how to understand spectral luminescence from thin film absorbers, absorber layer sequences and complete solar cells

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- **basics of steady state luminescence (Planck's generalized law)**
- **application to experimental results and requirements for evaluation**
  - **influence of temperature, spectral absorption, quasi-Fermi levels**
  - **lateral inhomogeneous absorbers**
  - **carrier depth profiles and depth dependent parameters**
- **numerical modeling of spectral pl**
- **interpretation of results (including multilayer optics) with re-absorption of luminescence photons, excess carrier depth profiles, lateral inhomogeneities…**
- **no summary**

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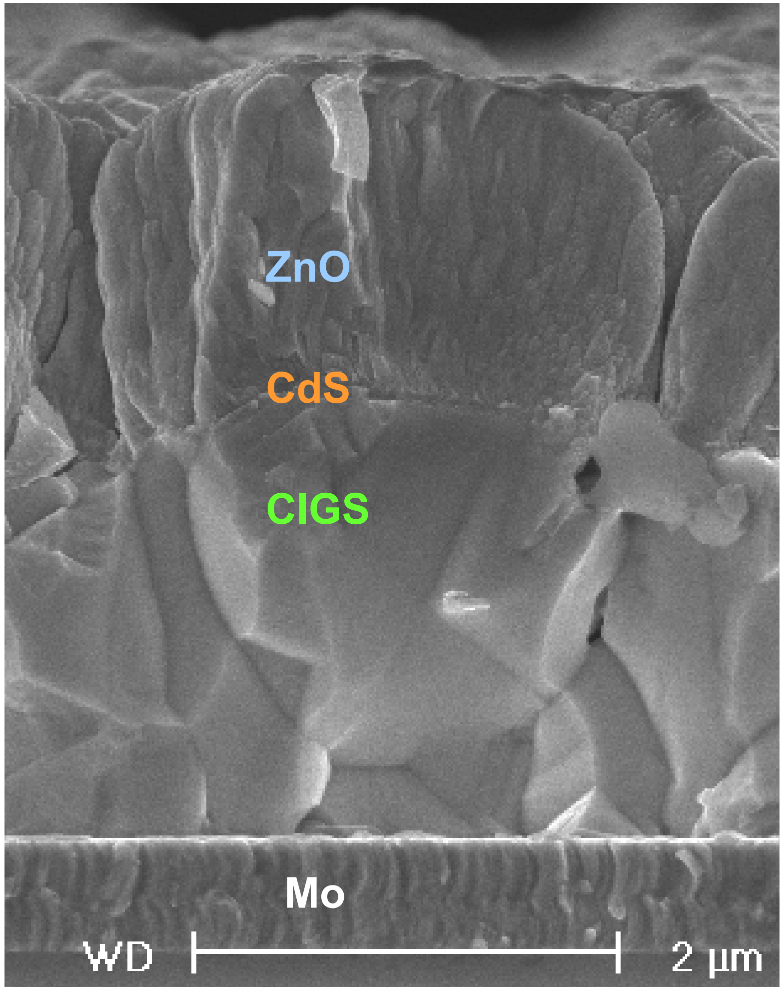
how to understand spectral luminescence from thin film absorbers, absorber layer sequences and complete solar cells

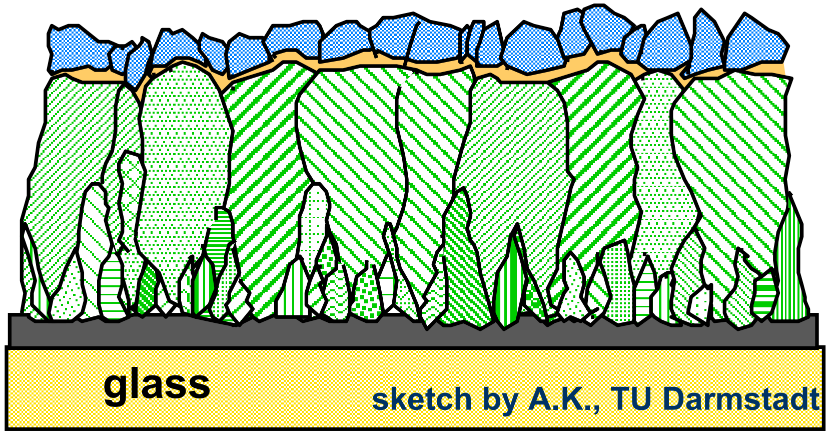
method applied to

- ***a-Si:H/c-Si heterodiodes (-> optimization of interface)***
- ***c-Si absorbers (-> passivation)***
- ***c-Si reference absorbers in 3rd generation approaches***
- ***polycrystalline semiconductors / diodes (CdTe, $Cu(Ga,In)Se_2$, $Cu(Ga,In)S_2$..)***
- ***thin polycristalline injection diodes***
- ***diodes of anorganic matrices with organic dyes***

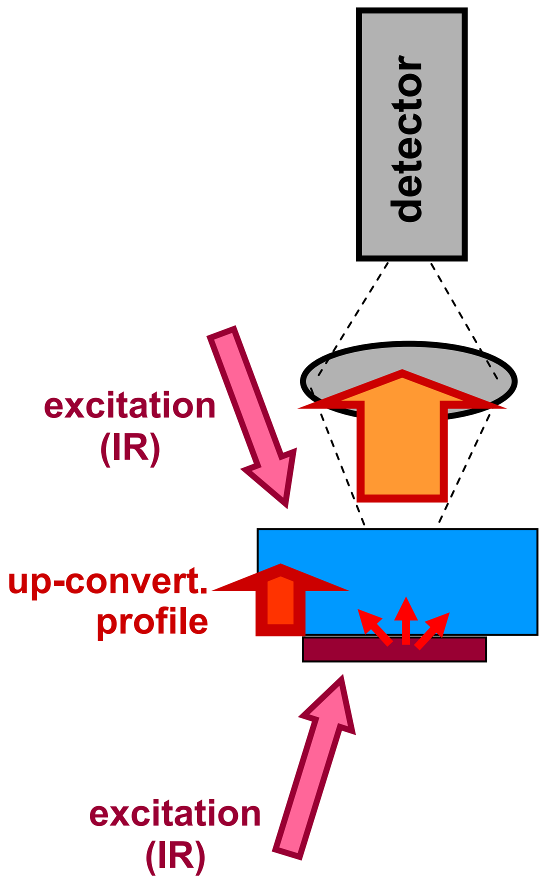
cross section of a $Cu(In_{0.7}Ga_{0.3})Se_2$ thin film on Mo coated glass substrate



SEM by ZSW Stuttgart



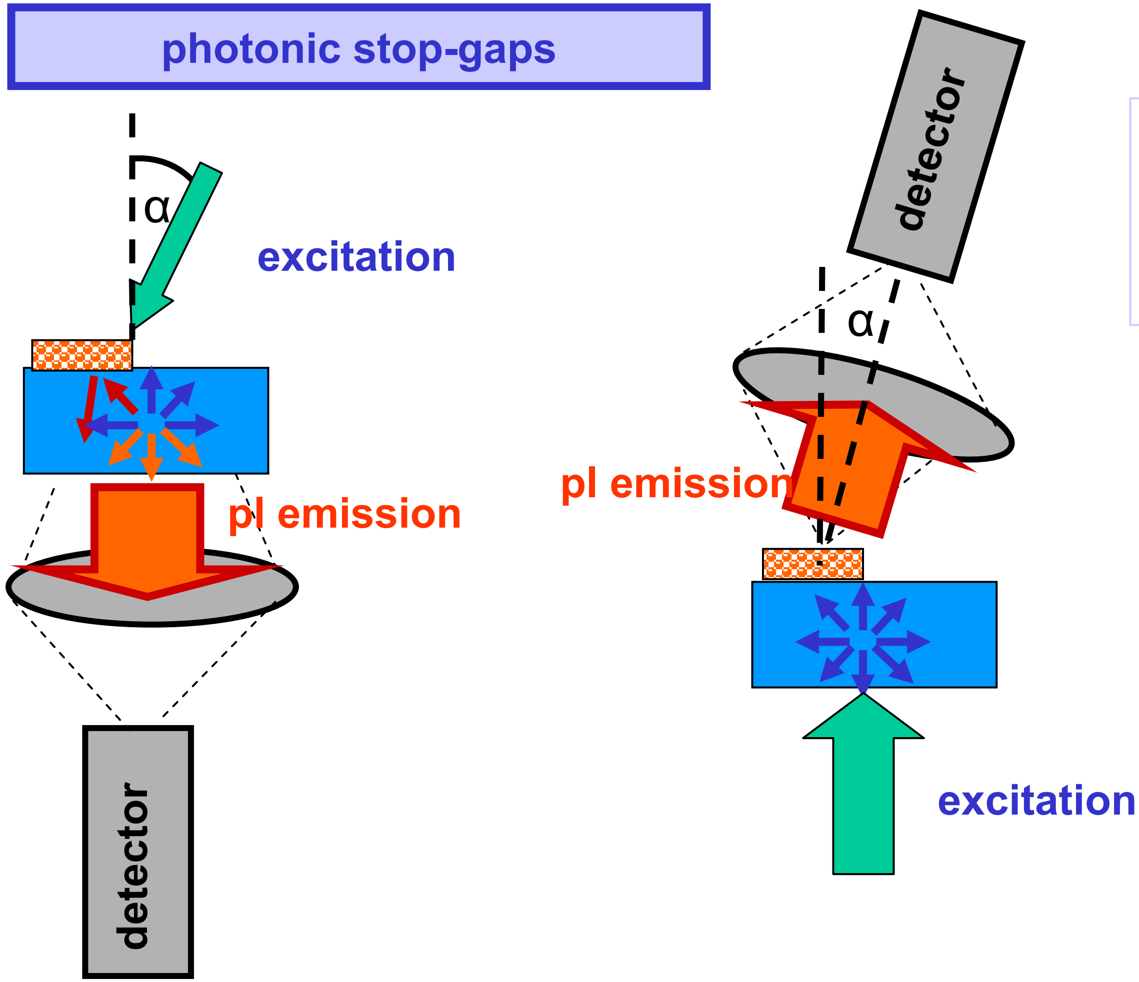
photoluminescence for determination of effects of manipulation of coupling solar light into absorbers



up-conversion

photoluminescence for determination of effects of manipulation of coupling solar light into absorbers

photonic stop-gaps

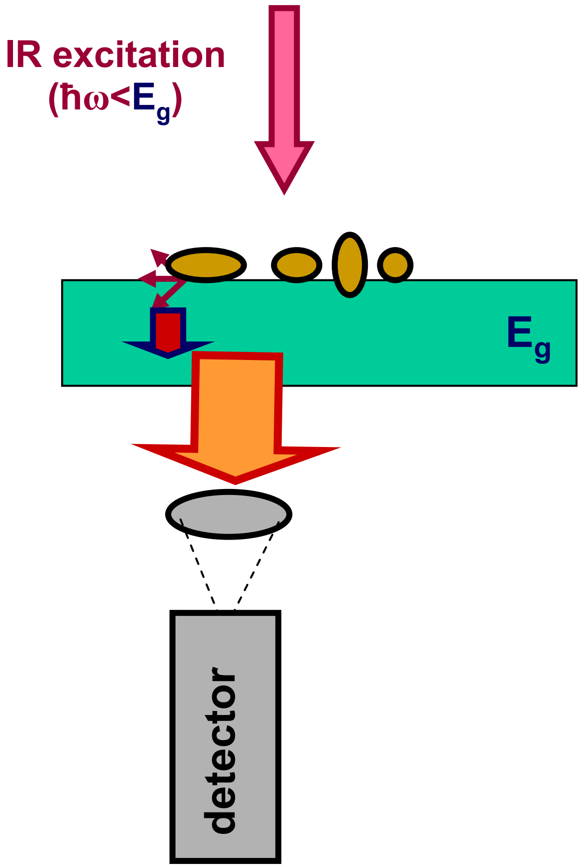


angle dependence

- excitation
- detection

photoluminescence for determination of effects of manipulation of coupling solar light into absorbers

metallic nano particles

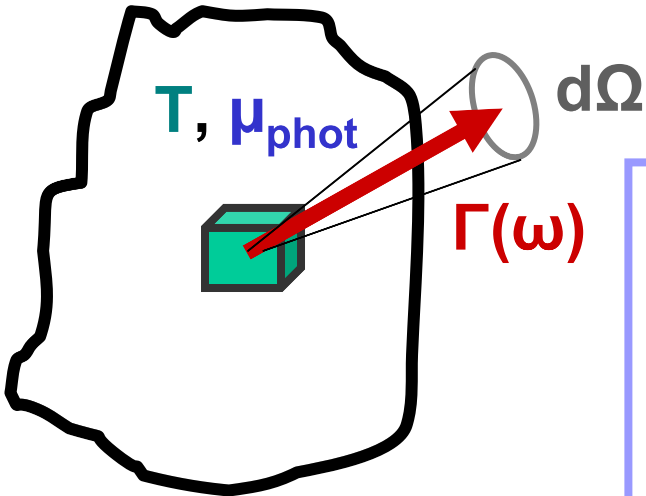


splitting of quasi-Fermi levels (ε_{Fn} - ε_{Fp}) via Planck's generalized law

photon flux from matter

$$\Gamma(\omega) = \varepsilon(\omega)\ \omega^2\ \{\exp[(\hbar\omega - \mu_{phot})/kT] - 1\}^{-1}$$

$\varepsilon(\omega)$ - spectral emissivity
μ_{phot} - chemical potential of the photon field



coupling of Bosons (μ_{phot}) and Fermions ($\mu_{n,p}$)
via rate equations of absorption and emission (spont. & stim.)
in an electronic 2-level/band system

$$\mu_{phot} = \mu_{n,p} = (\varepsilon_{Fn} - \varepsilon_{Fp}) \geq V_{oc}$$

(necessary condition in thermal non-equilibrium:
$\tau_{intraband}$ (momentum and energy relax.) << $\tau_{interband}$ (recomb.)
(maximum entropy distribution function -> temperature)

integration over entire volume of matter $\int \Gamma(\omega)\, d\Omega$
including wave optics (propagation, scattering, absorption, reflexion, photon recycling,..)

