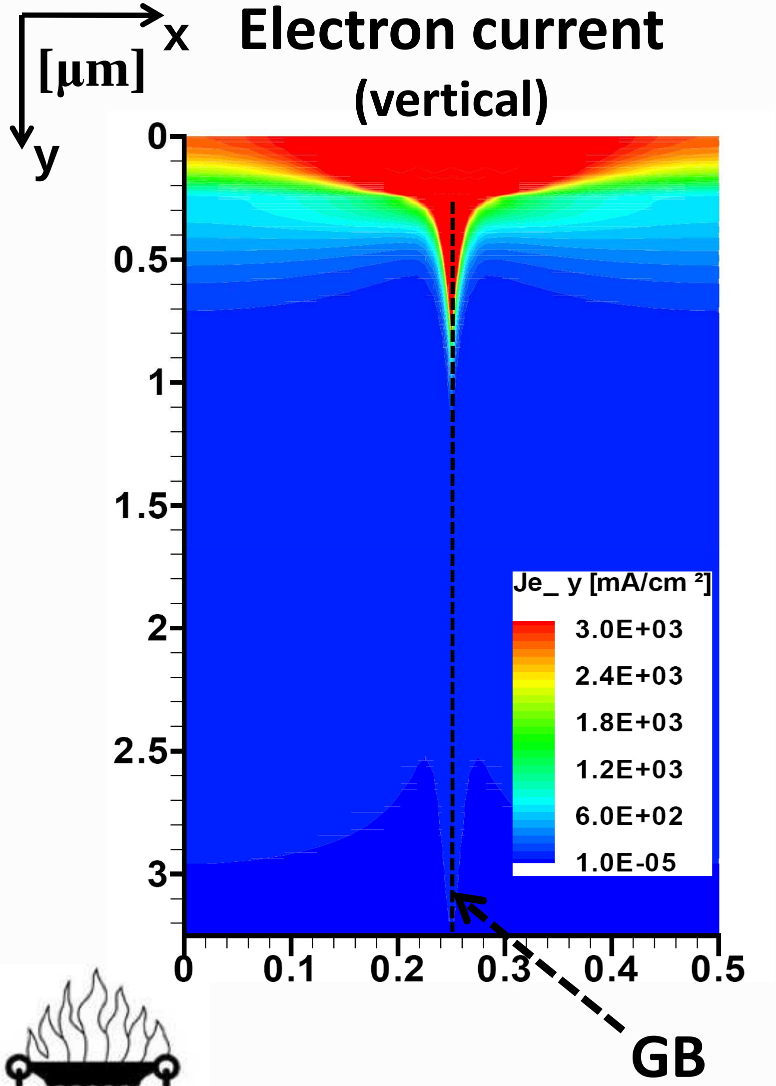


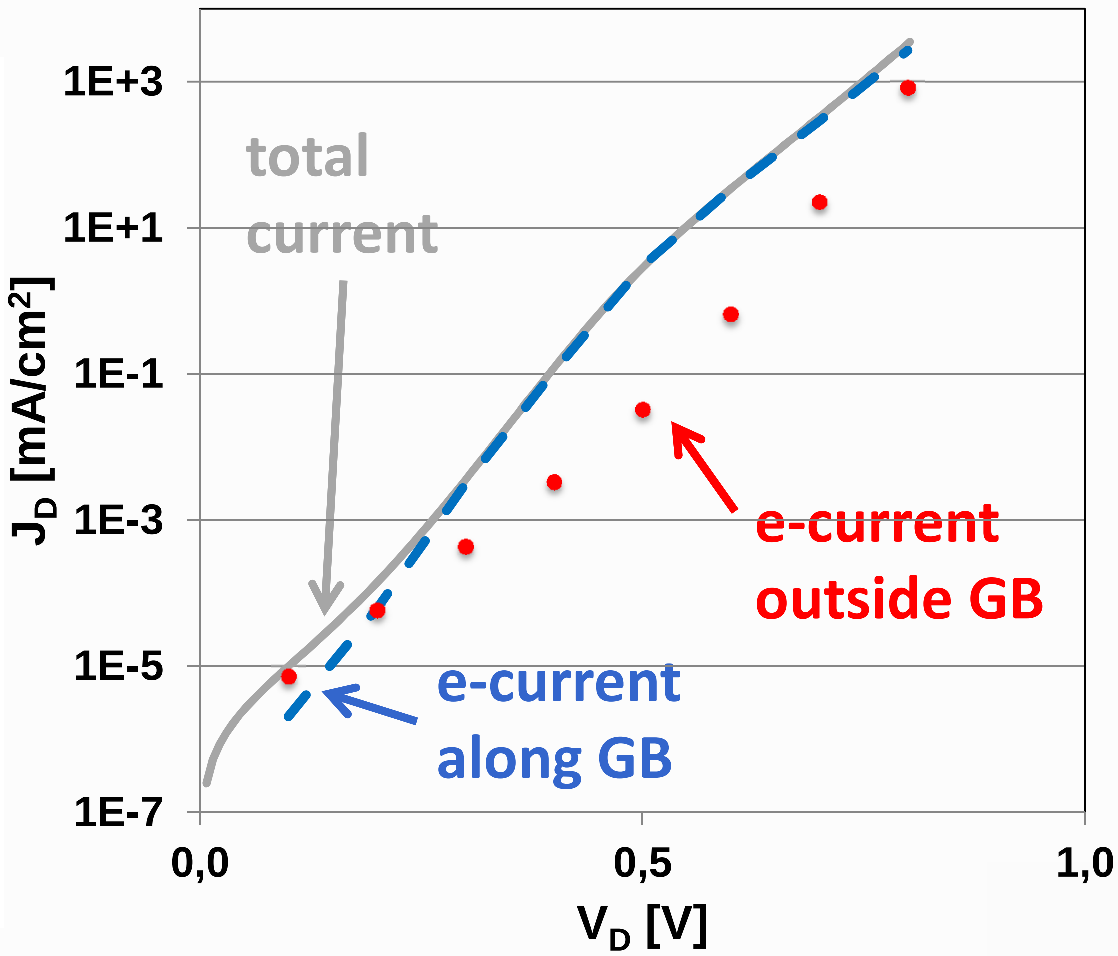
$$J_x = J_{0_x} \cdot \left(e^{\frac{q \cdot V_D}{n_x \cdot k \cdot T}} - 1\right)$$

