Analysis of modulated photoluminescence for lifetime determination in silicon

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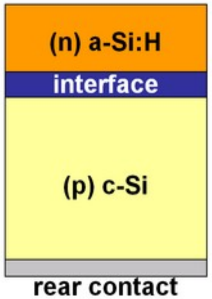
Overview

- Introduction
- Lifetime determination
- Concept of Modulated Photoluminescence (MPL)
- Linear models and experimental results
  - simple model
  - exact solution of diffusion equation
- Nonlinear models and experimental results
  - dispersive model
  - bimolecular approach
- MPL and open circuit voltage
- Summary

Introduction

- Open-circuit voltage V_{OC} of a-Si:H/c-Si heterodiode solar cells depends to large degree on interface defect density

- Efficient passivation of surfaces is required



- Effective lifetime = indicator for interface quality

- **Modulated photoluminescence (MPL)**: efficient and simple method for lifetime measurement allows investigation of influence of interface defects on minority carrier lifetime and estimation for V_{OC} in c-Si

Lifetime measurement

Established methods:

- Microwave photoconductance decay (µ-PCD)

- Quasi-steady-state photoconductance (QSSPC)

Problem: high concentration of free carriers (metallic defects, metallic rear contacts, high doped layers)

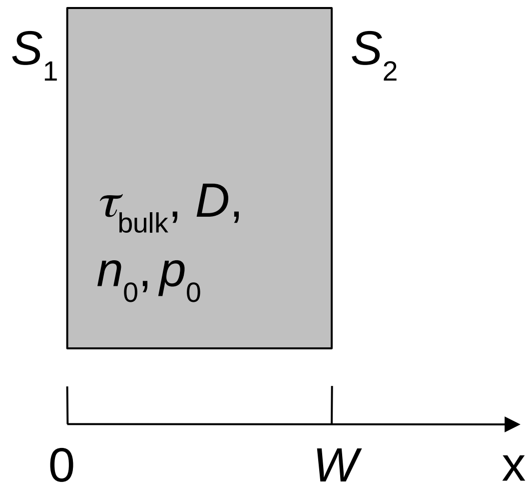
→ conductive methods fail because of shielding effects

→ alternative method: MPL

Concept: MPL

Considering high quality wafers with high bulk lifetime, the effective lifetime is determined by the contribution of surface/passivation layers (recombination velocities):

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{S_1}{W} + \frac{S_2}{W}$$



D: diffusion coefficient
S_1, S_2: recombination velocities
W: wafer thickness
n_0, p_0: carrier concentration

Concept: MPL

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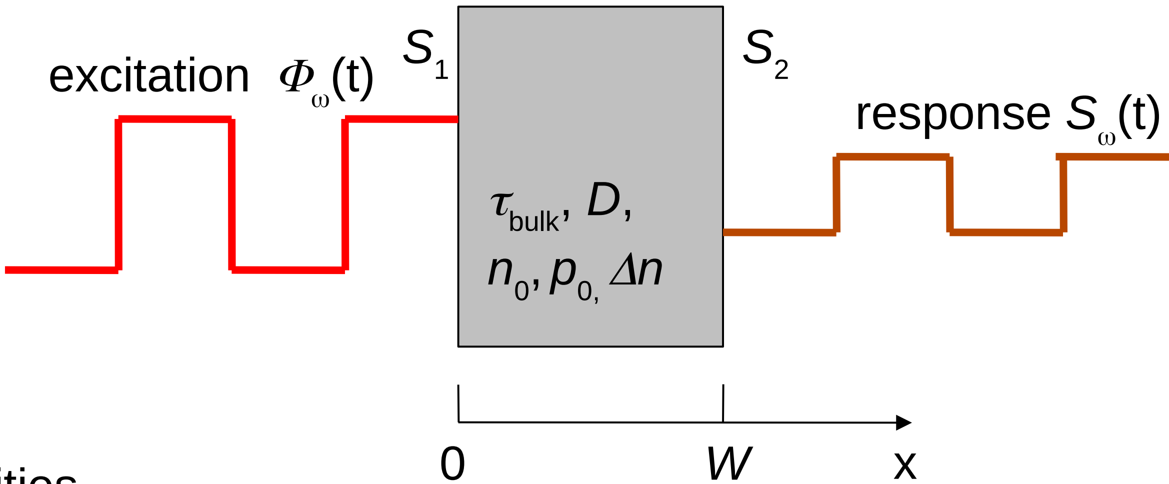


D: diffusion coefficient

S_1, S_2: recombination velocities

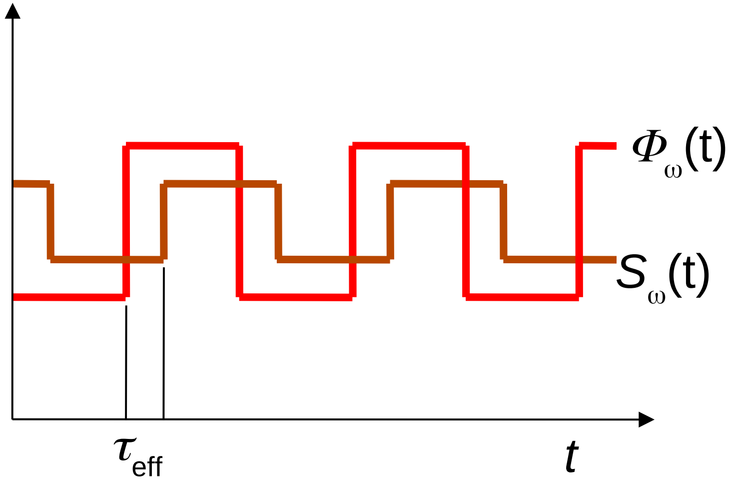
W: wafer thickness

n_0, p_0: carrier concentration; Δn: excess carrier density

Concept: MPL

Optical excitation with modulation frequency ω

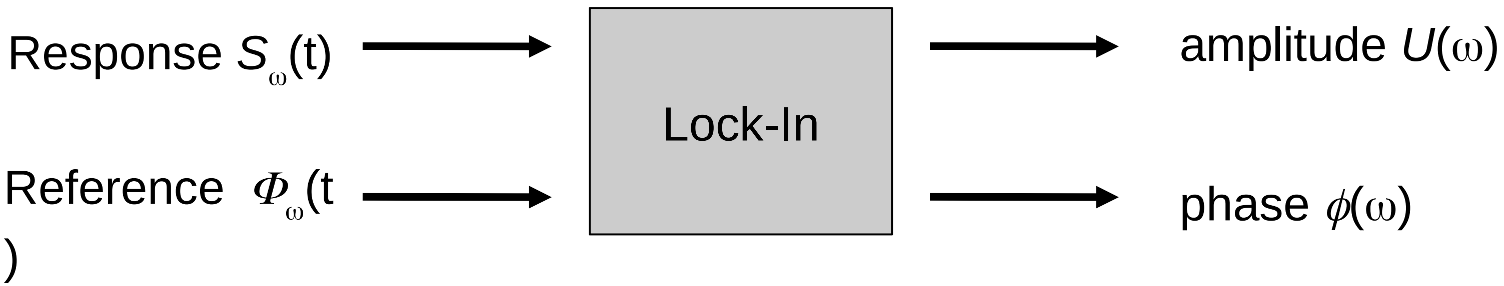
Response with modulation frequency ω and delay time = **effective lifetime τ_{eff}**