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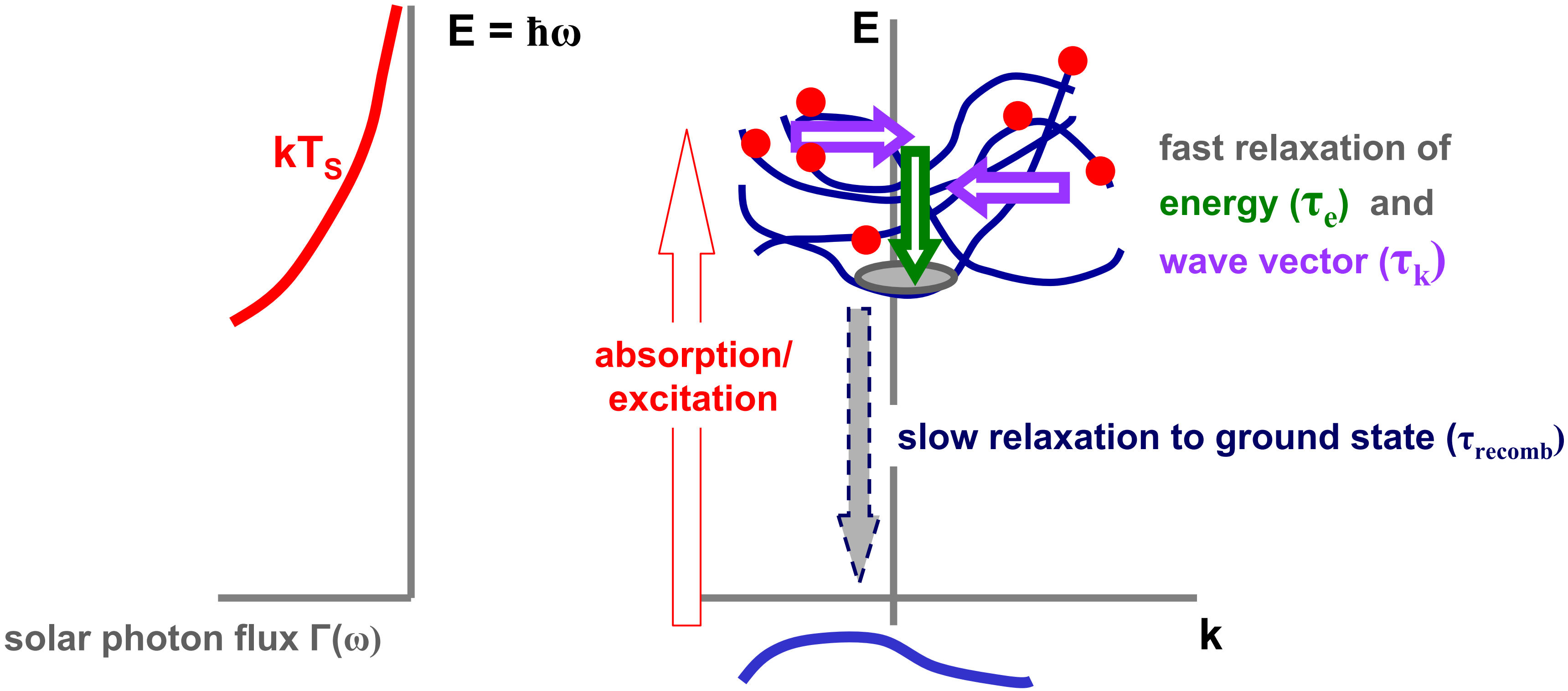
steady state conditions and fast intraband relaxation

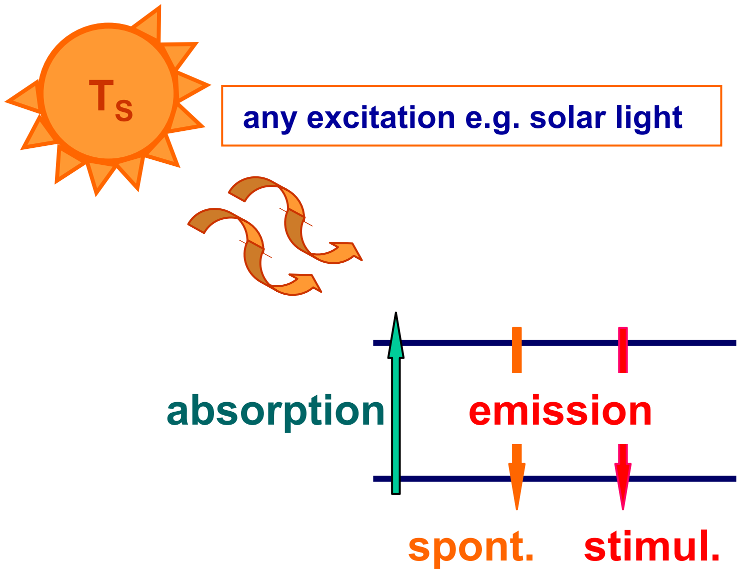
solar photons reflect sun surface temperature 6000 K
→ provide for „hot“ carriers



$\tau_e, \tau_k << \tau_{recomb}$ → max. entropy distribution (T)

maximum achieavable chemical potential of electron hole-ensemble

steady state balance of photon fluxes from sun (T_{sun}) absorbed by system at (T_{rec}) with chemical potential of electron hole ensemble $\mu_{n,p}$



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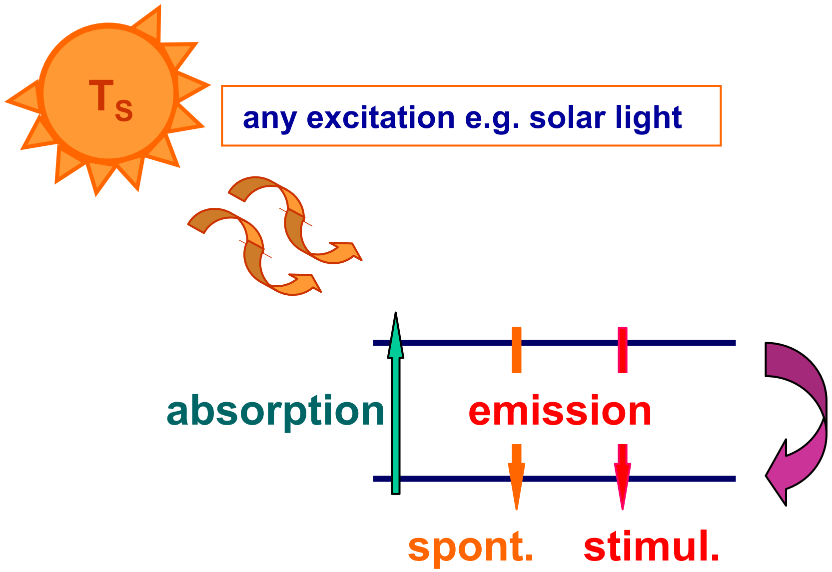
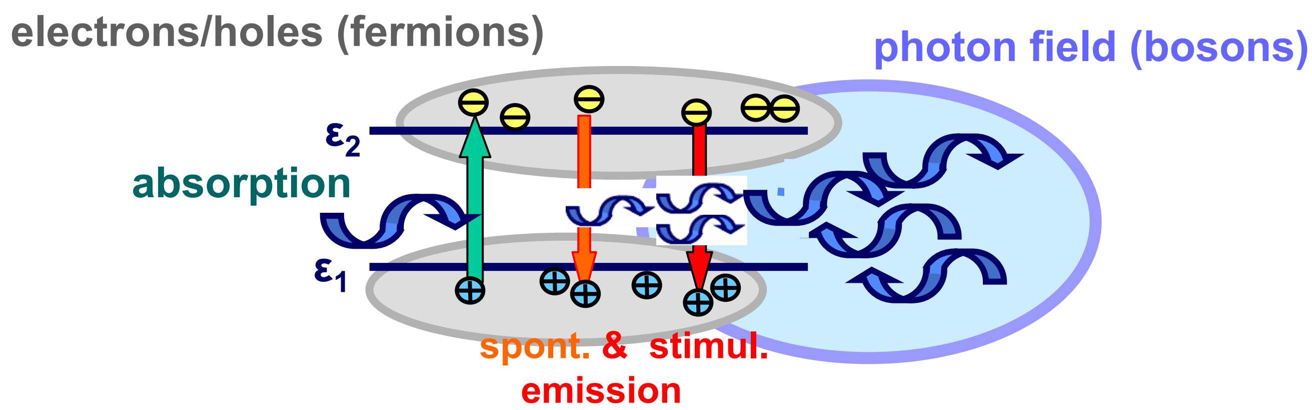


non-radiative

→ further decrease in excess carrier densities

→ drop in chemical potential μ_{np} ($\varepsilon_{Fn} - \varepsilon_{Fp}$)

chemical potential of photon field and of electron hole-ensemble



coupling of fermions with bosons
by rate equations for transitions between ε_1 and ε_2

COUPLING of BOSONS (PHOTONS) and FERMIONS (ELECTRONS-HOLES) in an ELECTRONIC TWO-LEVEL/BAND SYSTEM

- optical transitions $\hbar\omega = \varepsilon_2 - \varepsilon_1 = \varepsilon_g$

absorption, stimulated & spontaneous emission

$$B_{12}\, n(\varepsilon_1)\, p(\varepsilon_2)\, u_{phot}(\hbar\omega)\, 4\pi = B_{21}\, n(\varepsilon_2)\, p(\varepsilon_1)\, u_{phot}(\hbar\omega)\, 4\pi + A_{21}\, n(\varepsilon_2)\, p(\varepsilon_1)$$

$(B_{12} = B_{21})$

- level occupation by Fermi-/quasi-Fermi-statistics:

$n(\varepsilon_2) = D(\varepsilon_2)\, f_n^*(\varepsilon_2) = D(\varepsilon_2)\, \{\exp[(\varepsilon_2 - \varepsilon_{Fn})/kT] + 1\}^{-1}$ (conduction band)

$p(\varepsilon_1) = D(\varepsilon_1)\, f_p^*(\varepsilon_1) = D(\varepsilon_1)\, \{\exp[\varepsilon_{Fp} - \varepsilon_1)/kT] + 1\}^{-1}$ (valence band)

and via charge neutrality

$n(\varepsilon_1) = D(\varepsilon_1)[1 - f_p^*(\varepsilon_1)]$ (valence band)