- D_1: ideal diode current
- D_2:space-charge recombination current

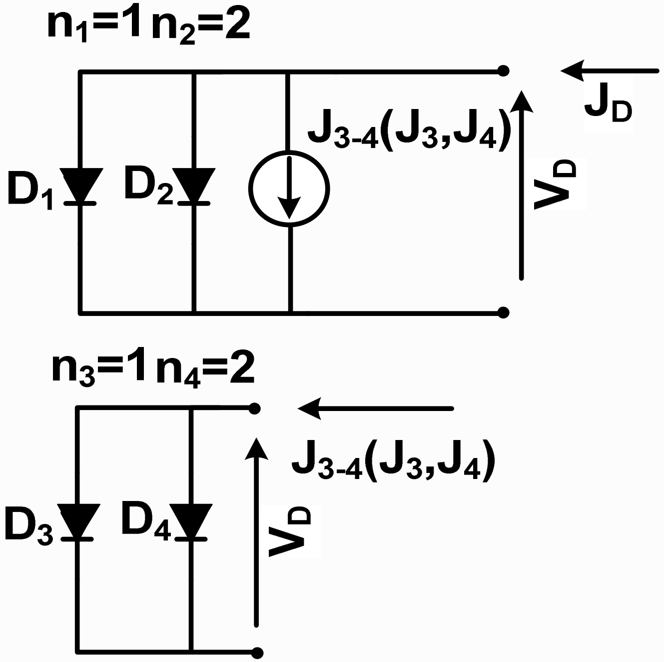


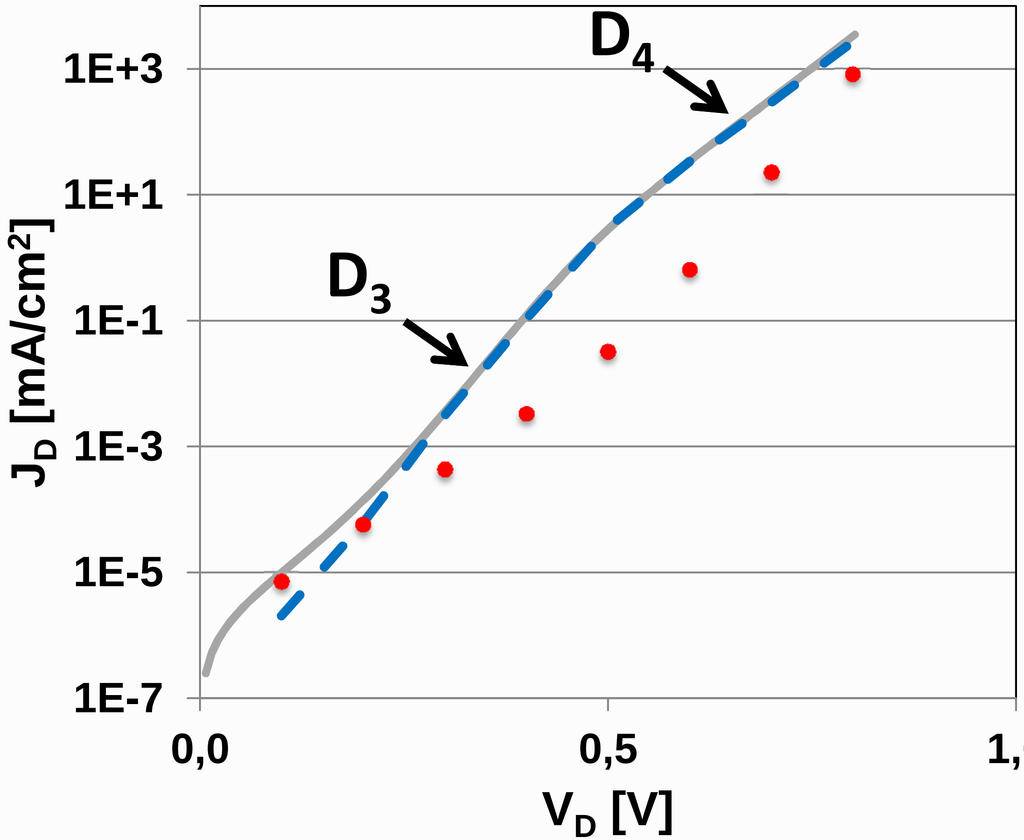
Polycrystalline cell





Compact model: polycrystalline cell