Amplitude and phase of response depend on effective lifetime τ_{eff}

With Lock-In technique get amplitude and phase spectra

Lock-in: phase-sensitive detection

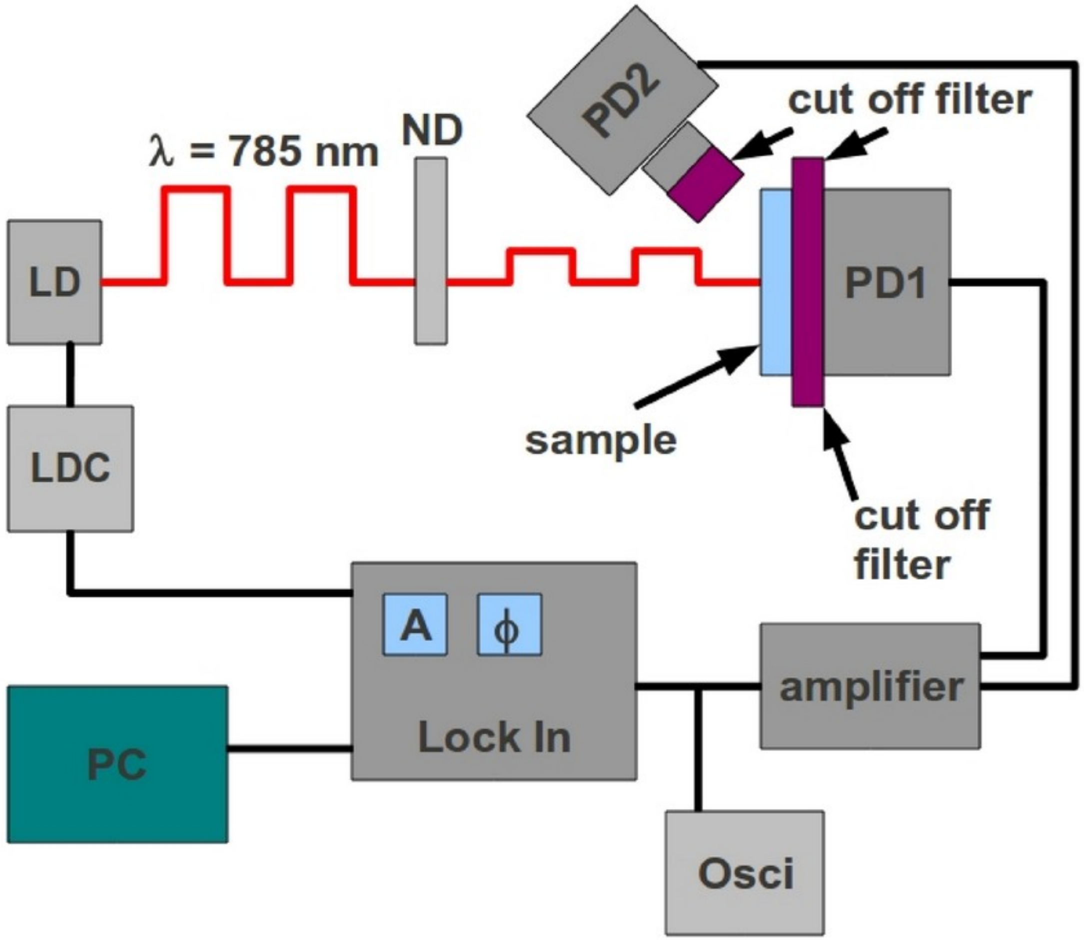


In-phase/ out-of-phase components:

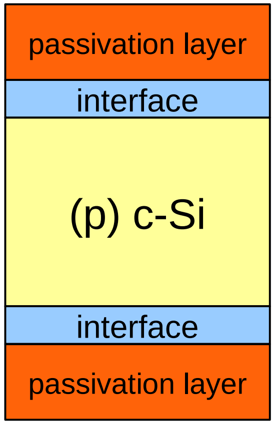
$$S_{IP}(\omega) = \frac{2}{T}\int_0^T S(t)\cos(\omega t)dt \qquad U(\omega) = \sqrt{S_{IP}(\omega)^2 + S_{OP}(\omega)^2}$$

$$S_{OP}(\omega) = \frac{2}{T}\int_0^T S(t)\sin(\omega t)dt \qquad \phi(\omega) = \tan^{-1}\left(\frac{S_{OP}(\omega)}{S_{IP}(\omega)}\right)$$

Experimental setup



Samples

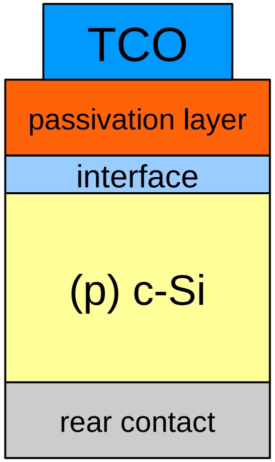


p,n-type c-Si wafer with different passivation:

- different passivation layers: n-type, intrinsic, SiC, a-Si:H, SiN

- different doping ($N_A=10^{15}$ cm^{-3}, $N_A=10^{16}$ cm^{-3})

- wafer with TCO and rear contact (solar cell)



Simple model [1]

Rateequation with sinusoidal modulation:

$$\frac{d\Delta n(t)}{dt} = G(t) - R(t) = G_0 + G_1 \sin(\omega t) - \frac{\Delta n(t)}{\tau}$$

$$\Delta n(t) = G_0\tau + G_1\tau \frac{\sin(\omega t + \arctan(\omega\tau))}{\sqrt{1+(\omega\tau)^2}}$$

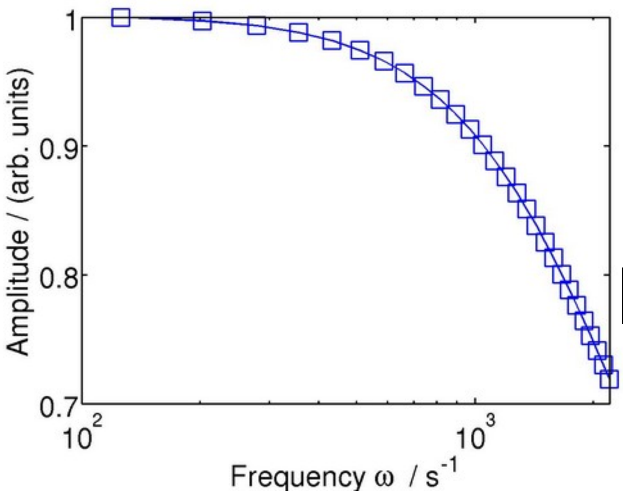
<u>spectral amplitude</u>: $$\Delta n_1(\omega) = \frac{\Delta G_1 \tau}{\sqrt{1+(\omega\tau)^2}}$$

<u>spectral phase</u>: $$\varphi(\omega) = -\arctan(\omega\tau) \Leftrightarrow \tan(\varphi) = -\omega\tau$$

[1] R. Brüggemann, S. Reynolds, J. Non-Cryst. Solids 352 (2006) 1888

Results: SiC-passivation (1 Ωcm)

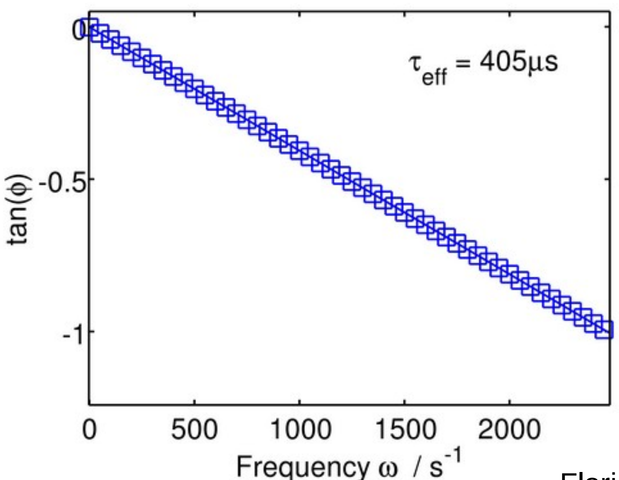
two procedures for lifetime extraction from experimental measurement