$p(\varepsilon_2) = D(\varepsilon_2)[1 - f_n^*(\varepsilon_2)]$ (conduction band)

maximum achieavable chemical potential of electron hole-ensemble

with rate equations → $\mu_{phot} = \mu_{n,p}$

steady state balance:
photon flux from sun (T_{sun}) absorbed by system at (T_{rec})
vs. photon flux emitted by system at (T_{rec}) with chemical potential $\mu_{n,p}$

$$\Omega_{inc}\int_0^\infty \frac{A(\omega)\omega^2 d\omega}{\exp\left[\frac{\hbar\omega}{kT_{sun}}\right]-1} = \Omega_{emiss}\int_0^\infty \frac{E(\omega)\omega^2 d\omega}{\exp\left[\frac{\hbar\omega-\mu_{n,p}}{kT_{rec}}\right]-1}$$

$$A(\omega)=E(\omega)$$

luminescence

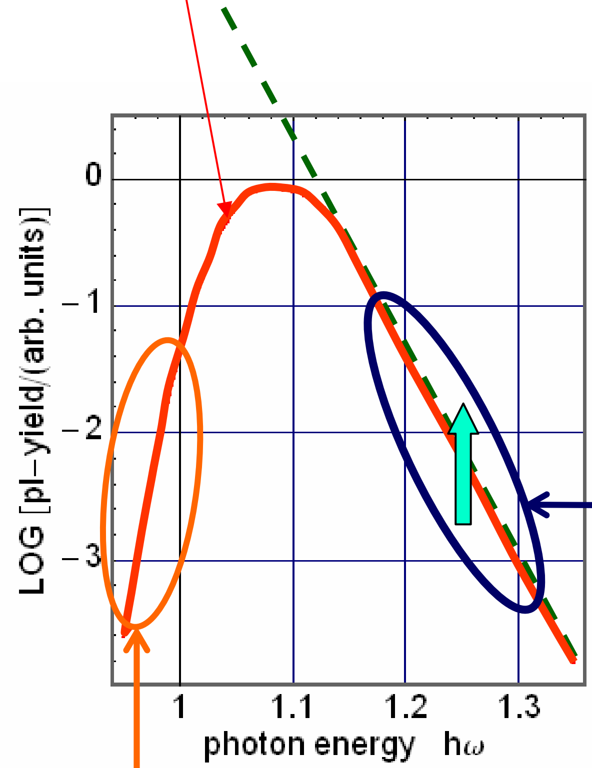
$$+rate_{non-radiative\_recomb.} + rate_{carrier-injection/-extration}$$

access to actual chemical potential of electron hole ensemble (E_{Fn}-E_{Fp})

messages included in the spectral pl-yield (Planck's generalized law)

$$\Gamma(\omega) = C \;\; \alpha(\omega) \;\; \omega^2 \;\; \{\exp[(\hbar\omega - \mu_{phot})/ kT] - 1\}^{-1}$$

$$\alpha(\omega) = \varepsilon(\omega) \; ; \quad \mu_{phot} = \mu_{n,p}$$



slope in log-plot → kT

amplitude → chemical potential μ

1- exp[-αd] ≈ 1 (complete absorption)

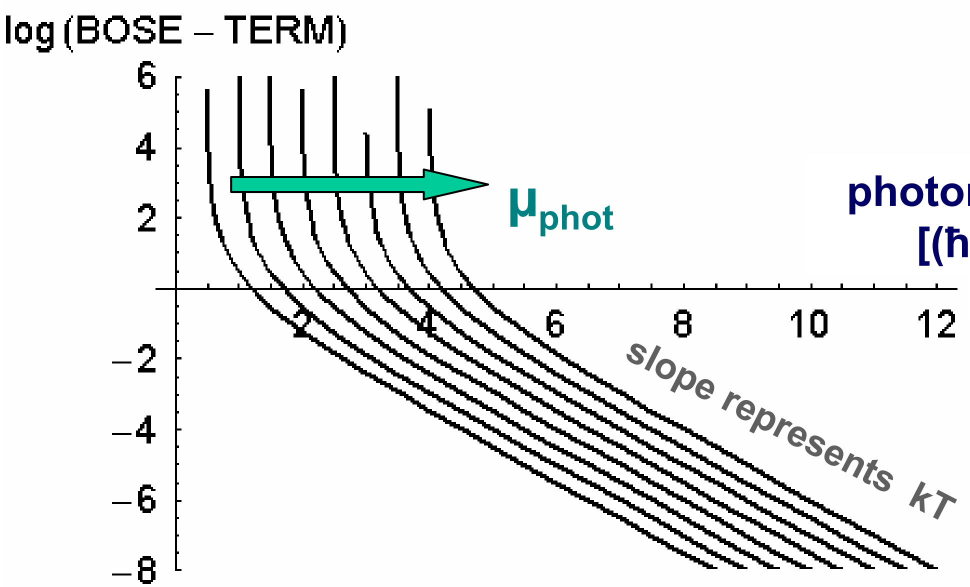
~ αd (weak absorption)

chemical potential of the electron-hole-ensemble μ_{np} via Bose-Term of Planck's Generalized Law

Bose-term $\{\exp[(\hbar\omega-\mu_{phot})/kT]-1\}^{-1}$

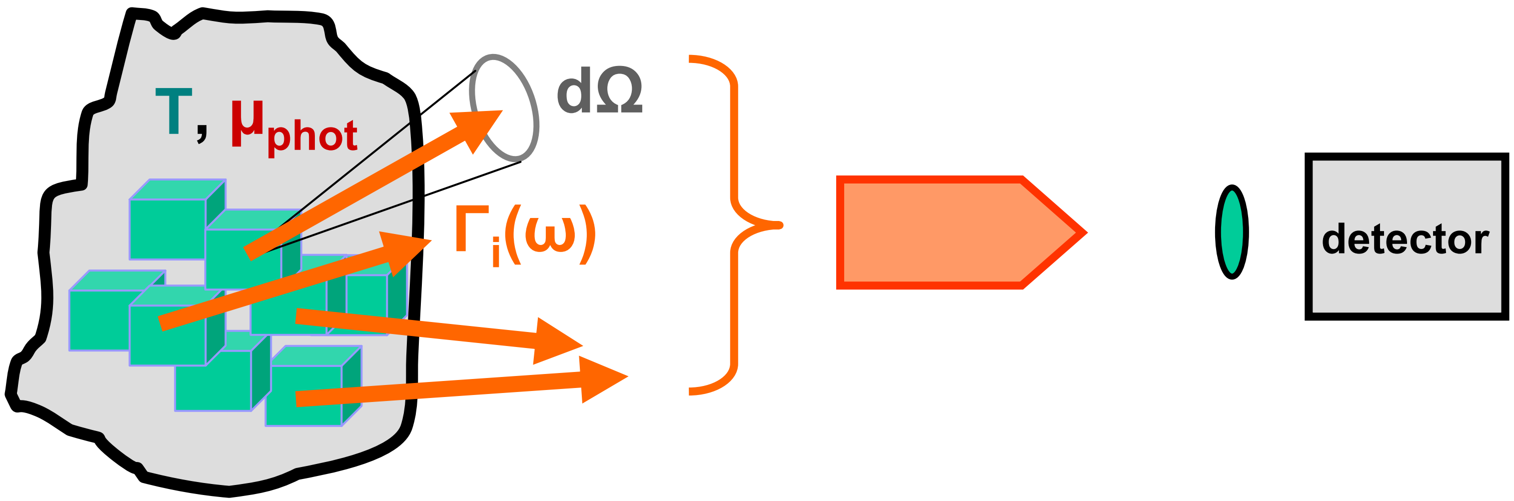
steady state $\mu_{phot} = \mu_{np} = (\varepsilon_{Fn} - \varepsilon_{Fp}) = V_{oc,max}$

Log [Bose-term] (a.u.)



photon energy [(ħω)/kT]

contribution to photon flux from many volume elements



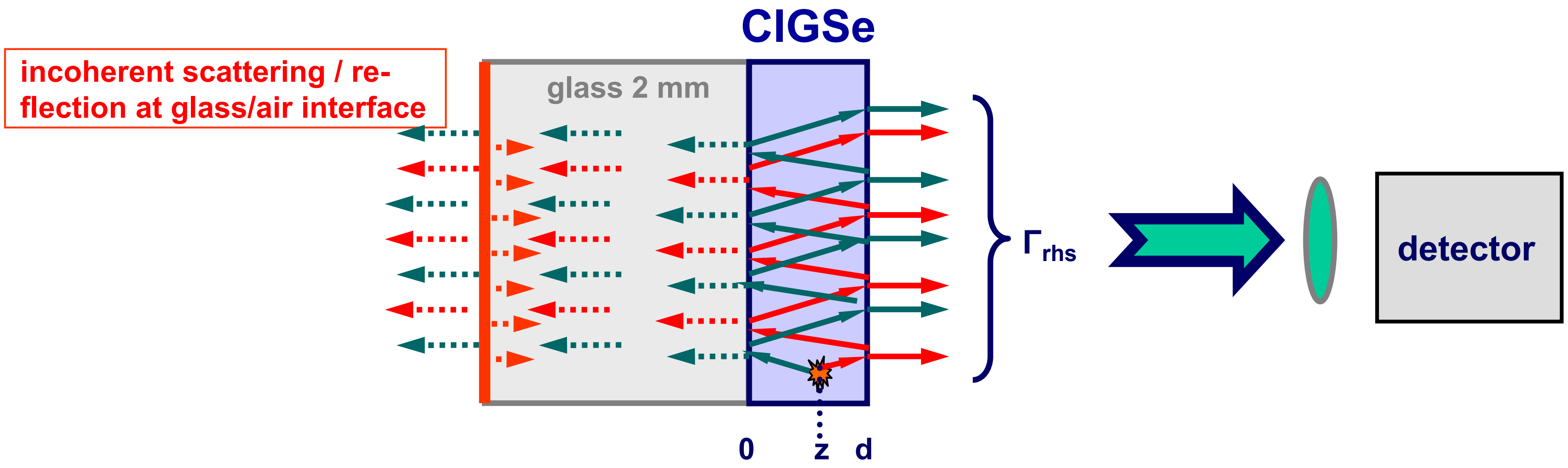
$\Gamma_{tot}(\omega)$ by integration of over entire volume dΩ

$$\Gamma_{tot}(\omega) = \int \Gamma_i(\omega)\, d\Omega$$

including wave optics (propagation, scattering, absorption, reflection, photon recycling,..)

multilayer optics for the formulation of total photon flux to detector

formalization of luminescence photon propagation (**plane wave approach**)



$$\Phi_{rhs}(z) \propto \Phi_B \left\{ (t_{12})^2 \exp(-2\alpha(d-z)) \left| \frac{1+2r_{10}\exp(-2\alpha z)\exp[i2kz]+(r_{10})^2\exp(-4\alpha z)}{1-2r_{01}r_{12}\exp(-2\alpha d)\exp[i2kd]+(r_{01}r_{12})^2\exp(-4\alpha d)} \right|^2 + \right.$$

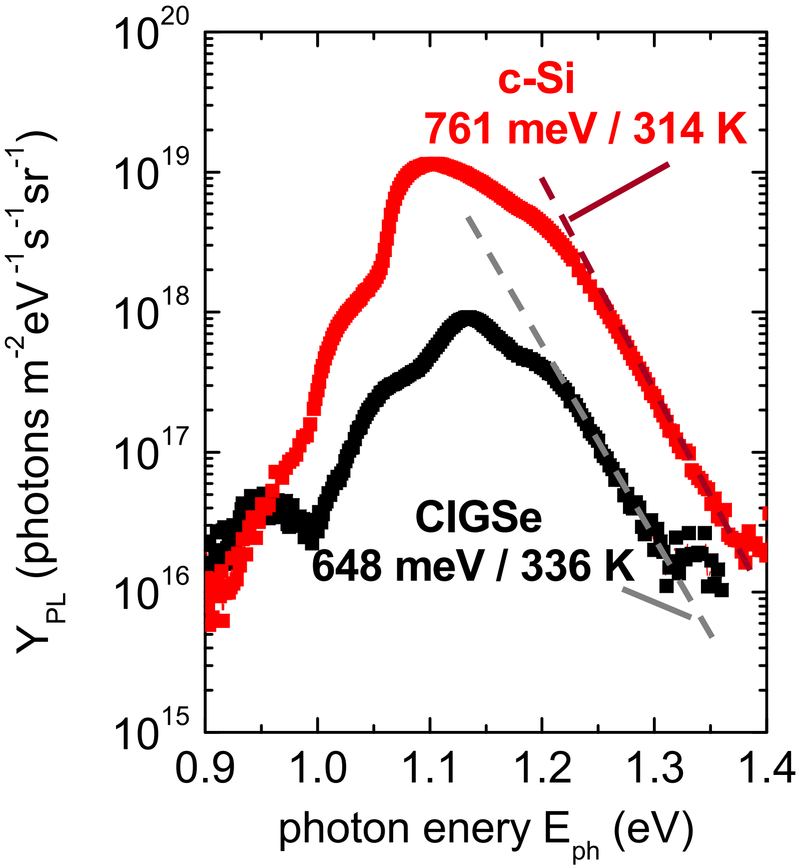
$$\Phi_B = \varepsilon(\omega)\frac{1}{4}\Gamma_{phot}(z)\omega^2 \left[\exp[\frac{\hbar\omega-\mu_{n,p}}{kT}]-1 \right]^{-1}$$