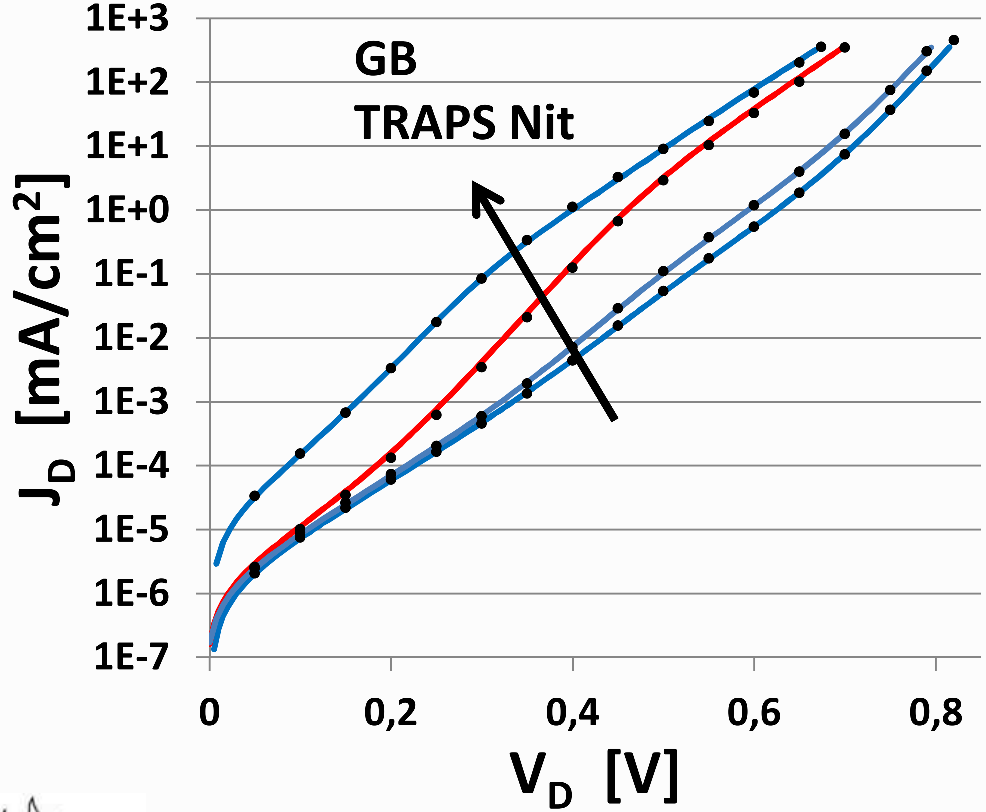
$$J_x = J_{0_x} \cdot \left(e^{\frac{q \cdot V_D}{n_x \cdot k \cdot T}} - 1\right)$$

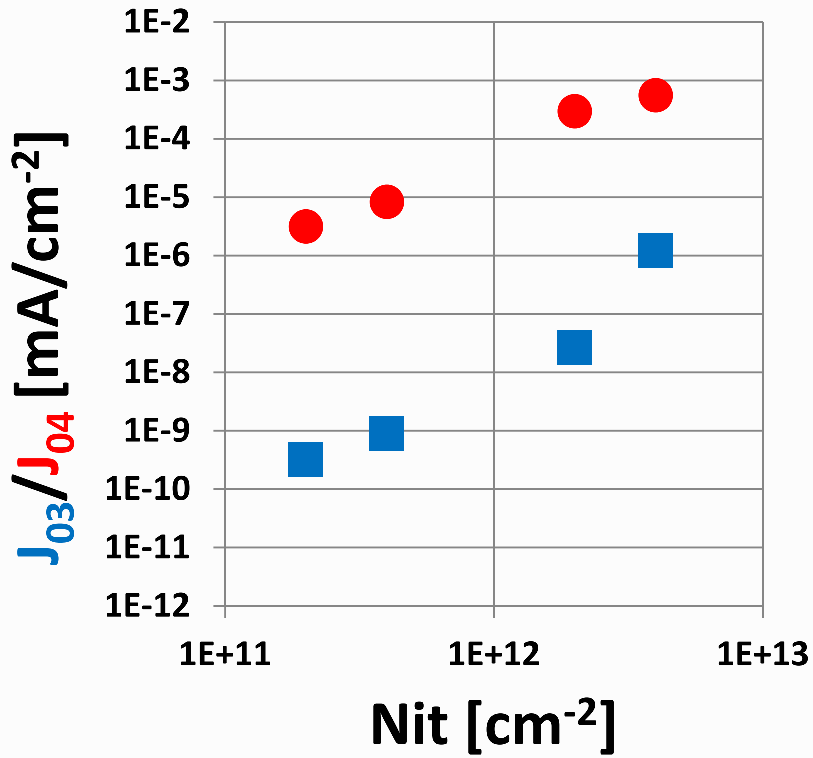
- D_3: ideal GB current
- D_4: High injection GB current