fit amplitude

$$\tau_n = 397\mu s$$

$$|\Delta n_1| = \frac{\tau_n G_1}{\sqrt{1+(\omega\tau_n)^2}}$$

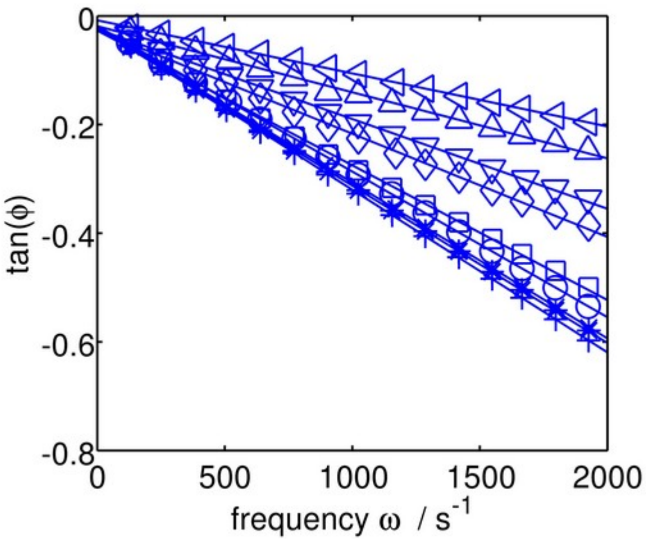


fit tangent

$$\tau_n = 405\mu s$$

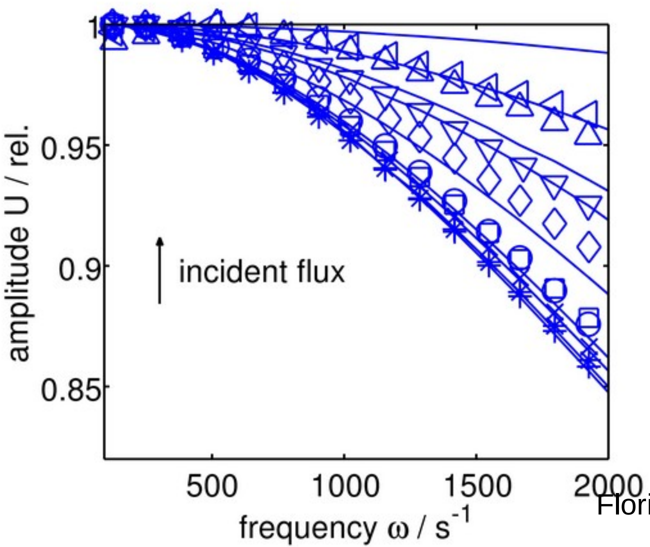
$$\tan(\wp) = -\omega\tau_n$$

Results: SiN passivation (1 Ωcm)

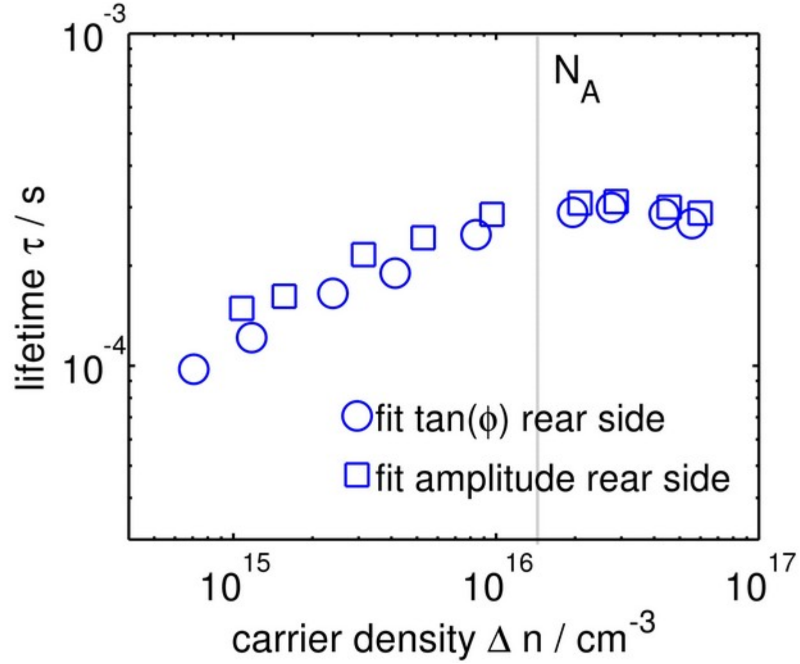


lifetime measurement by phase more reliable in contrast to amplitude

τ_{φ}



$\tau_{amplitude}$



$$\Delta n = G\tau_{eff}$$

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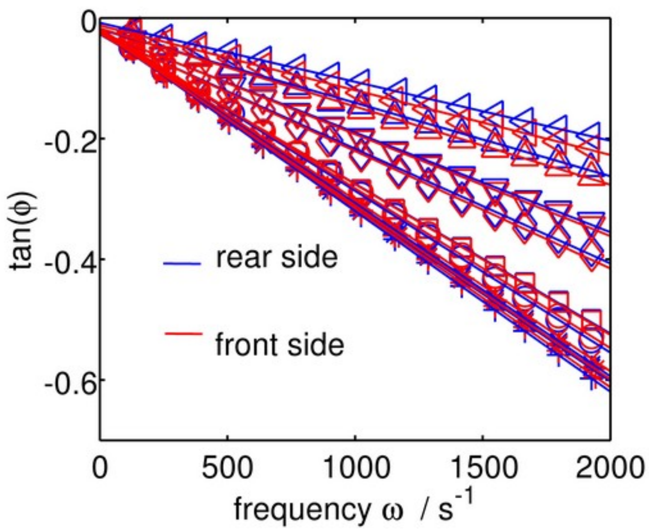
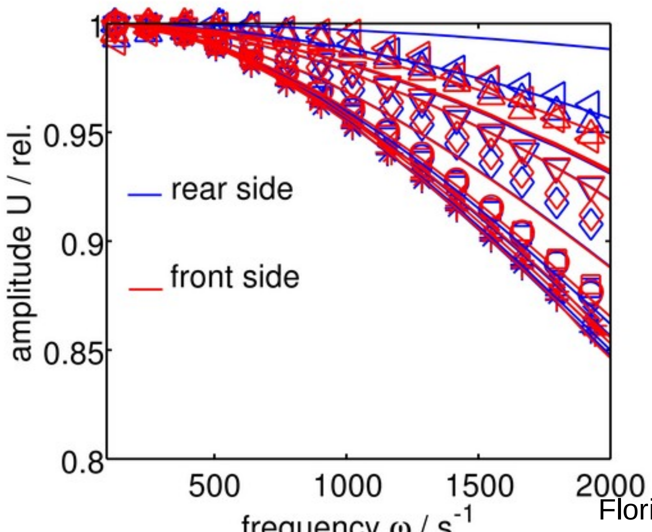
Results: SiN passivation (1 Ωcm)