$$\left. (r_{01})^2 (t_{10})^2 \exp(2\alpha z) \left| \frac{\left[\frac{(t_{12}t_{01})^2 \exp(-2\alpha d)}{1-(r_{12})^2\exp(-2\alpha d)\exp[ikd]} \right] \left(1+(r_{12})2\exp(-2\alpha(d-z))\exp(ik(d-z))+(r_{12})^2\exp(-4\alpha(d-z))\right)}{1+2(r_{01}r_{12})^2\exp(-4\alpha d)-(r_{01}r_{12})2\exp(ikd)\exp(-2\alpha d)} \right|^2 \right\}$$

no photon recycling considered since in CIGSe (300 K) $r_{non-rad} >> r_{rad}$

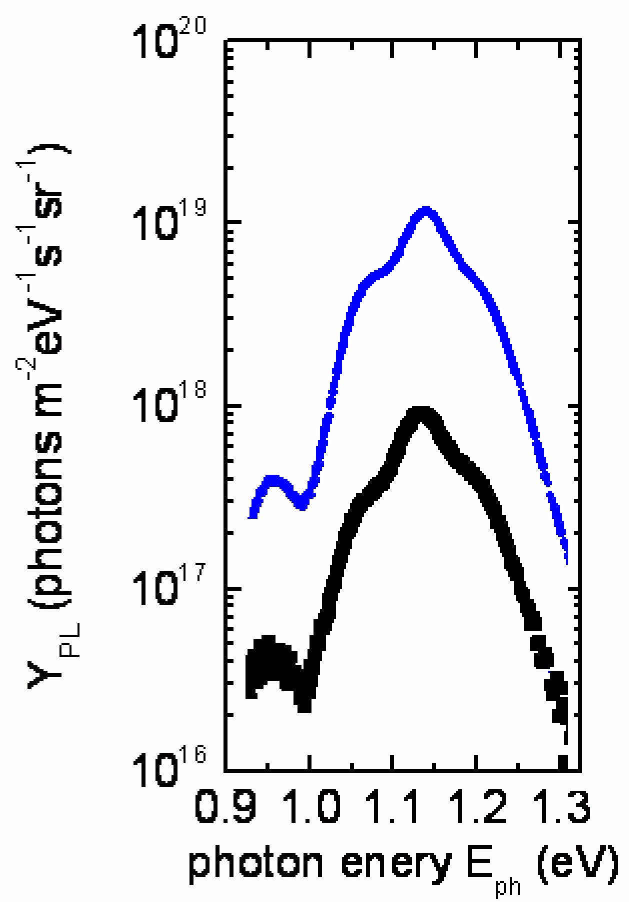
calibrated room temperature photoluminescence at AM1-equivalent excitation from optimally passivated monoc-Si and thin film $Cu(In_{0.7}Ga_{0.3})Se_2$

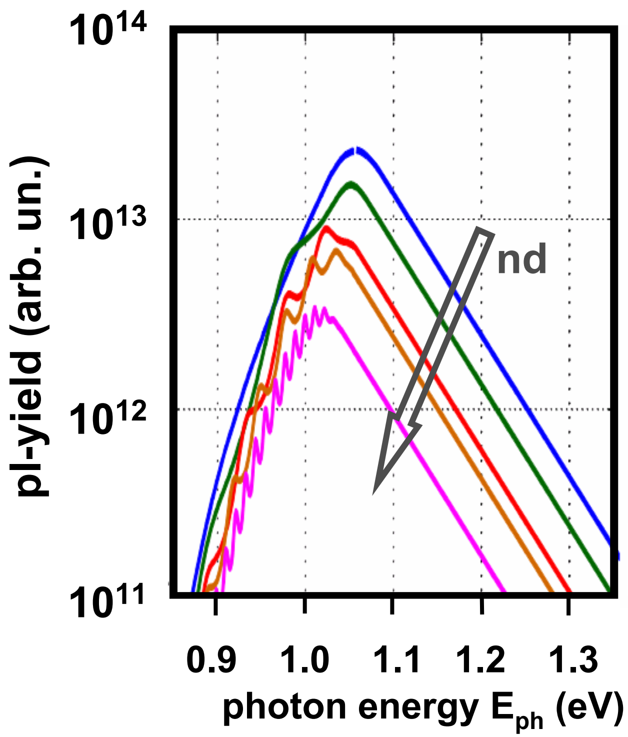
excess carrier depth profile most flat → V_{oc}-equivalent



CIGSe- pl shows interference pattern

comparison of experimental and calculated pl-yields

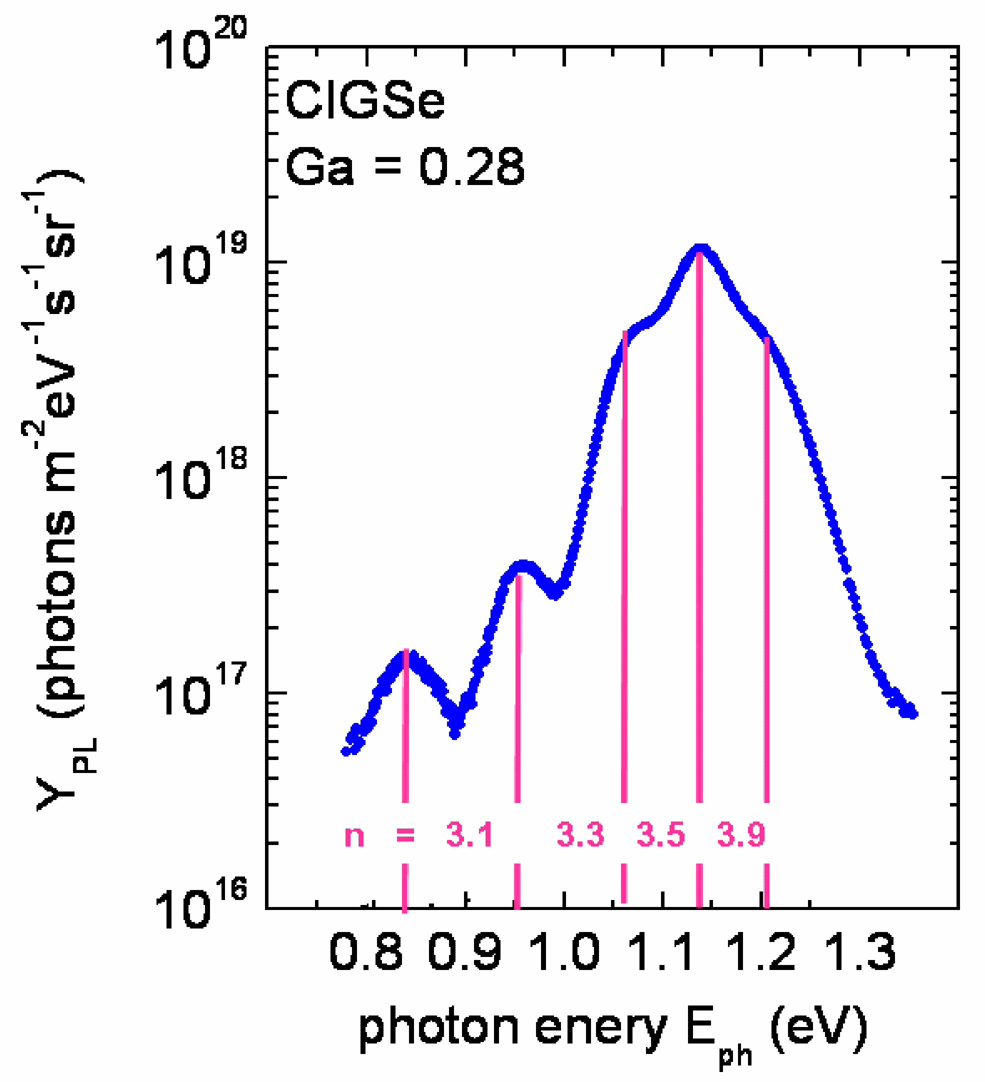




excess carrier depth profile almost flat (S_0=S_d= 10^4 cm/s)