$$J_{3-4}(J_3, J_4) = \left(J_3(V_D)^{-1} + J_4(V_D)^{-1}\right)^{-1}$$

Compact model: polycrystalline cell

$N_b=10^{14}$ cm^{-3} $\Delta E_v=0$ eV g=0.5 µm





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$Zn_{1-x}Mg_xO$ properties

- Good transparency in the solar spectrum range
- Band gap (E_G) increases with increasing Mg content
- Electron affinity decreases with increasing Mg content

x = 0.19

$\chi_{CIGS} - \chi_{ZnMgO} = 0.04$ eV

$E_{G,ZnMgO} = 3.49$ eV

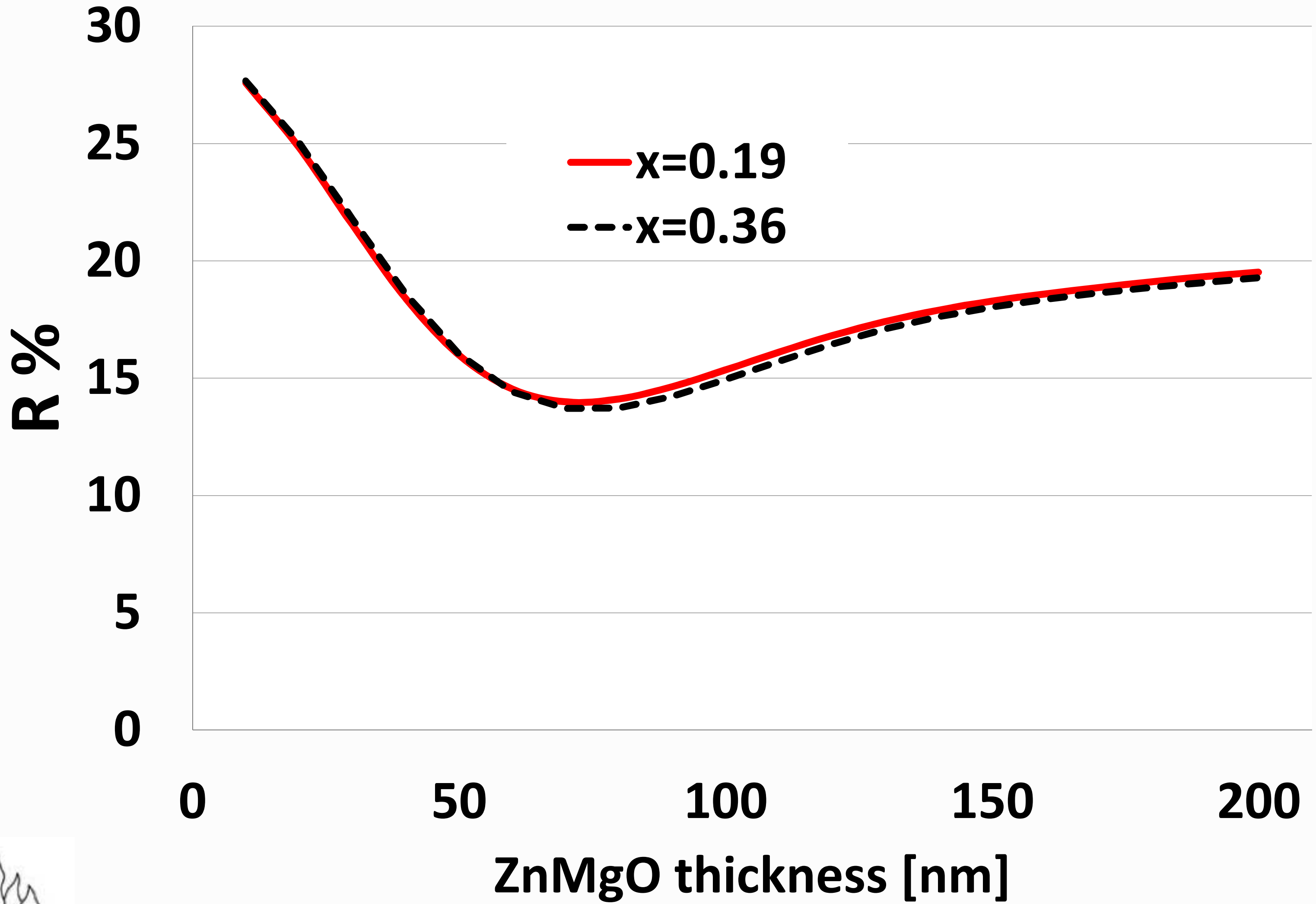
x = 0.36

$\chi_{CIGS} - \chi_{ZnMgO} = 0.22$ eV

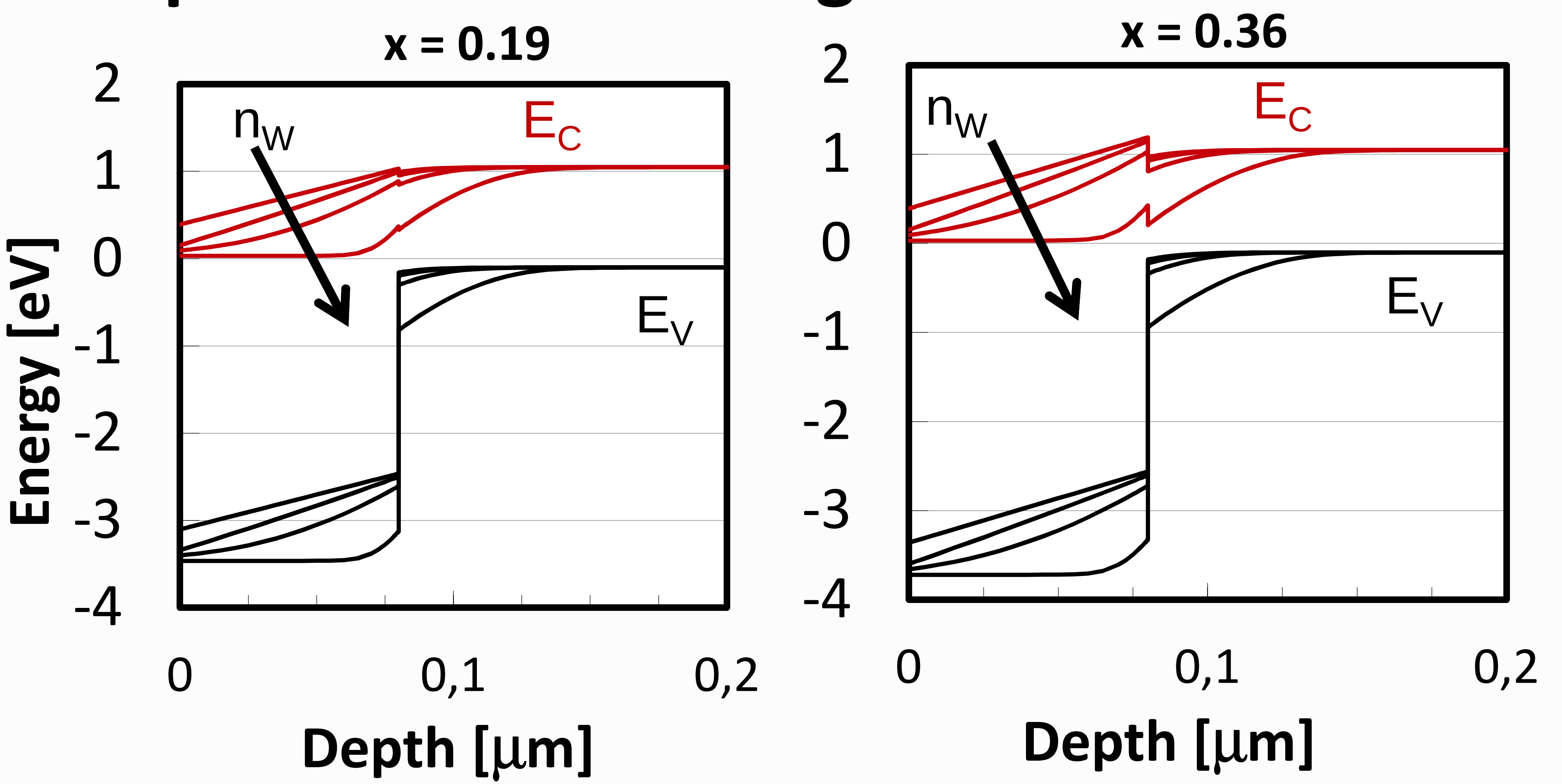