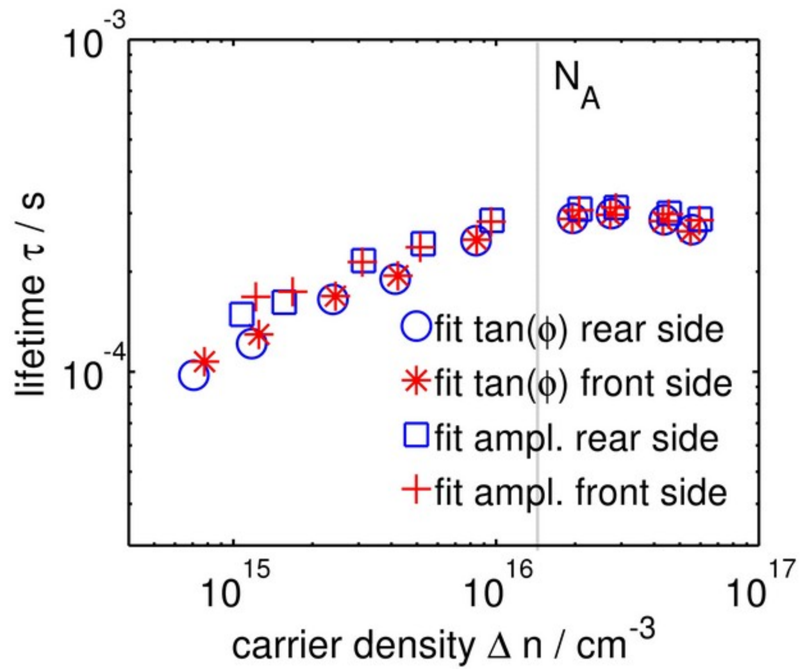




good agreement between measurement at rear and front side

τ_{φ}

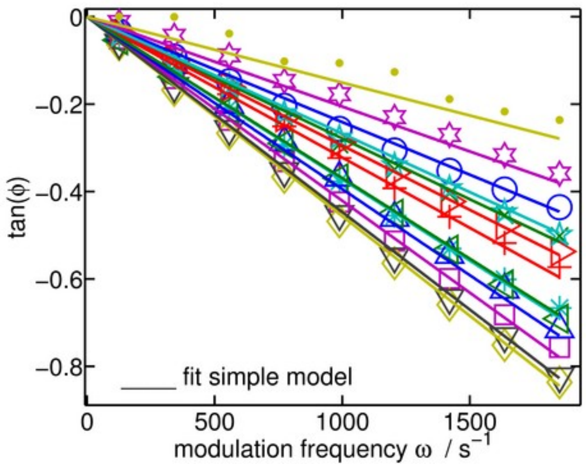
$\tau_{amplitude}$

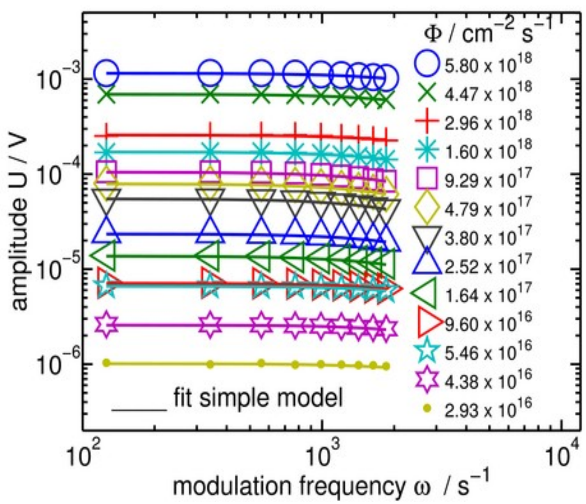


$$\Delta n = G\tau_{eff}$$

Results: (n)a-Si-H/(i)a-Si:H pass. (1 Ωcm)

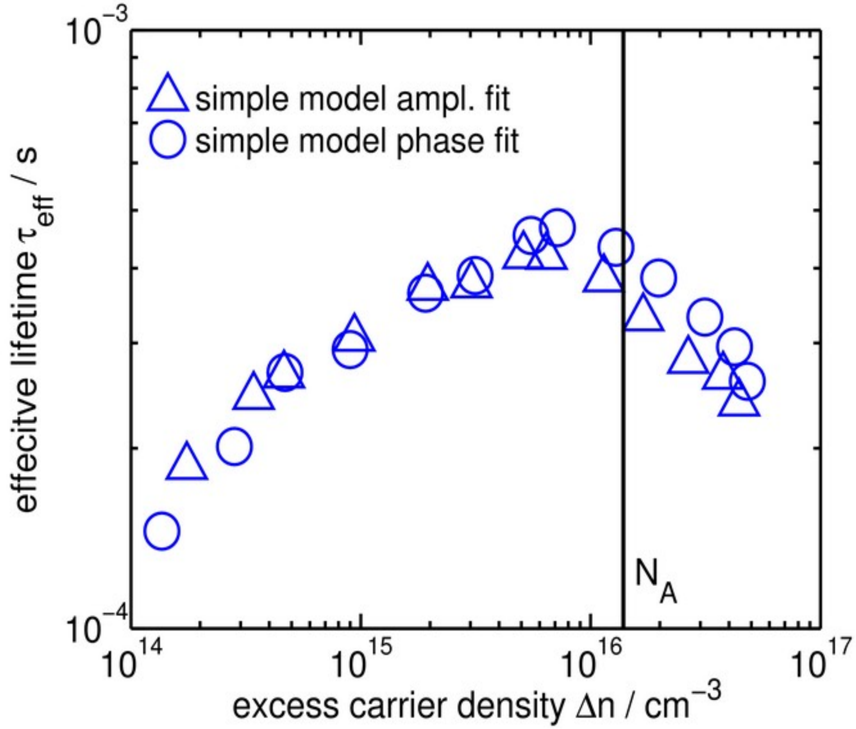
applied to solar cell (only in reflection mode)





τ_{φ}

$\tau_{amplitude}$



$$\Delta n = G\tau_{eff}$$

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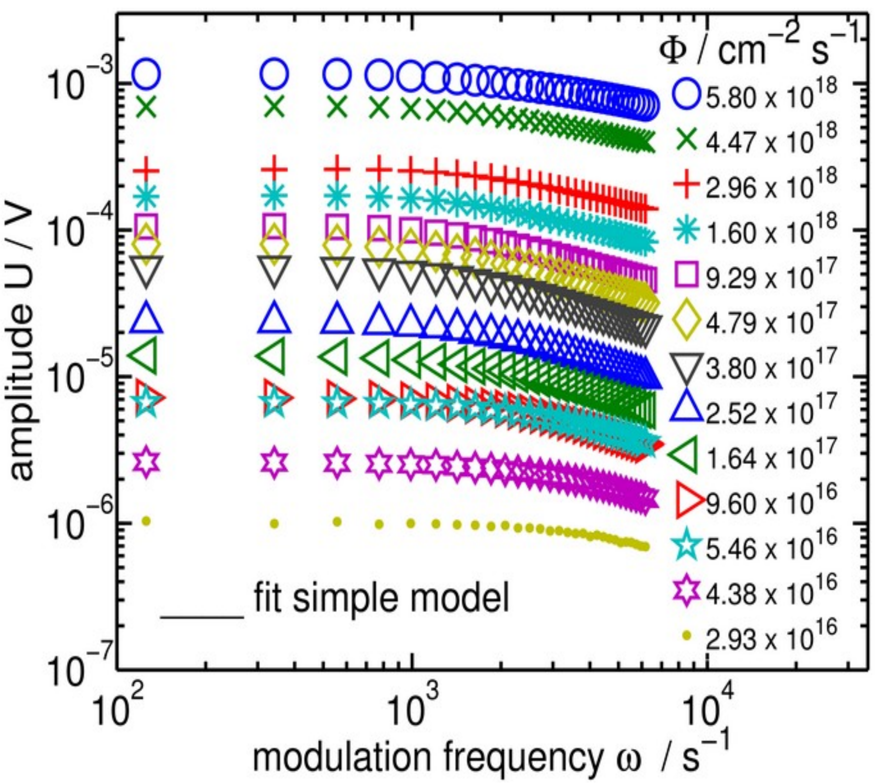
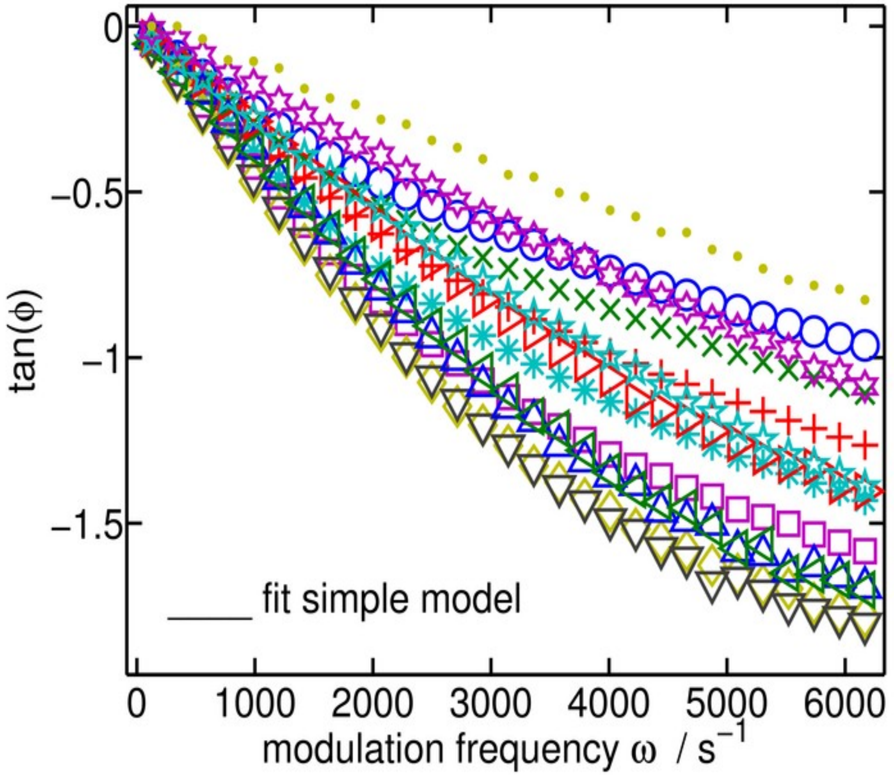
high frequency range: deviations from linear variation of the tangens