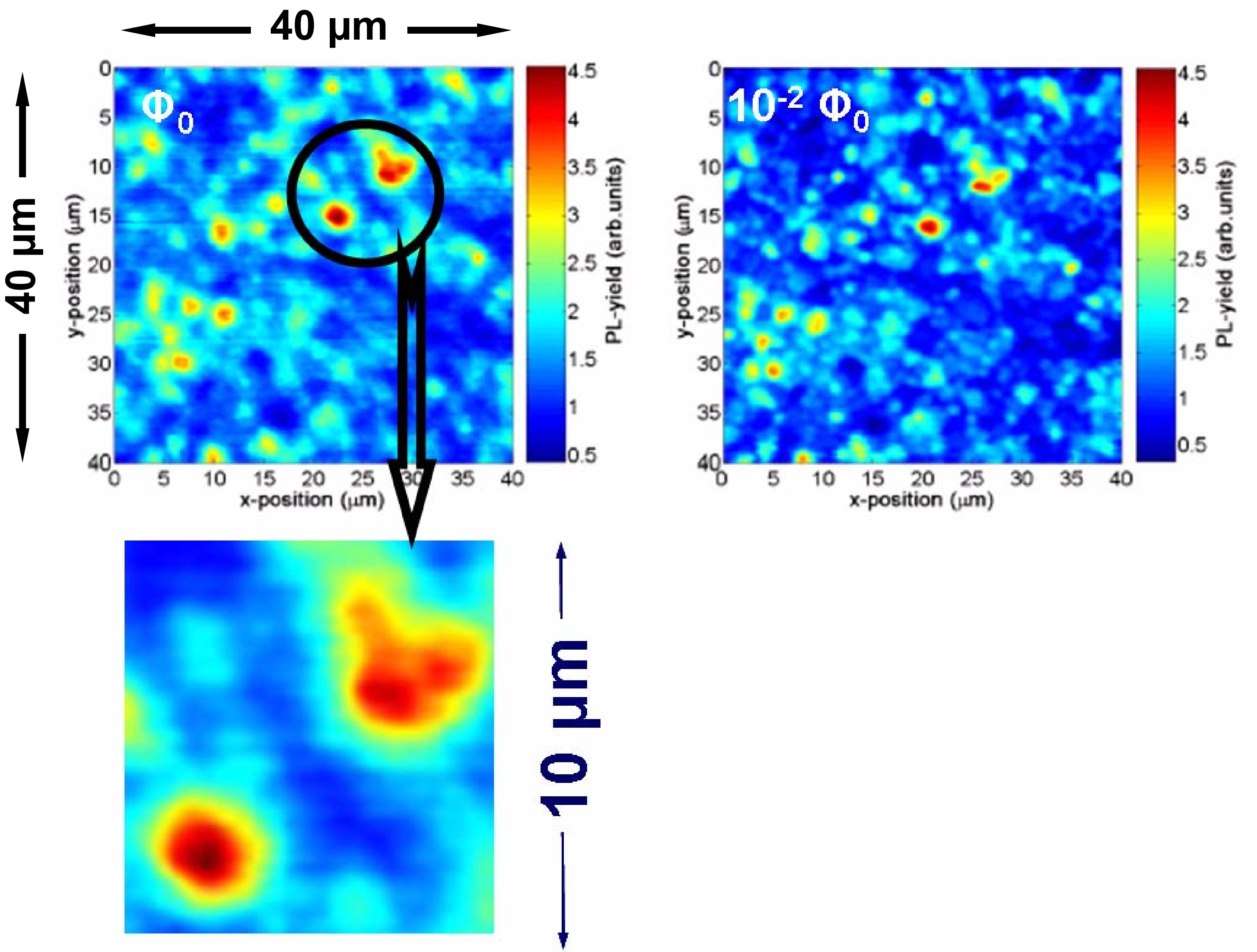
nd ≤ nd ≤ nd

calibrated luminescence from $CuInGaSe_2$ with interference pattern

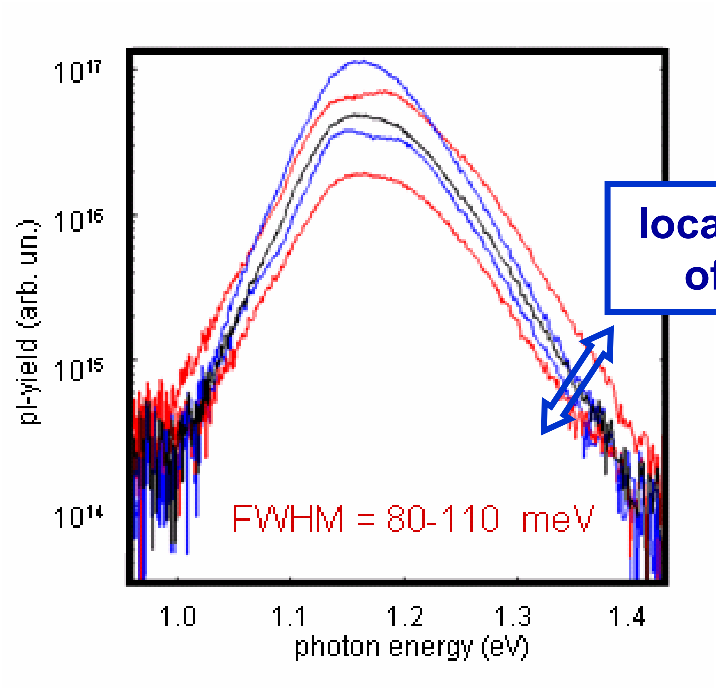


interfrerence peaks with refractive index $n = n(\hbar\omega)$

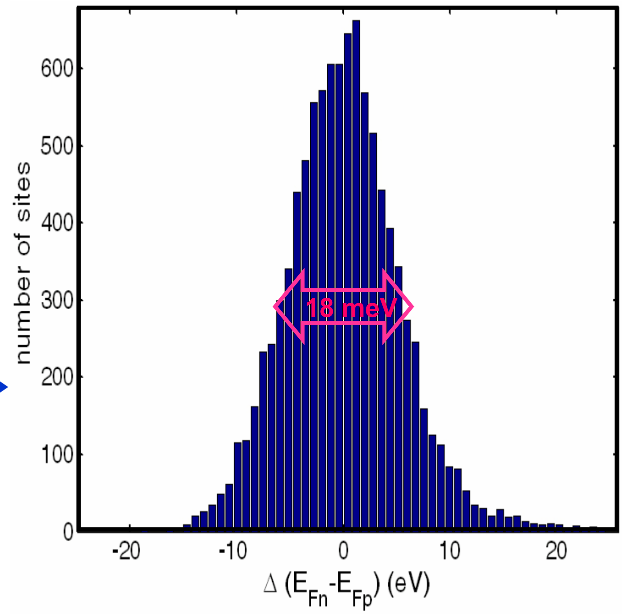
laterally resolved photoluminescence from $Cu(In_{0.7}Ga_{0.3})Se_2$



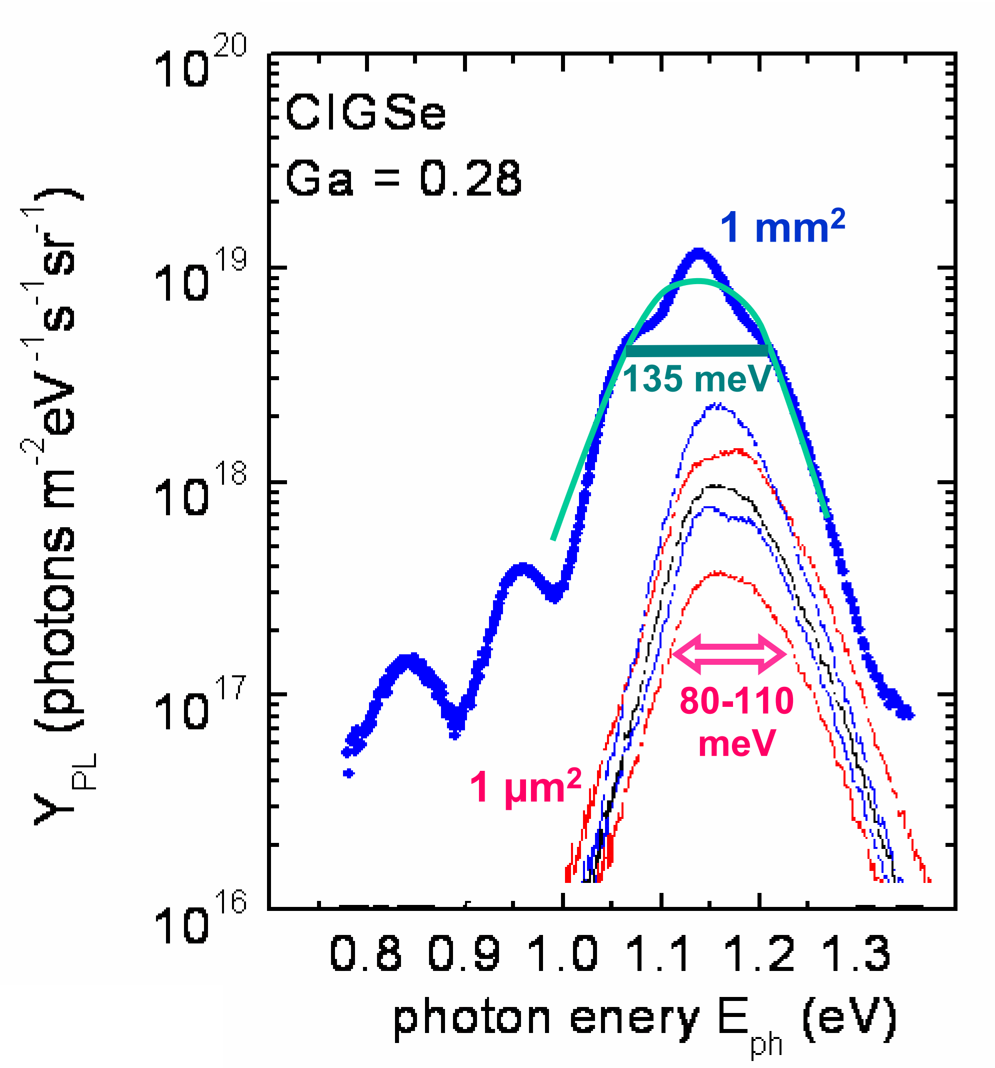
yield of confocally recorded photo-luminescence of $CuInGaSe_2$ (L. Gütay et al., 2004)



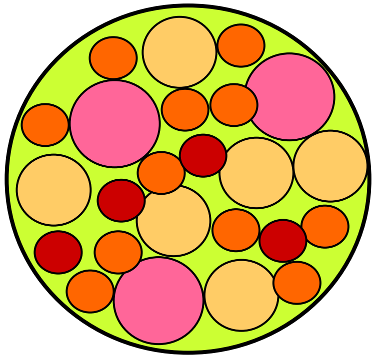
local variation of E_{Fn}-E_{Fp}



calibrated room temperature luminescence (AM1 equivalent excitation) versus confocally resolved luminescence



problems by averaging photon fluxes



lateral pattern of photon fluxes with different chemical potentials

avereging of photon individual fluxes

$$\sum Y_{pl,i}$$

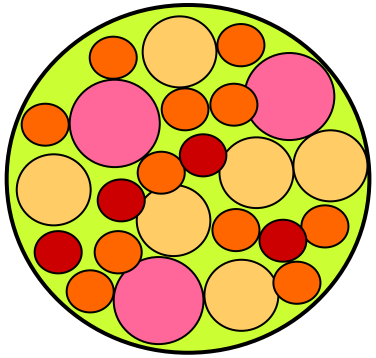
→ **extraction of quasi Fermi level splitting**

$$E_{Fn}-E_{Fp} \sim kT \ln(\sum Y_{pl,i}))$$

averaging of individual chemical potentials

$$E_{Fn}-E_{Fp} \sim kT \sum \ln(Y_{pl,i}))$$

problems by averaging photon fluxes



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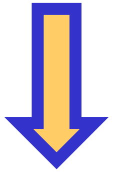
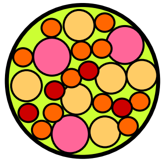


analyze distribution function (FWHM)

problems by averaging photon fluxes



lateral pattern of photon fluxes with different chemical potentials

$$\delta = kT\,\frac{\displaystyle\int_{Ypl0-\Delta}^{Ypl0+\Delta} \ln\big((Ypl)\big(f(Ypl)\big)\big)\,dYpl - \ln\left(\int_{Ypl0-\Delta}^{Ypl0+\Delta} (Ypl)\, f(Ypl)\,dYpl\right)}{\displaystyle\int_{Ypl0-\Delta}^{Ypl0+\Delta} \ln\big[(Ypl)\big(f(Ypl)\big)\big]\,dYpl}$$

avereging of photon individual fluxes

$\sum Y_{pl,i}$

→ extraction of quasi Fermi level splitting

$E_{Fn}-E_{Fp} \sim kT \ln\left(\sum Y_{pl,i}\right)$

avereging of individual chemical potentials

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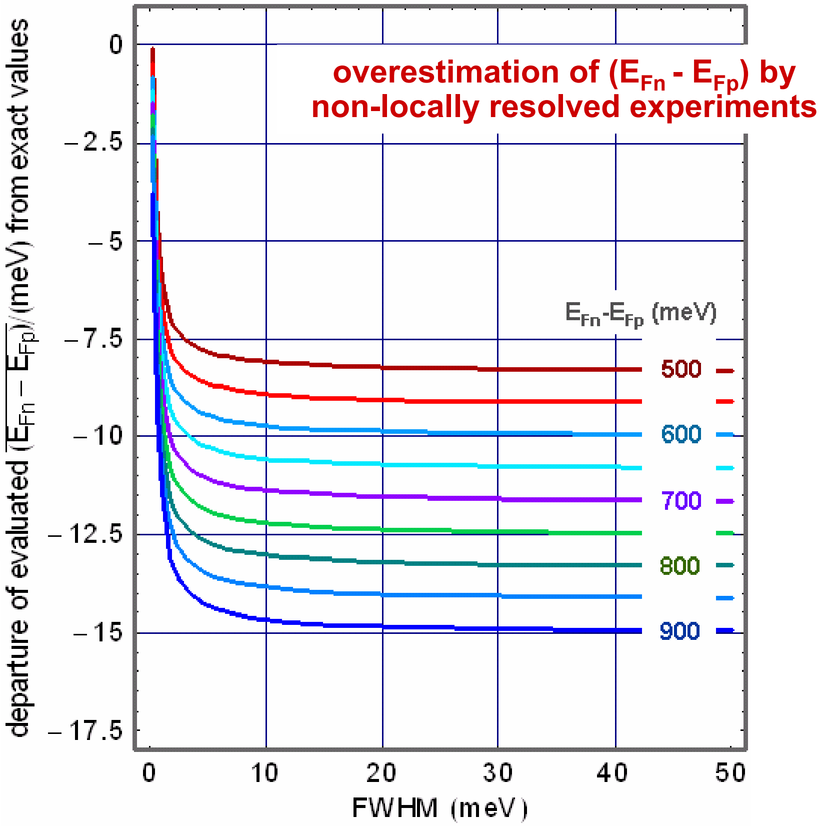
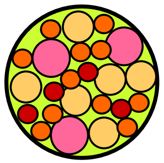


problems by averaging photon fluxes



lateral pattern of photon fluxes with different chemical potentials

avereging of photon individual fluxes

$\sum Y_{pl,i}$

→ extraction of quasi Fermi level splitting

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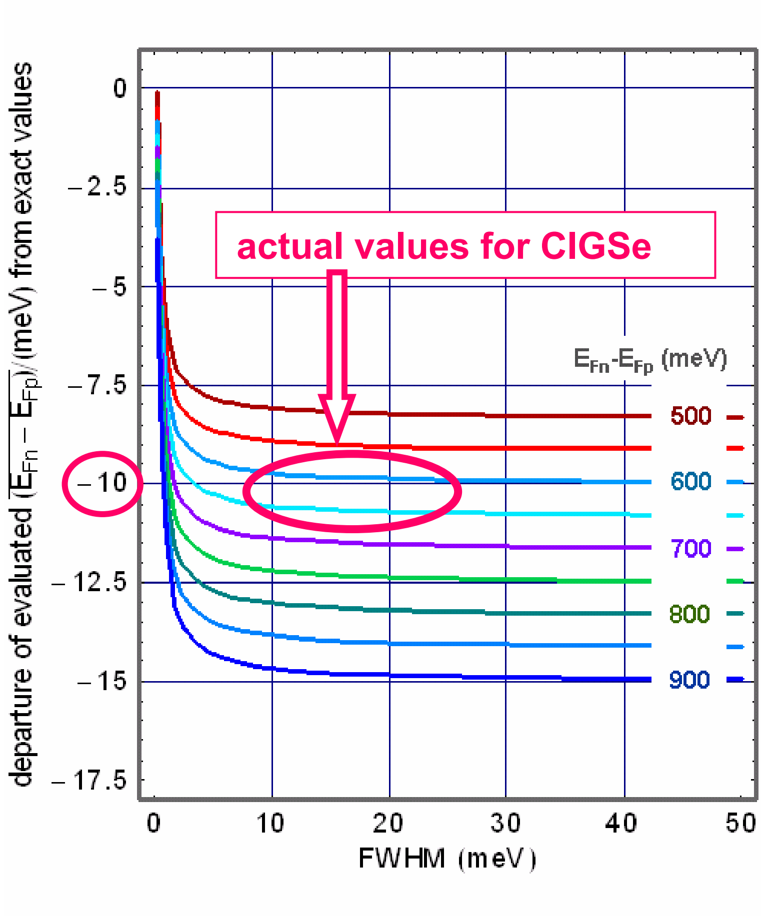
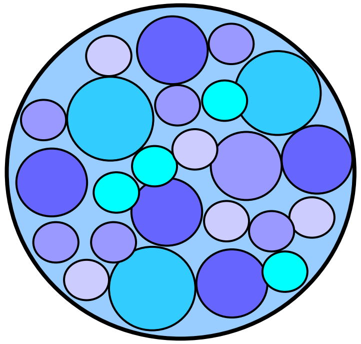


spectral absorption coefficient of $Cu(In_{0.7}Ga_{0.3})Se_2$ extracted from laterally highly resolved (1 µm) white light transmission