$E_{G,ZnMgO} = 3.75$ eV

$E_{G,CIGS} = 1.15$ eV

Thickness and reflectivity



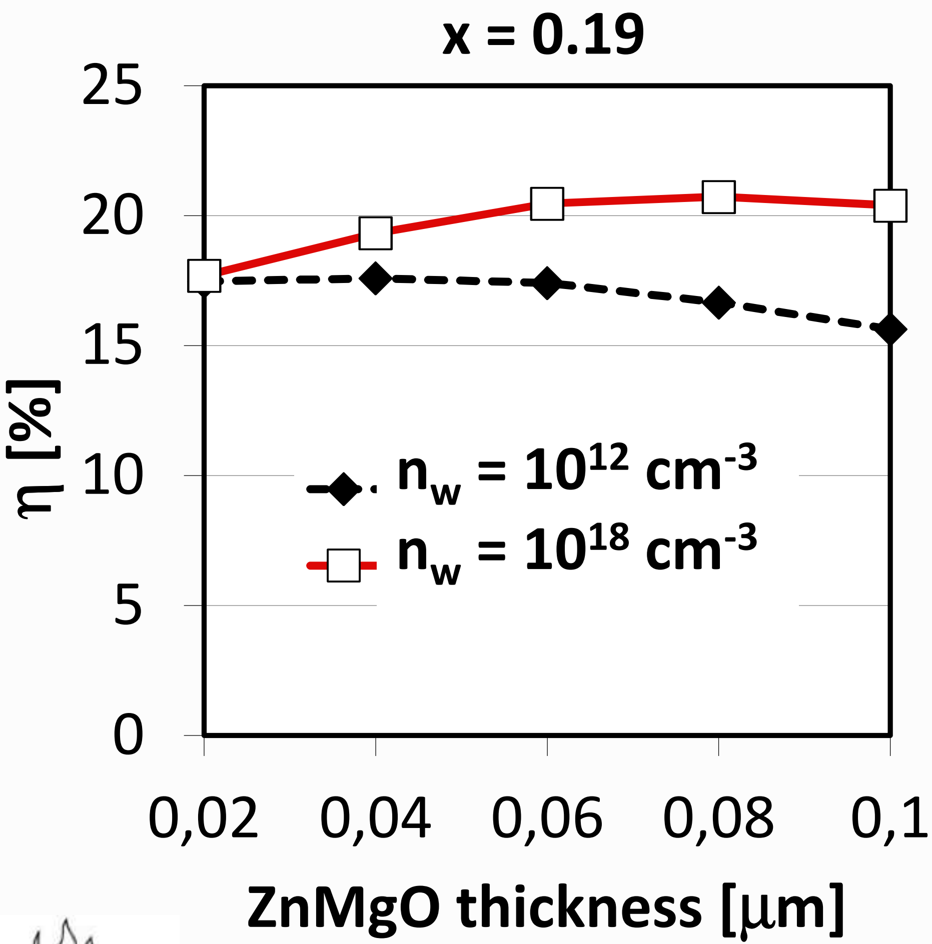
Equilibrium band diagram

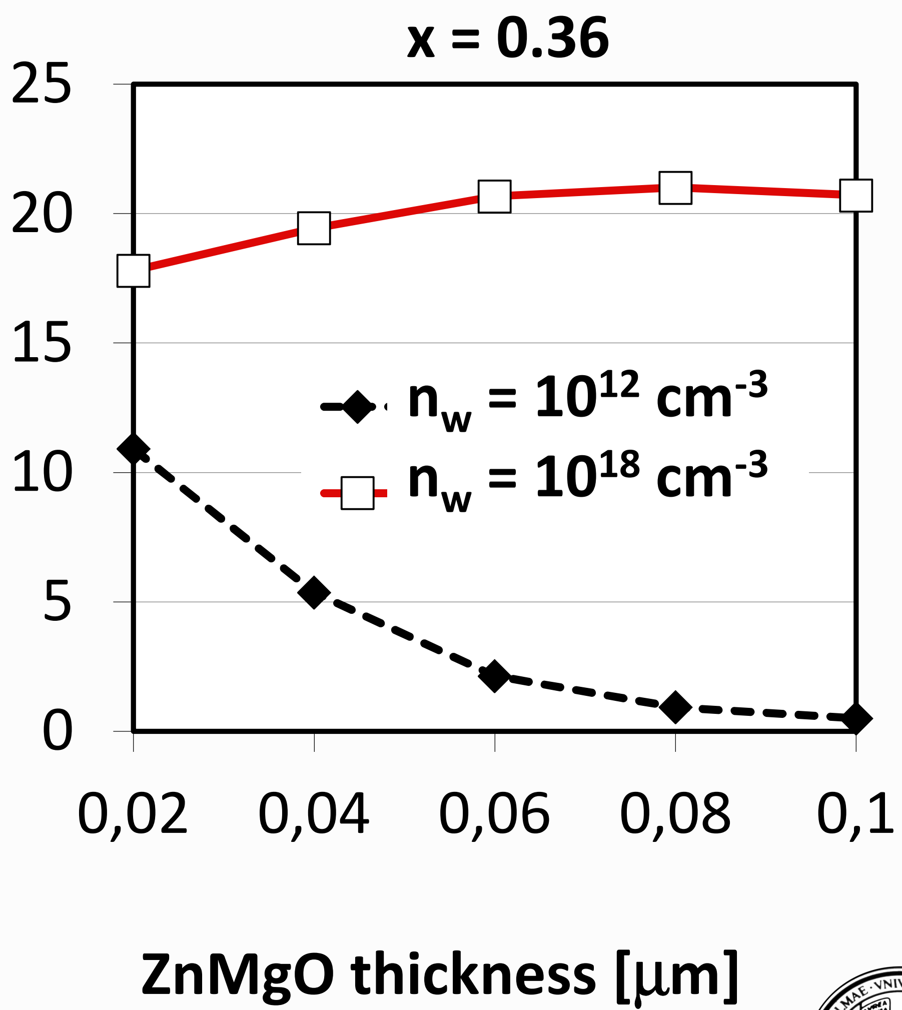


Doping: ZnMgO $n_W = 10^{12}, 10^{16}, 10^{17}, 10^{18}\ cm^{-3}$, CIGS $N_A = 3\cdot10^{17}\ cm^{-3}$