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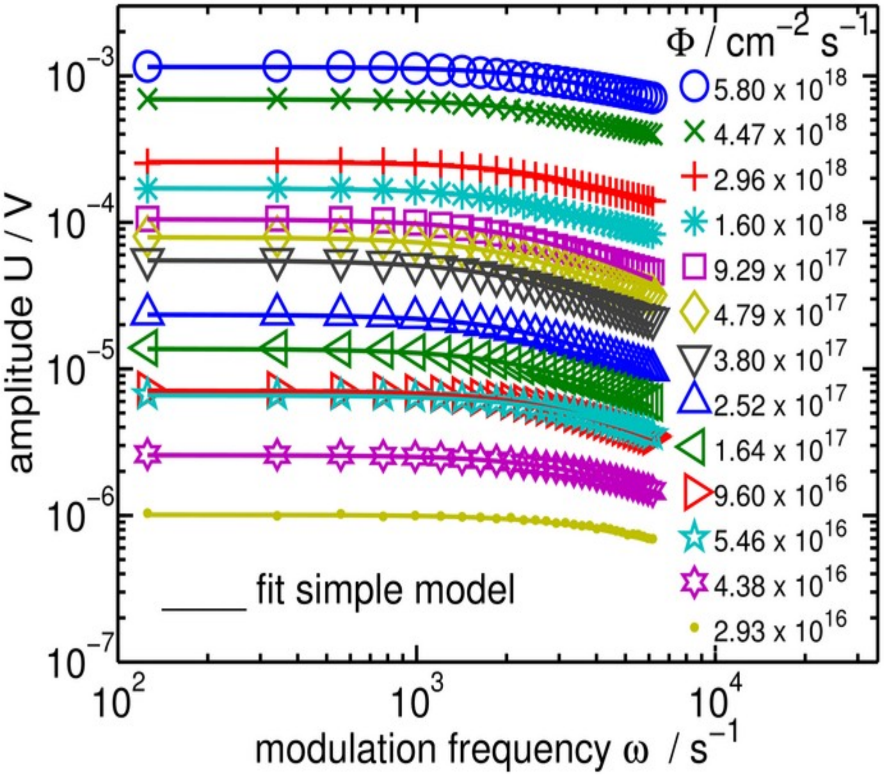

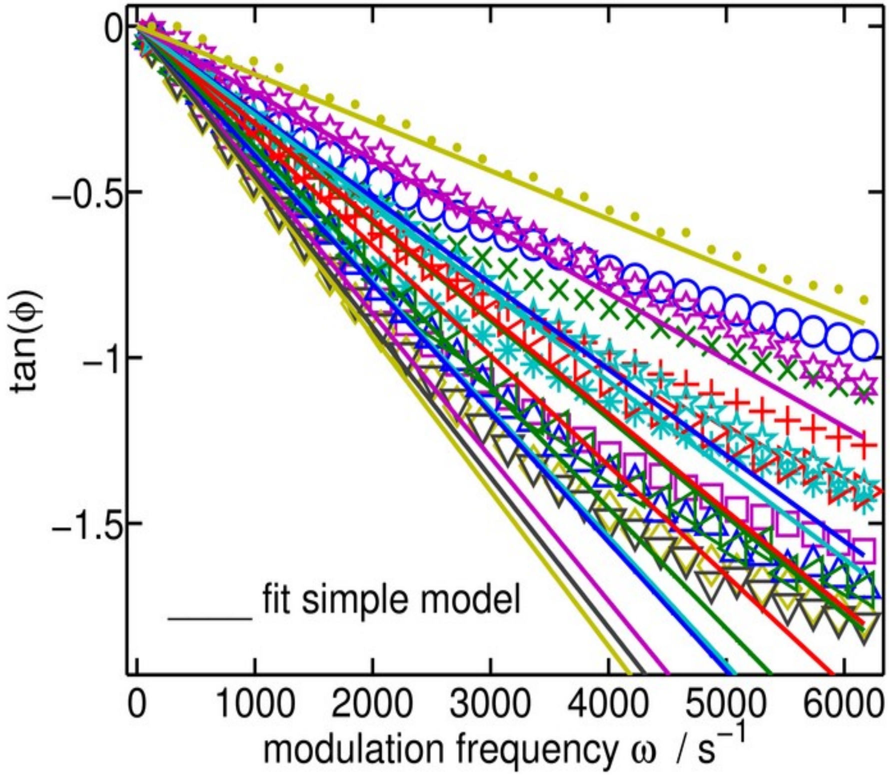

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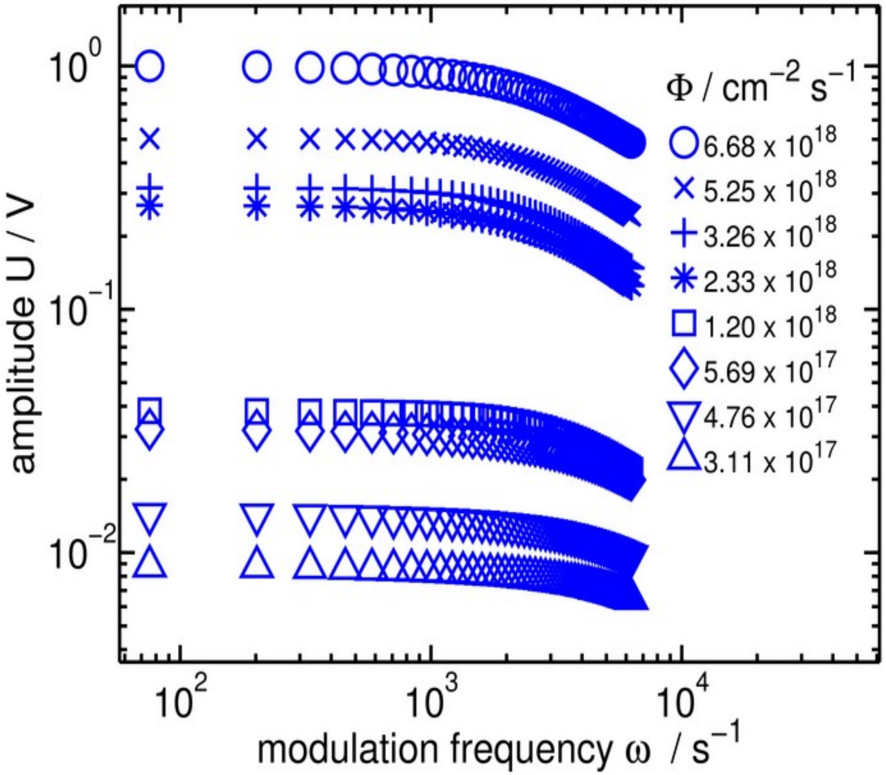