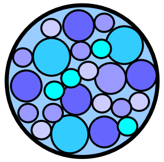
lateral pattern of white light transmitted photons (variation of (αd))

$$A_{average}(\omega) = \sum_i \left(1 - \exp[-\alpha_i d_i]\right)$$

average absorption coefficient ??

$$\alpha_{average}(\omega) = -\frac{1}{d}\ln\left(1 - A_{average}(\omega)\right)$$

critical / inappropriate averaging of relevant magnitudes

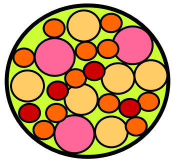


lateral pattern of white light transmitted photons (variation of (αd))

$$< A(\omega) >= A_{average}(\omega) = \sum_i \left(1-\exp[-\alpha_i(\omega) d_i]\right)$$

$$< \alpha(\omega)d >= (\alpha(\omega)d)\Big|_{average} = \ln\left[\frac{1}{1-\sum_i 1-\exp\left[-\alpha_i(\omega)d_i\right]}\right]$$

average absorption coefficient ??



lateral pattern of photon fluxes with different chemical potentials

average chemical potential

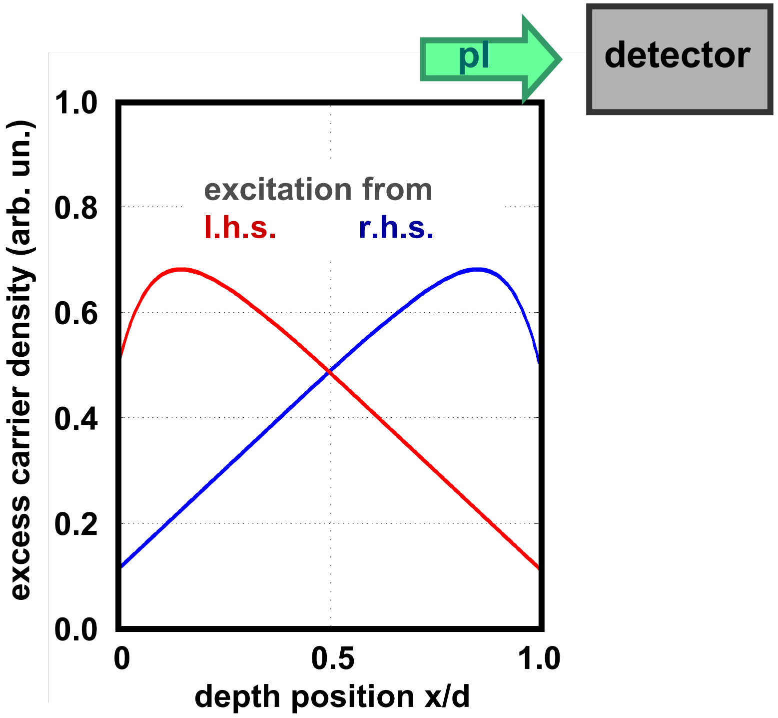
$$< E_{Fn} - E_{Fp} > \sim kT \sum_i \ln\left[Y_{pl,i}\right]$$

$$Y_{pl,i} \sim \alpha_i(\omega) \frac{\omega^2}{\exp\left[\frac{\hbar\omega-(E_{Fn}-E_{Fp})}{kT}\right]-1}$$

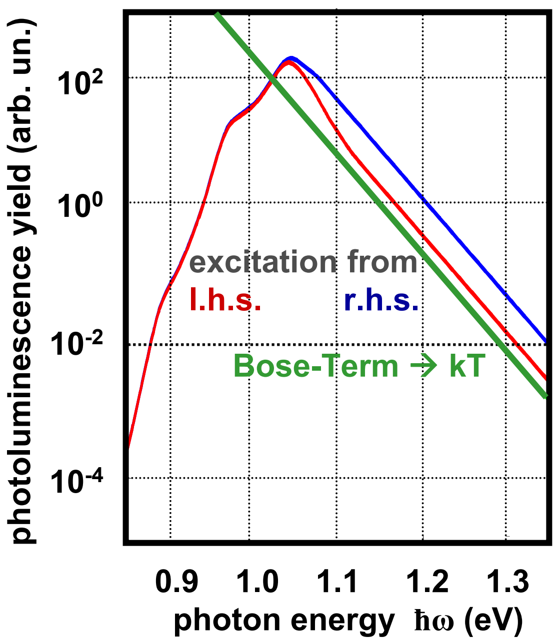
avoid inappropriate averaging of magnitudes that superimpose non-linearly

dependence of spectral luminescence signal on carrier depth profile

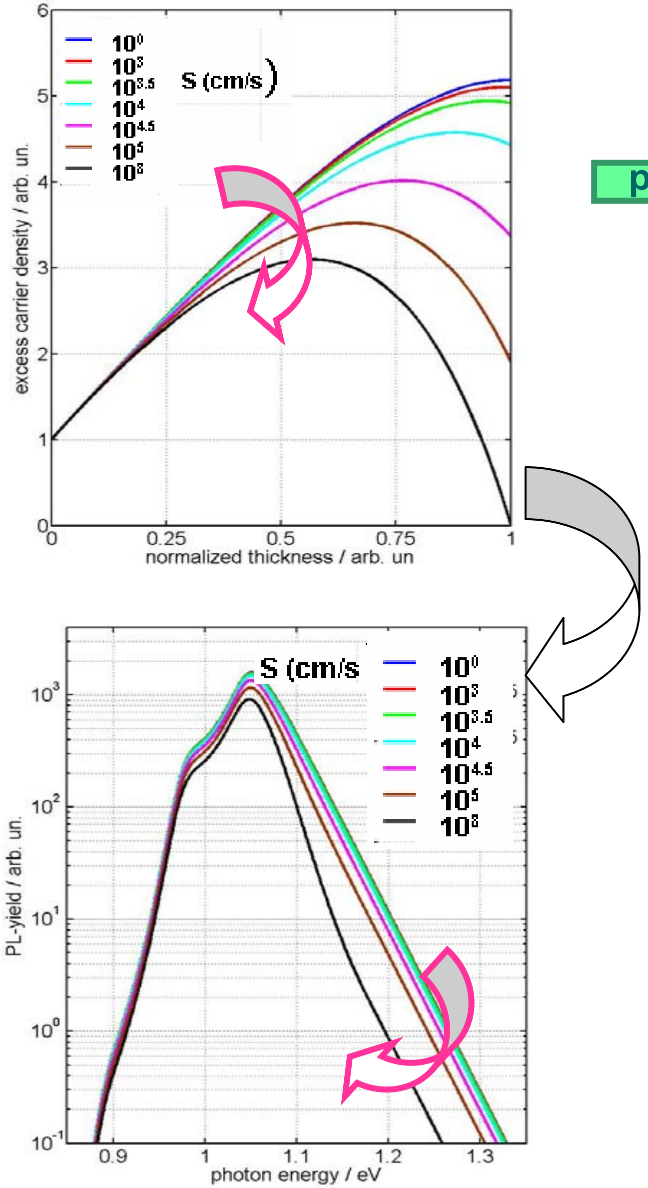
excess carrier depth profiles
for numerical calculation of

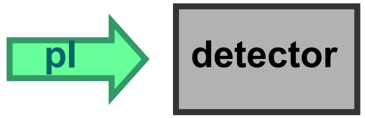


pl signal at the detector



numerical modelling for examination of influence of carrier depth profile on spectral pl





excess carrier depth profiles and according spectral pl-yields
(plane wave approach)

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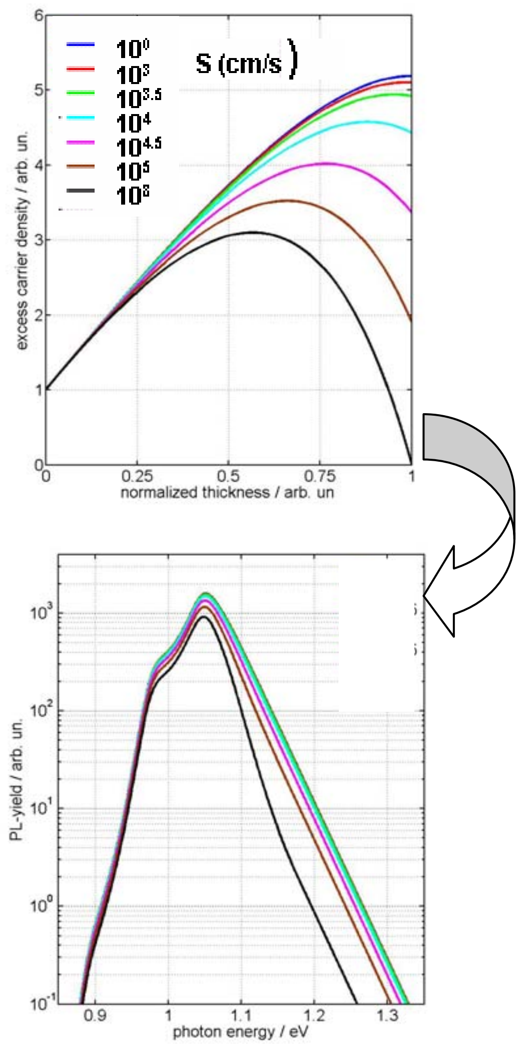

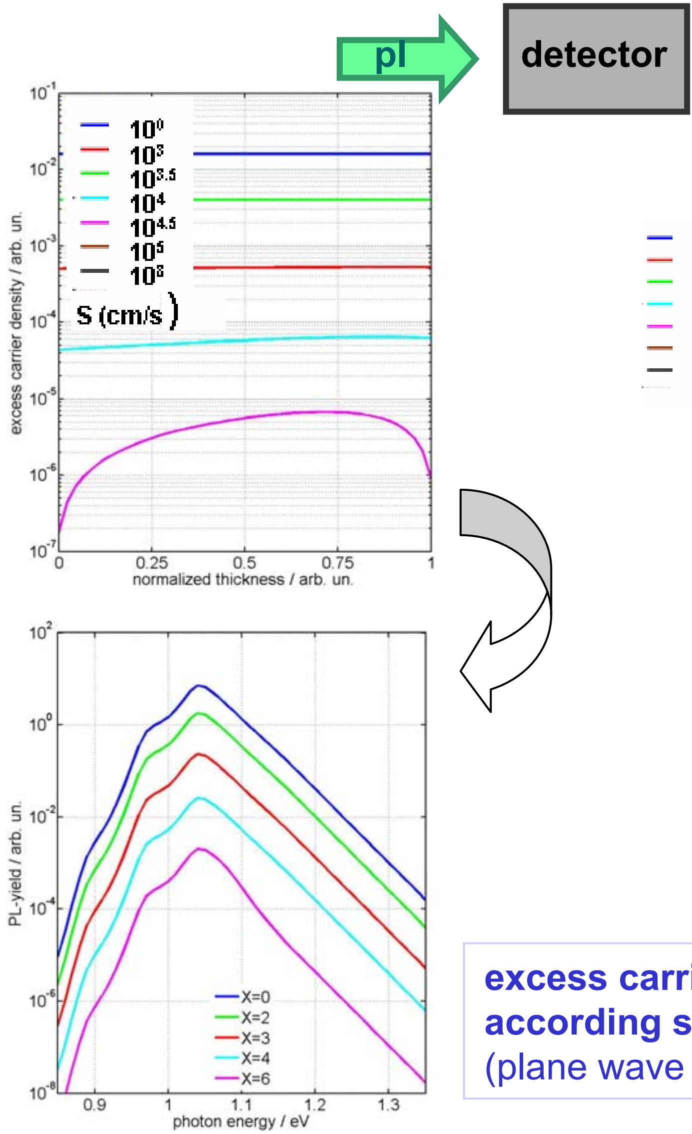

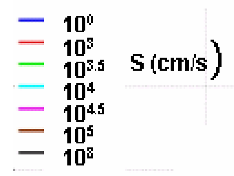

excess carrier depth profiles and according spectral pl-yields
(plane wave approach)