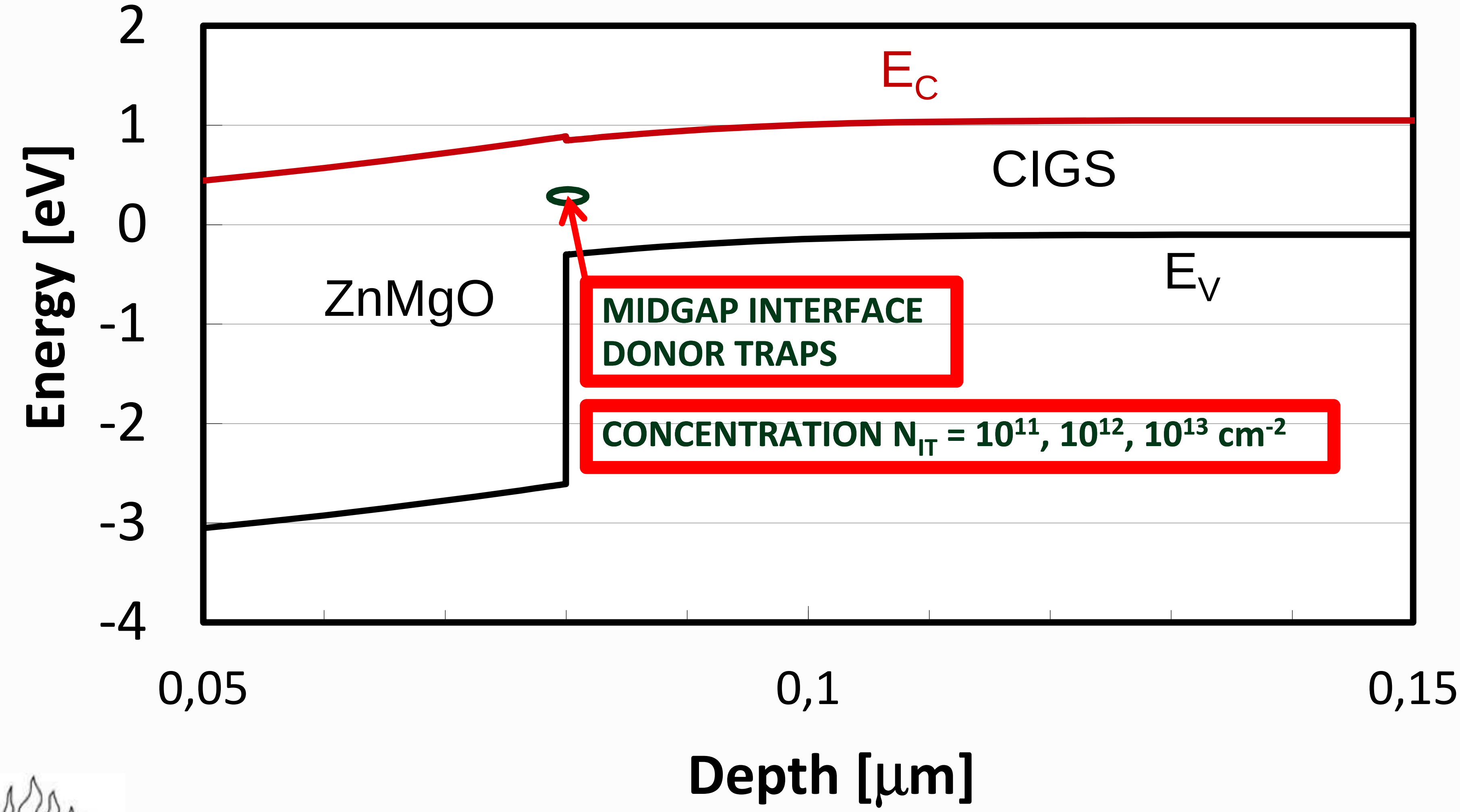
ZnMgO thickness: 80 nm

Ideal ZnMgO/CIGS interface: efficiency



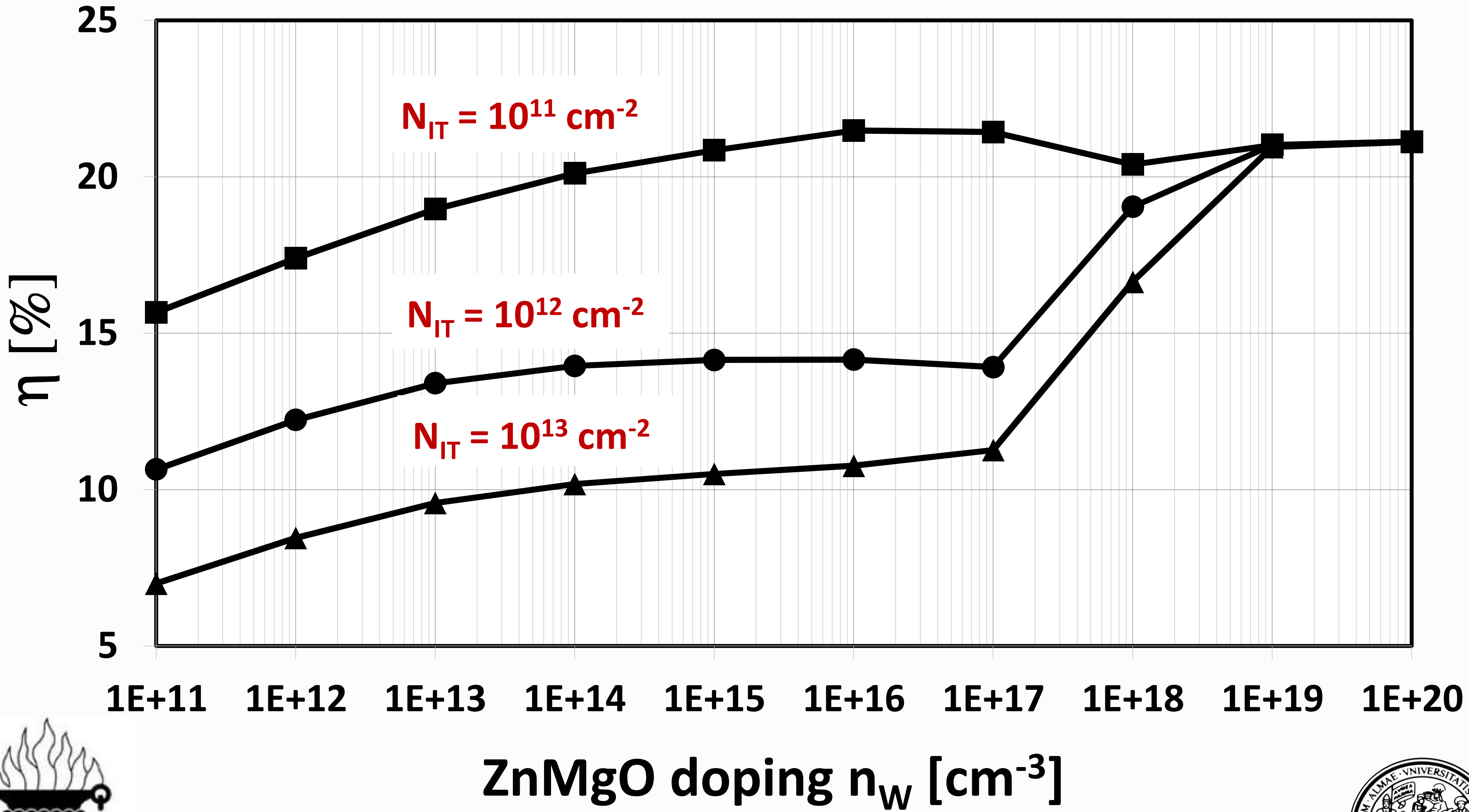


Effect of interface states



ZnMgO thickness: 80 nm, x = 0.19

Effect of interface states



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Conclusions

•CIGS electrical behavior:
Bulk traps, grain boundaries, localized band-gap variations

•Physics-based compact model of the cell in the dark:
2-diode single-crystal
4-diode polycrystalline

•Cd-free CIGS solar cell:
✓impact of ZnMgO thickness on the reflectivity
✓effects of thickness, composition, doping, traps of the ZnMgO buffer-window layer

Material parameters (poly-CIGS)

Layer	ZnO	CdS	CIGS
Eg [eV]	3.3	2.4	1.15
Doping [cm^{-3}]	$N_D = 10^{18}$	$N_D = 6 \cdot 10^{17}$	$N_A = 3 \cdot 10^{17}$
$\varepsilon/\varepsilon_0$	9	10	13.6
m_e/m_0	0.2	0.2	0.09
m_h/m_0	1.2	0.8	0.72
μ_e [$cm^2/(Vs)$]	100	100	100
μ_h [$cm^2/(Vs)$]	25	25	12.5

Bulk traps	ZnO	CdS	CIGS
Density [cm^{-3}]	10^{16}	10^{16}	10^{15}
Energy	midgap	midgap	midgap
σ_e[cm^2]	10^{-16}	10^{-15}	$2 \cdot 10^{-14}$
σ_h[cm^2]	10^{-13}	10^{-12}	$2 \cdot 10^{-14}$

GB traps	Density [cm^{-2}]	Energy [eV]	$\sigma_e = \sigma_h$ [cm^2]