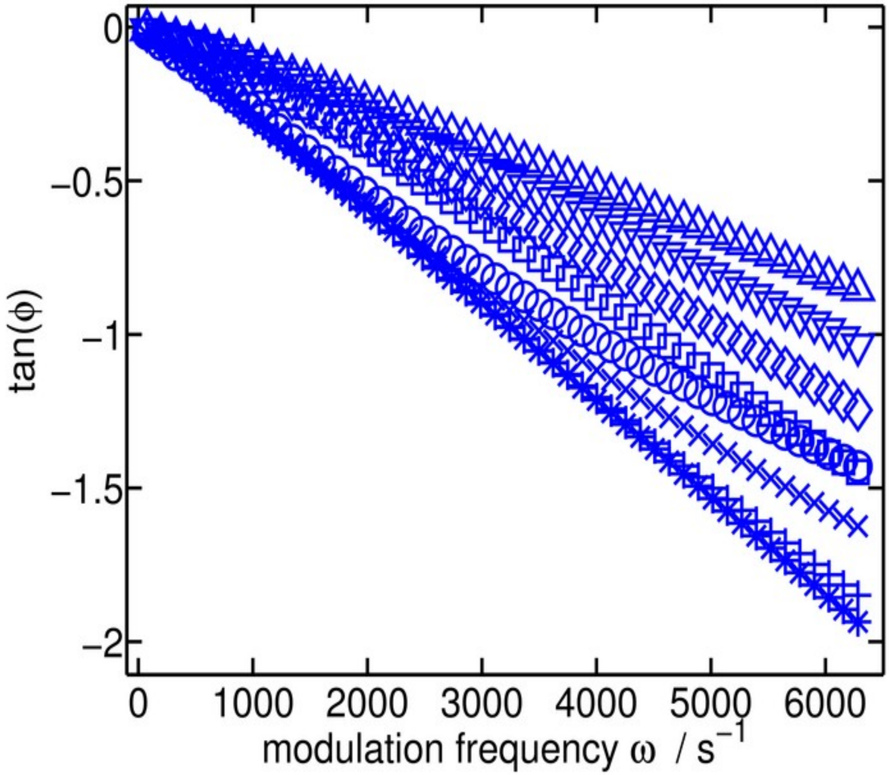

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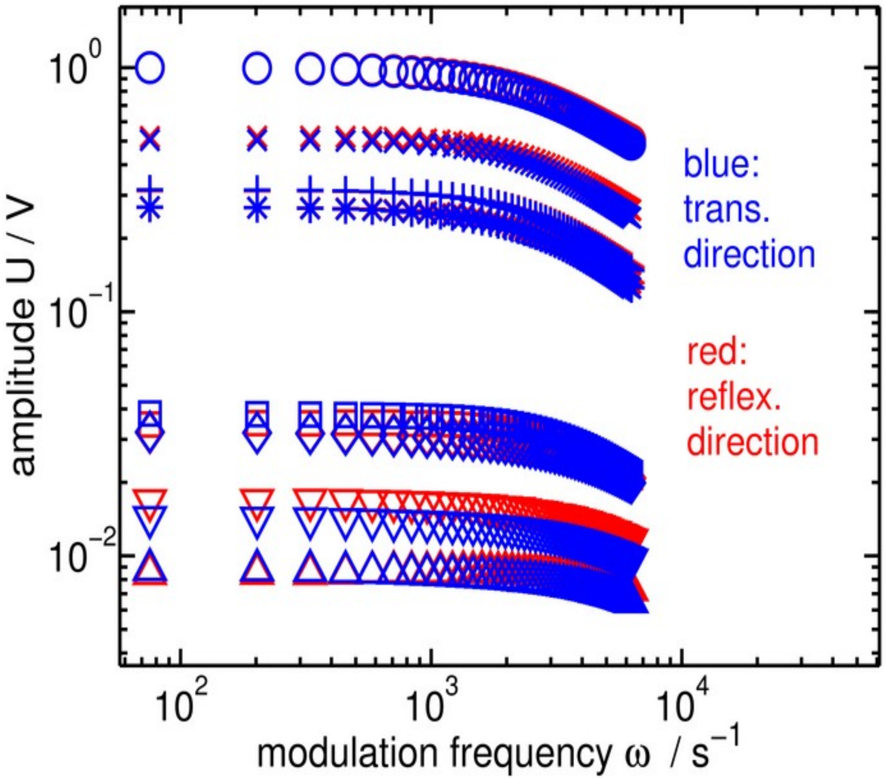

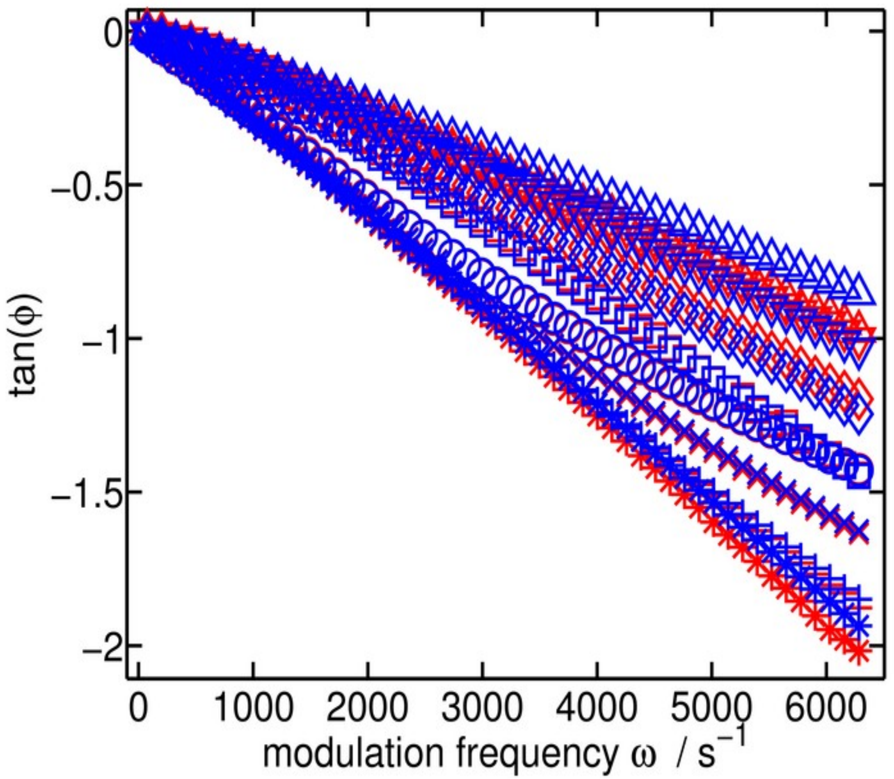

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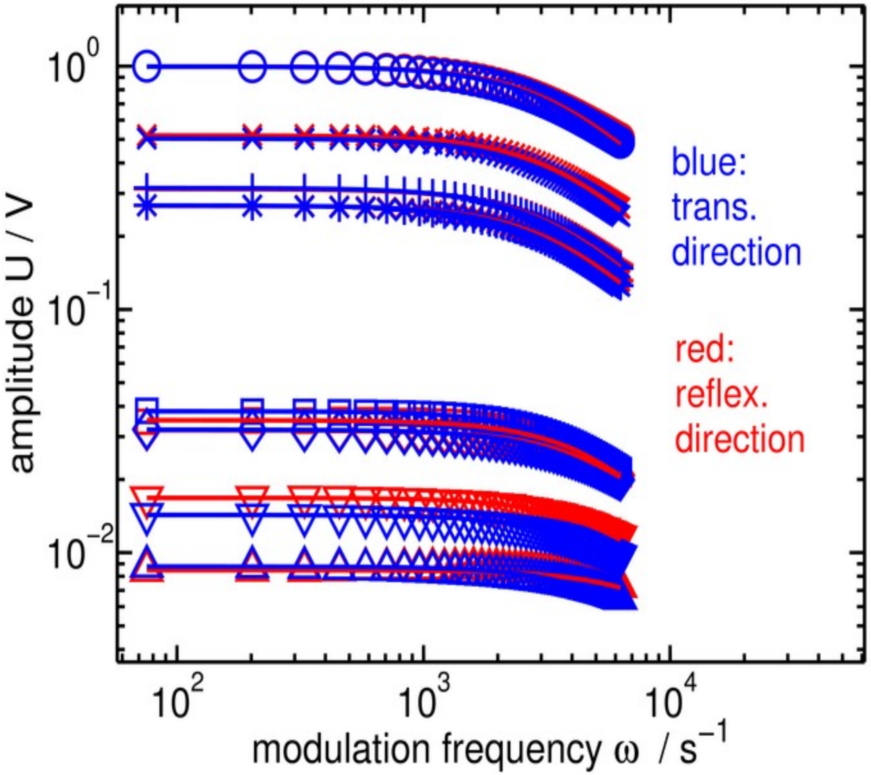