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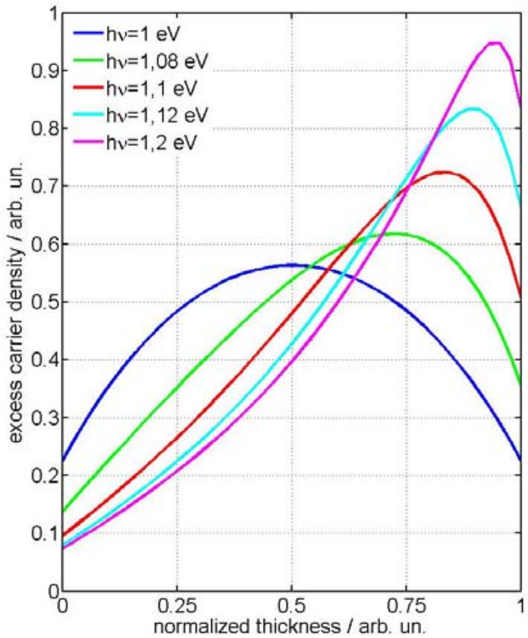
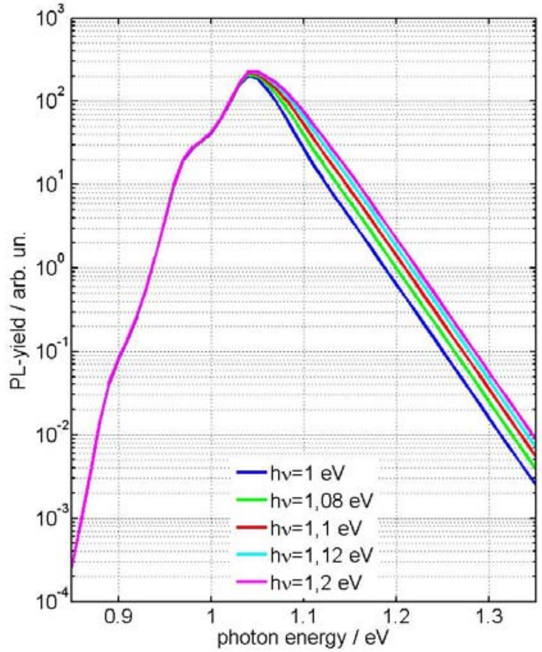
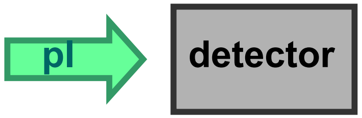
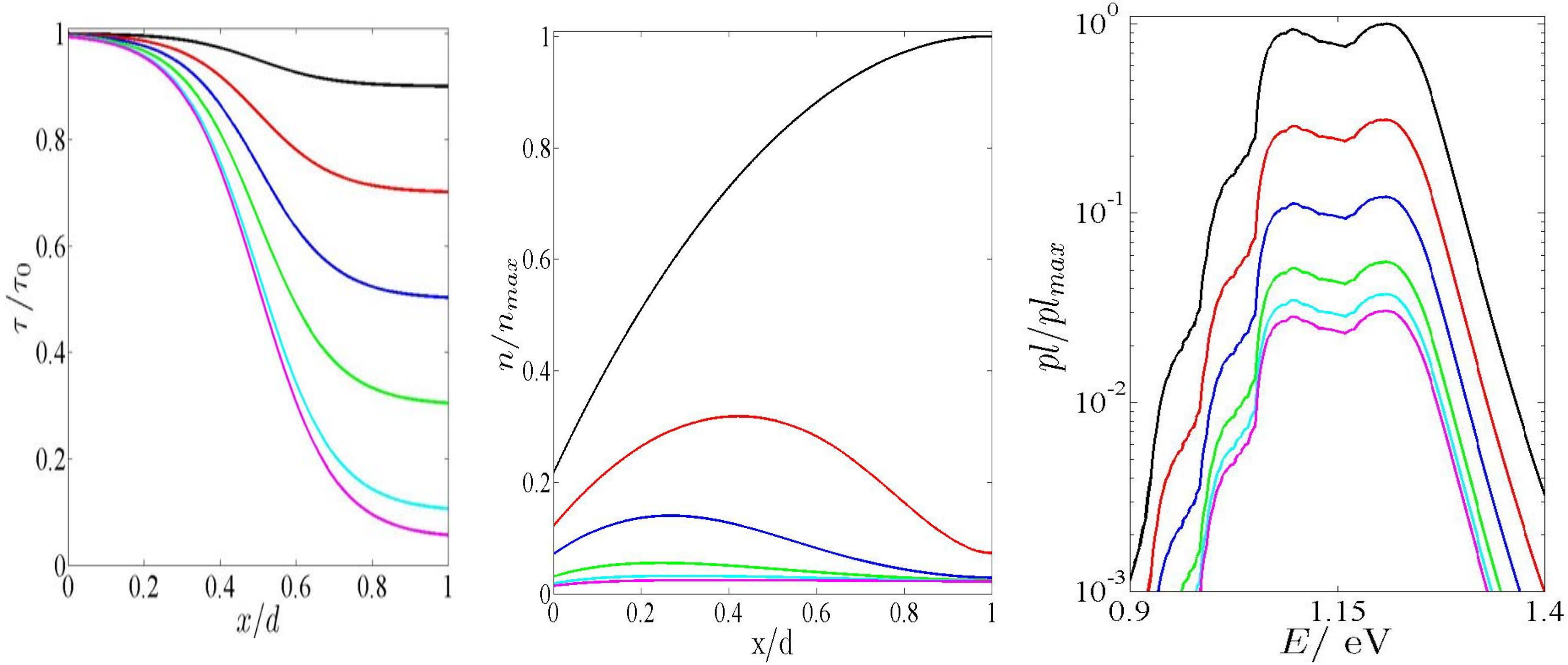




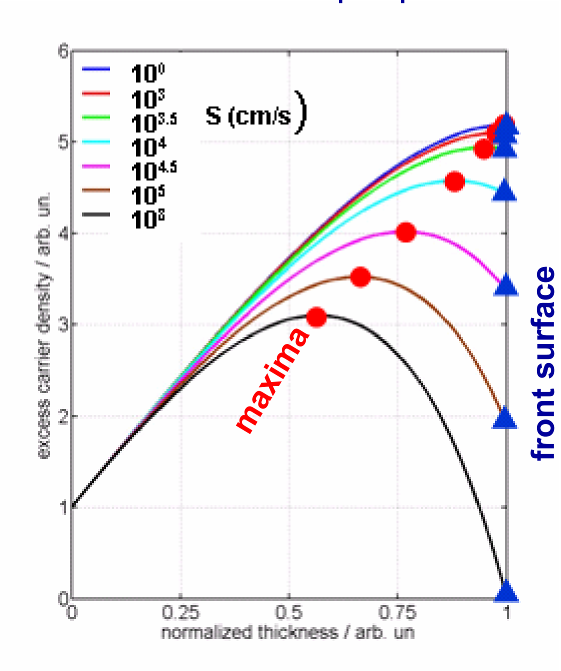


carrier depth profiles and according spectral luminescence yields

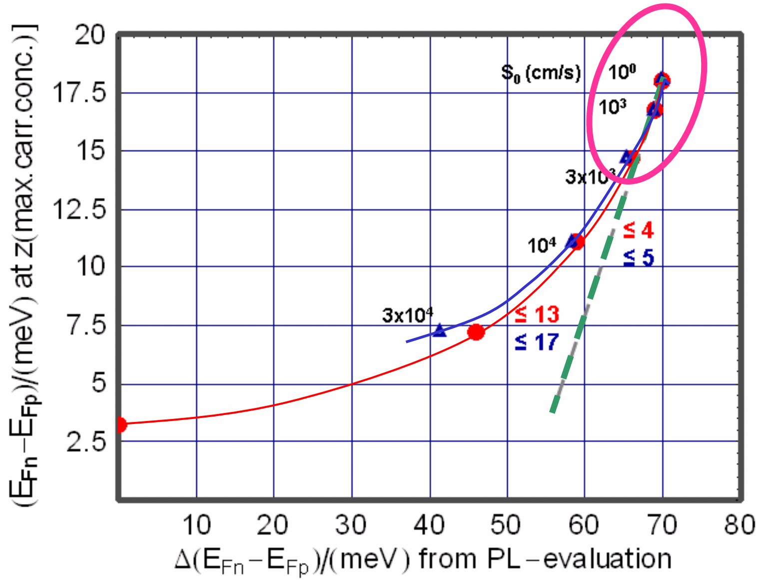


determination of quasi-Fermi level splitting

excess carrier depth profiles

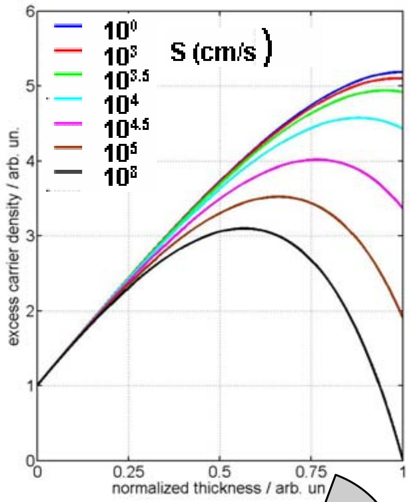


(E_{Fn}-E_{Fp}) calculated from carrier profiles versus (E_{Fn}-E_{Fp}) from pl-evaluation



for surface recombination velocities $S \leq 3x10^3$ cm/s
→ departure of (E_{Fn}-E_{Fp}) by pl-evaluation from exact value **< 1 meV**

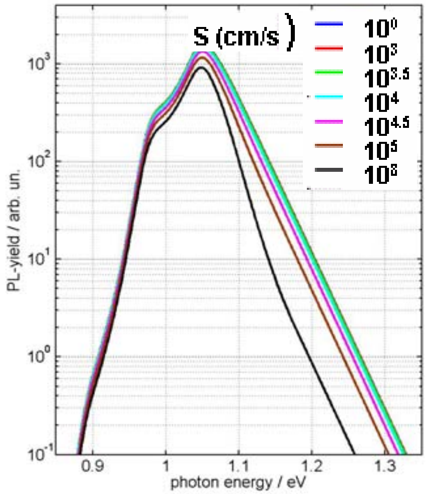
excess carrier depth profiles and according spectral pl-yields

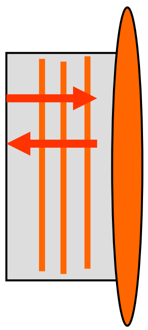


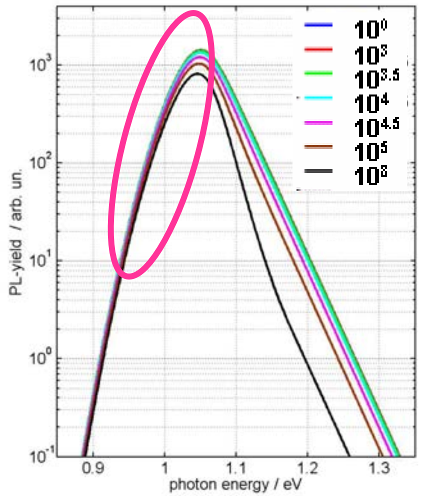
spherical wave approach

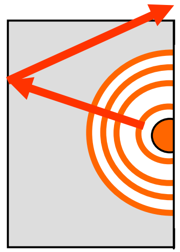
confocal setup (?) / SNOM

plane wave approach





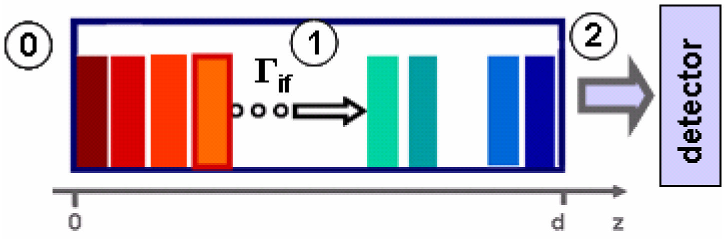


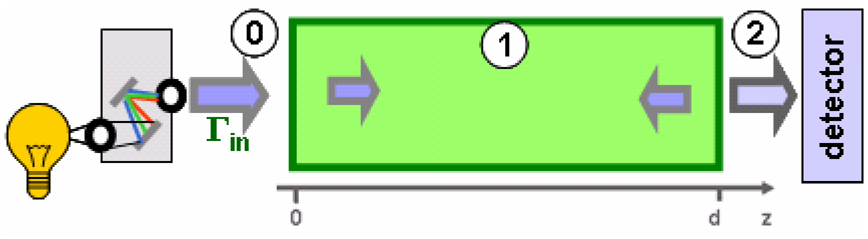


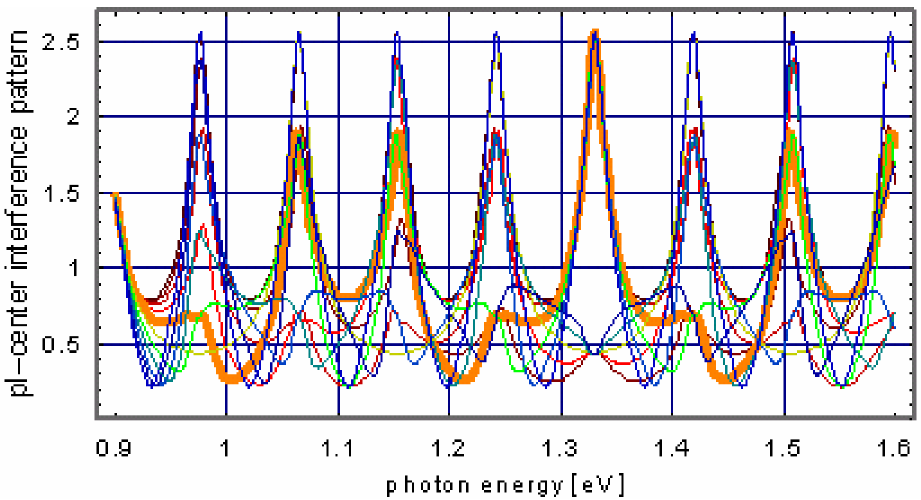
interference pattern from luminescence (centers distributed across depth) and from spectral transmission