Donor	$2 \cdot 10^{12}$	E_v+0.880	10^{-15}

Material parameters (ZnMgO)

Layer	CIGS	ZnMgO
Eg [eV]	1.15	3.208+1.509 x
χ [eV]	4.6	4.6+0.16-1.056 x
Doping [cm^{-3}]	$N_A = 3 \cdot 10^{17}$	$N_D = 10^{11}$ to 10^{18}
$\varepsilon/\varepsilon_0$	13.6	9
m_e/m_0	0.09	0.2
m_h/m_0	0.72	1.2
μ_e [$cm^2/(Vs)$]	100	10
μ_h [$cm^2/(Vs)$]	12.5	10

Bulk traps (acceptor)	CIGS
Density [cm^{-3}]	10^{15}
Energy	midgap
$\sigma_e = \sigma_h$ [cm^2]	$2 \cdot 10^{-14}$

Interface traps (donor)	ZnMgO/CIGS
Density [cm^{-2}]	10^{11} to 10^{13}
Energy	midgap
$\sigma_e = \sigma_h$ [cm^2]	10^{-15}

Shockley-Read-Hall:

$$R = \frac{N_0 v_{th}^n v_{th}^p \sigma_n \sigma_p (np - n_i^2)}{v_{th}^n \sigma_n (n + n_1) + v_{th}^p \sigma_p (p + p_1)}$$

$$n_1 = n_i e^{E_{trap}/kT} \quad p_1 = n_i e^{-E_{trap}/kT} \quad v_{th}^{n,p} = \sqrt{\frac{3kT}{m_{n,p}}}$$

Poisson:

$$\nabla \cdot (\varepsilon \nabla \phi) = -\mathrm{q}(\mathrm{p} - \mathrm{n} + \mathrm{Nd} - \mathrm{Na}) - \rho_{trap}$$

Continuity:

$$\nabla \cdot \vec{J}_n = -\nabla \cdot \vec{J}_p = \mathrm{q}(\mathrm{R} - \mathrm{G})$$

Drift-diffusion:

$$\vec{J}_{n,p} = q \cdot n, p \cdot \mu_{n,p} \cdot \nabla \frac{E_{F_{n,p}}}{q}$$

Fermi-Dirac:

$$f(E) = \frac{1}{1 + e^{(E - E_F)/kT}}$$