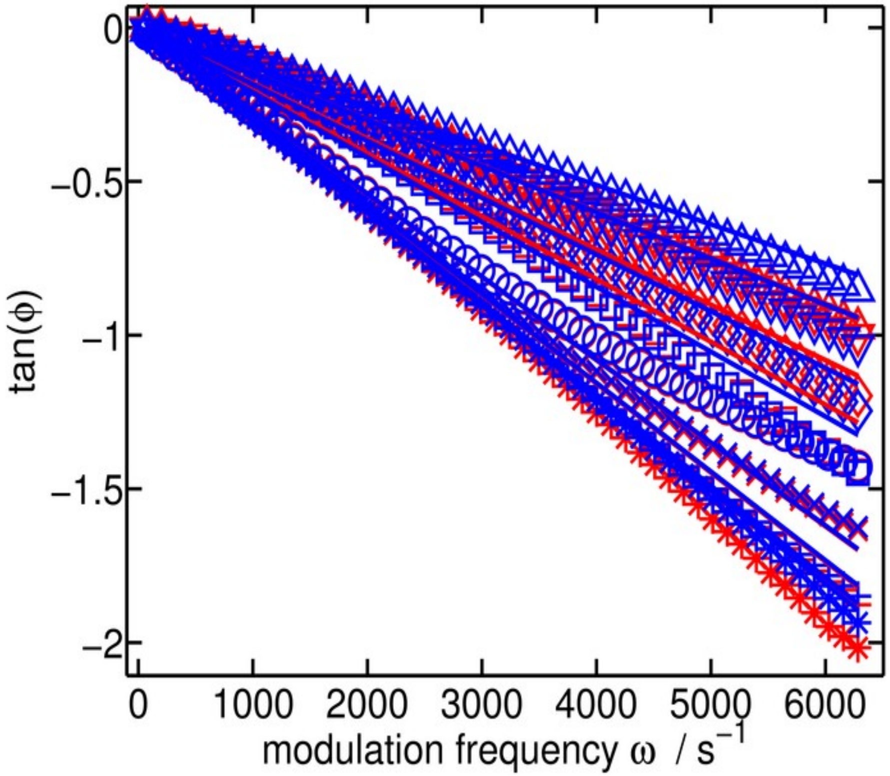

Better approach: solving diffusion equation [2]

$$\frac{\partial \Delta n(x,t)}{\partial t} = D\nabla^2 \Delta n(x,t) - \frac{\Delta n(x,t)}{\tau_{bulk}} + G(x,t)$$

Δn: excess carrier density
D: diffusion coefficient
G: generation rate

[2] M. Orgeret, J. Boucher, Rev. de Phys. Apl. 13(1), 29-37 (1987)

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$$\frac{\partial \Delta n(x,t)}{\partial t} = D\nabla^2 \Delta n(x,t) - \frac{\Delta n(x,t)}{\tau_{bulk}} + G(x,t)$$

$$G(x,t) = \sum_{m=-\infty}^{\infty} G_m e^{im\omega t} e^{-\alpha x}$$

$$D \frac{\partial \Delta n(x,t)}{\partial x}\bigg|_{x=0} = S_1 \Delta n(0,t)$$

$$-D \frac{\partial \Delta n(x,t)}{\partial x}\bigg|_{x=W} = S_2 \Delta n(W,t)$$

Δn: excess carrier density
D: diffusion coefficient
G: generation rate
α: apsorption coefficient
S_1,S_2 surface recombination velocity

[2] M. Orgeret, J. Boucher, Rev. de Phys. Apl. 13(1), 29-37 (1987)

Complex solution: local excess carrier concentration

$$\Delta n(x,t) = \sum_{m=-\infty}^{\infty} \Delta n_m^*(x,\omega) e^{im\omega t}$$

Solution: complex excess carrier concentration

$$\Delta n(x,t) = \sum_{m=-\infty}^{\infty} \Delta n_m^*(x,\omega) e^{im\omega t}$$

$$\sum_{m=-\infty}^{\infty} \int_0^W \Delta n_m^*(x,\omega) e^{im\omega t} dx = \sum_{m=-\infty}^{\infty} \Delta N_m^*(\omega) e^{im\omega t}$$

W: wafer thickness

Lock-In detection: only fundamental component (ω)

$$\Delta n_1^*(x,\omega) = \frac{G_1\left(C_1 e^{(x-W)/L_1} + C_2 e^{-(x-W)/L_1} - e^{\alpha x}\right)}{D\left(\alpha^2 - \frac{1}{L_1^2}\right)}$$

$$C_1 = \frac{1}{2}\frac{(\alpha D + S_1)\left(\frac{D}{L_1} - S_2\right) - (\alpha D - S_2)\left(\frac{D}{L_1} + S_1\right)e^{-W(\alpha - \frac{1}{L_1})}}{\left(\frac{D^2}{L_1^2} + S_1 S_2\right)\sinh(\frac{W}{L_1}) + \frac{D}{L_1}(S_1 + S_2)\cosh(\frac{W}{L_1})}$$

$$\tau_1(\omega) = \frac{\tau_{bulk}}{1 + i\omega\tau_{bulk}}$$

$$L_1(\omega) = \sqrt{D\tau_1(\omega)}$$

$$C_2 = \frac{1}{2}\frac{(\alpha D + S_1)\left(\frac{D}{L_1} + S_2\right) - (\alpha D - S_2)\left(\frac{D}{L_1} - S_1\right)e^{-W(\alpha + \frac{1}{L_1})}}{\left(\frac{D^2}{L_1^2} + S_1 S_2\right)\sinh(\frac{W}{L_1}) + \frac{D}{L_1}(S_1 + S_2)\cosh(\frac{W}{L_1})}$$

L_1: diffusion length

Extended model

→ more precise model including independent values for front and back surface recombination velocities, wavelength dependent absorption, sample thickness and dopant type

$$U_{ampl} \sim \|\int_0^W \Delta n_1^*(x,\omega)dx\| = \|\Delta N_1^*(\omega)\|$$

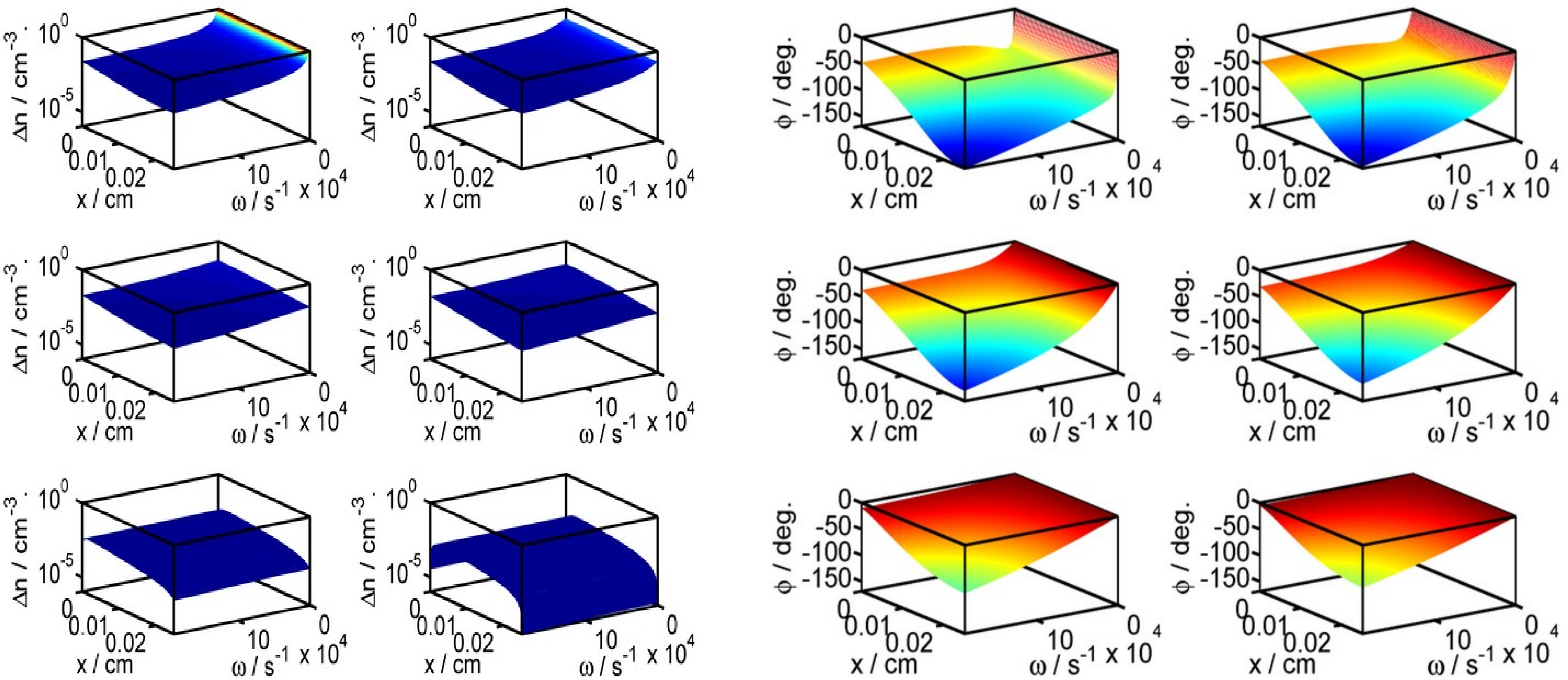
$$\phi(\omega) = \tan^{-1}\left(\frac{\Im(\Delta N_1^*(\omega))}{\Re(\Delta N_1^*(\omega))}\right)$$