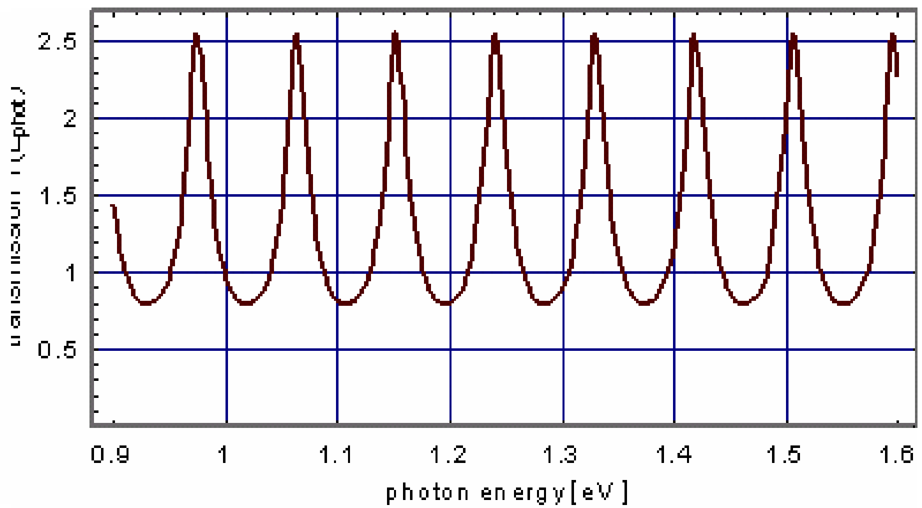
$$\Xi_{if,PL}(k) \propto \frac{1}{4}(t_{12})^2\, \Gamma_{phot}(k,z) \left|\frac{1+2r_{10}\exp[i2kz]+(r_{10})^2}{1-2r_{01}r_{12}\exp[i2kd]+(r_{01}r_{12})^2}\right|^2$$

$$T_{\Gamma_{in}}(k) \propto (t_{12})^2\, \Gamma_{in}(k) \left|\frac{1+2r_{10}+(r_{10})^2}{1-2r_{01}r_{12}\exp[i2kd]+(r_{01}r_{12})^2}\right|^2$$

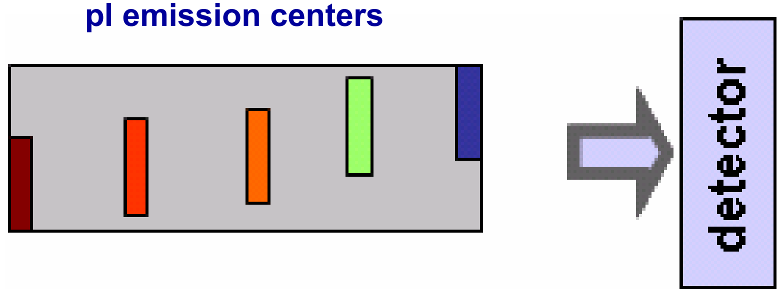


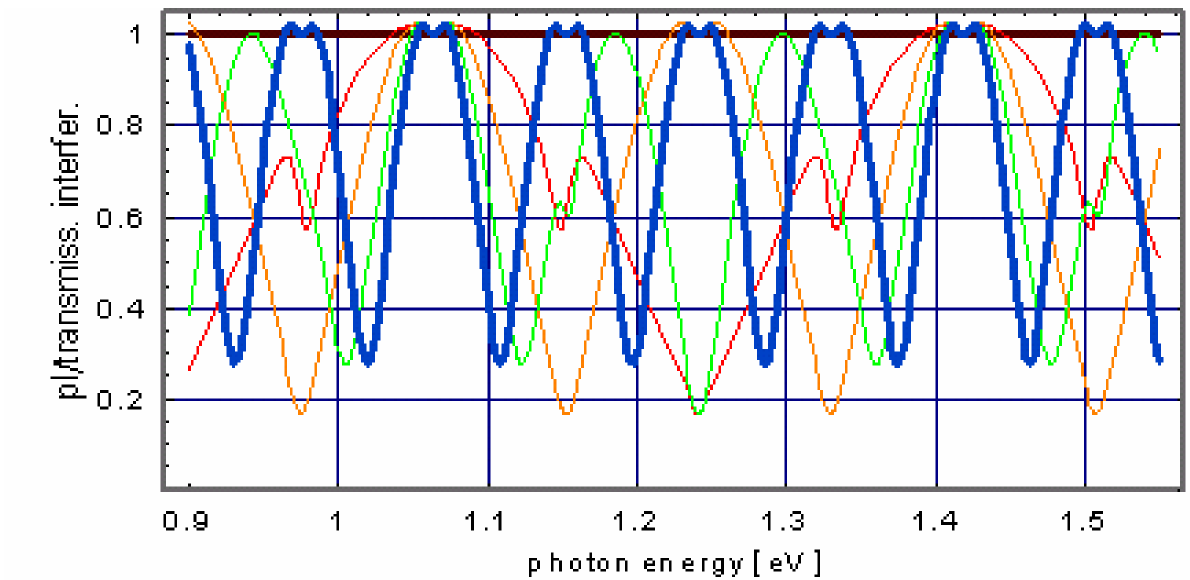






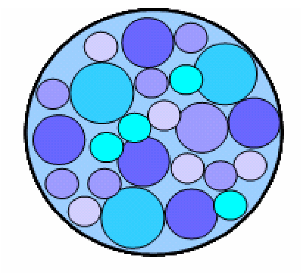
interference patterns from spectral luminescence versus those from spectral transmission

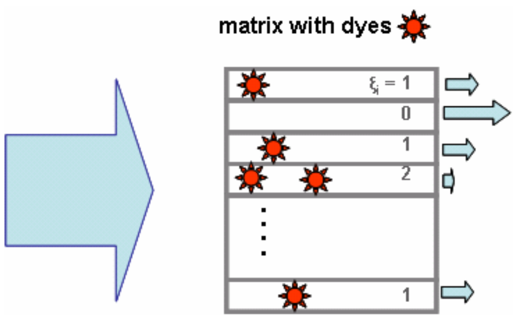


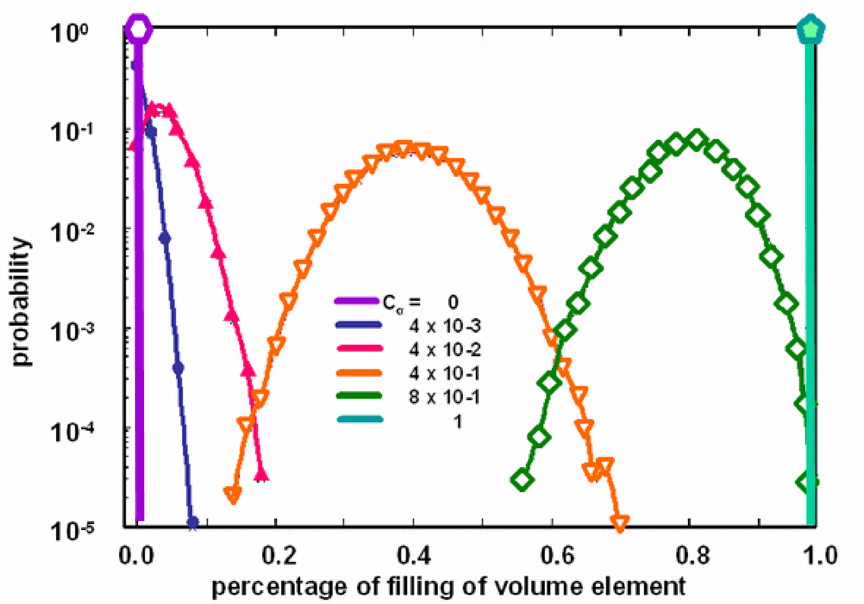


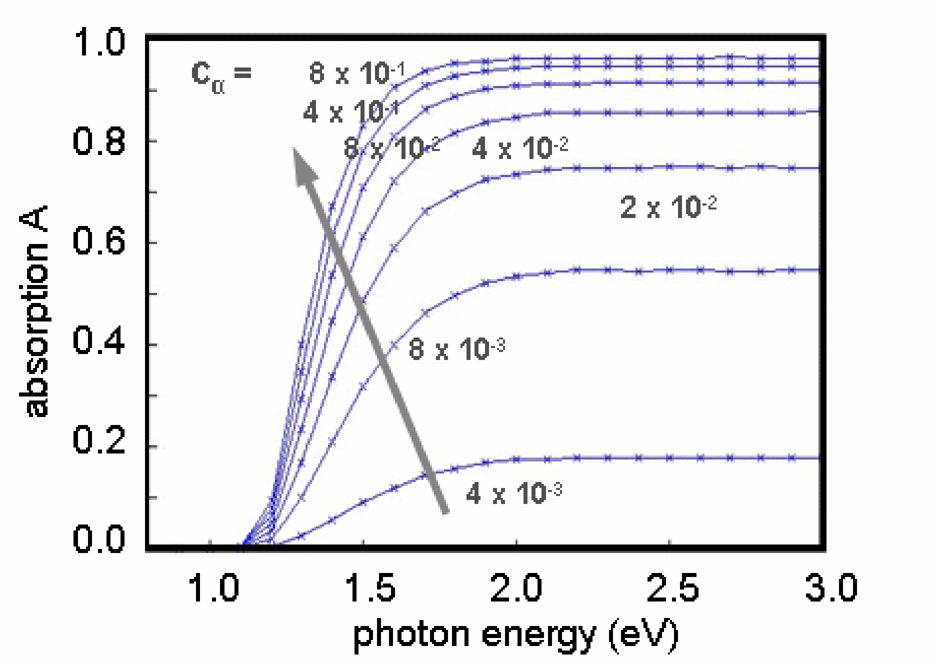
lateral, inhomogeneous with "percolative" transmission (low concentration of absorbing centers (dyes))

lateral distribution of absorption centers









NO summary

→calibrated spectral luminescence yields information on relevant parameters
for quantum solar energy conversion (pv) → $(E_{Fn}-E_{Fp})$, $\alpha(\omega)$, T

→ don't mix magnitudes (luminescence, absorption, etc.)
that superimpose non-linearly !!

→ front side / light entrance = position of hetero junction,
for decent front layer passivation $(E_{Fn}-E_{Fp})$ → e Voc;

→ departure of high energy pl-photon fluxes from ideal Bose-behavior
indicates
by positive curvature → shift of maximum carrier concentration deep in the absorber
by negative curvature → depth dependent optoelectronic properties of absorber (gradient in band gap, life time etc.)

luminescence as tool for analyses of quality of photo excited states in matter

persons involved in pl-studies

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H. Graaf (→ TU Chemnitz)
F. Heidemann
L. Gütay (→ Uni Luxb)
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M. Meesen
M. Suhlmann
P. Pargmann
K.-Ch. Schersich
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T. Unold (→ HMI)
F. Voigt
S. Vignoli (UCB Lyon)
S. Wilken
R.B. Wehrspohn (→ U/MPI Halle-Witt.)

GHB

„thanx"

funds over the years

BMBF
BMU
HBFG (DFG/ State Nds)
VW
PROCOPE / DAAD