→ model allows depth profile of amplitude and phase spectra

Space depending amplitude and phase spectra

D = 12 cm² s⁻¹; τ_{bulk} = 20 ms; W=0.025 cm; α= 1010 cm⁻¹;

<u>symmetrical sample</u>: $S_1 = S_2$= 20, 100, 500, 10^3, 10^4, 10^6 cm s⁻¹



Integrated amplitude and phase spectra

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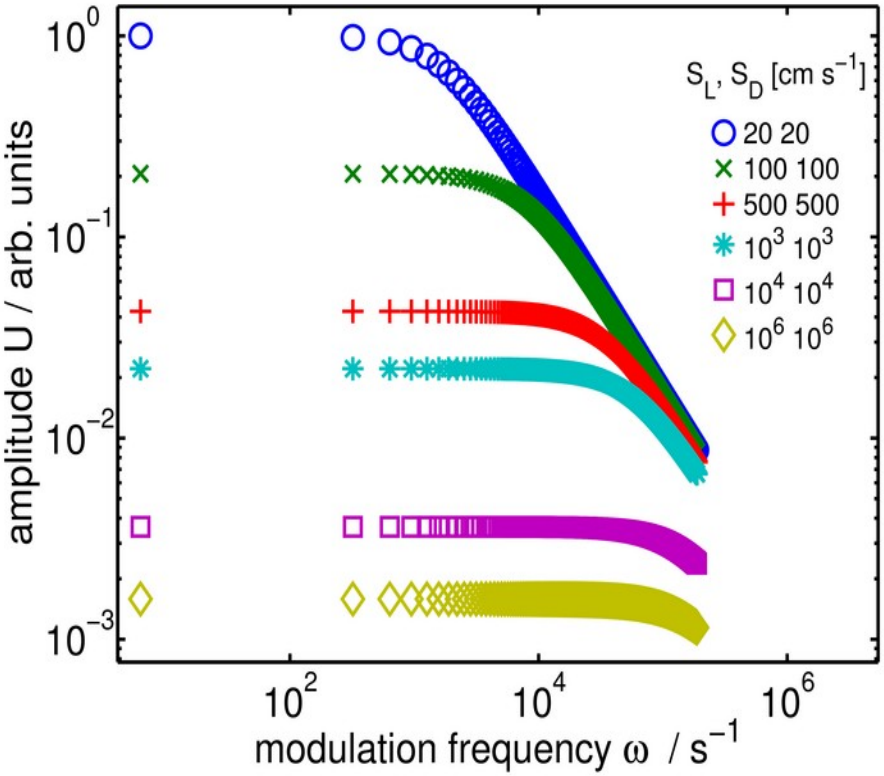

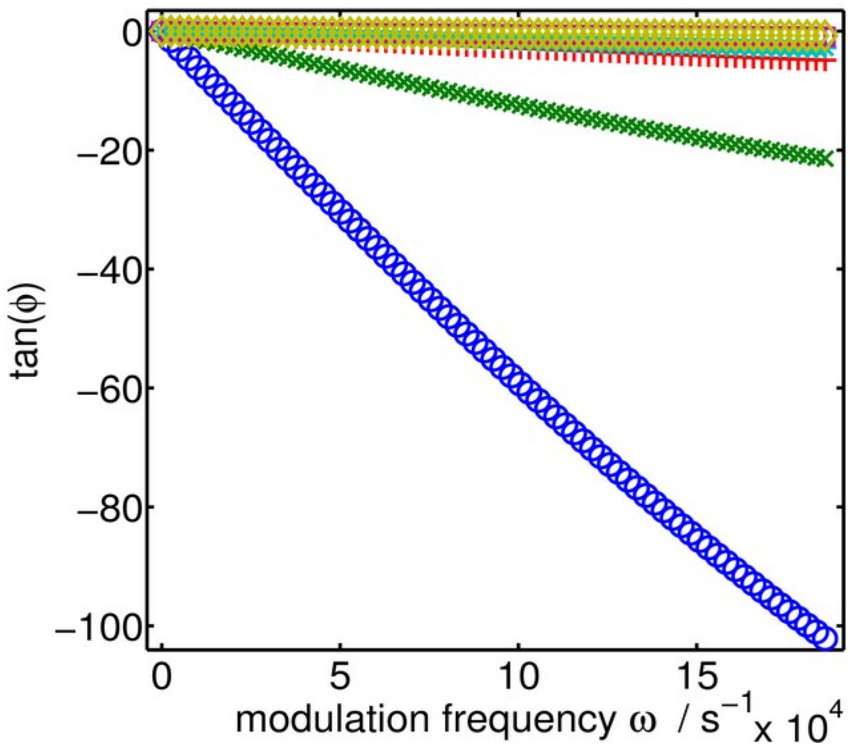

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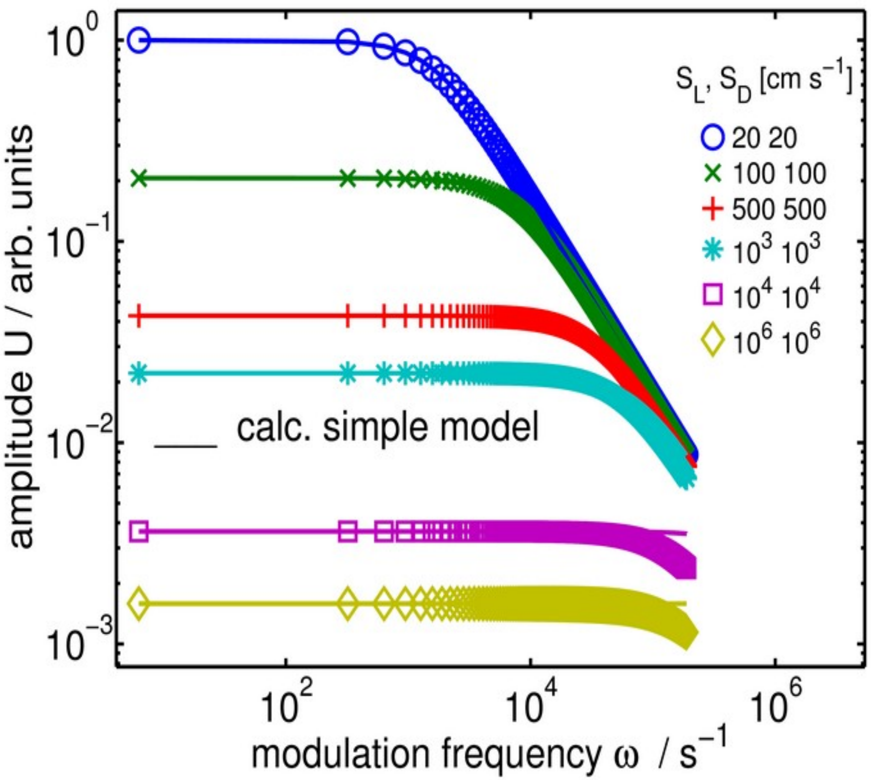

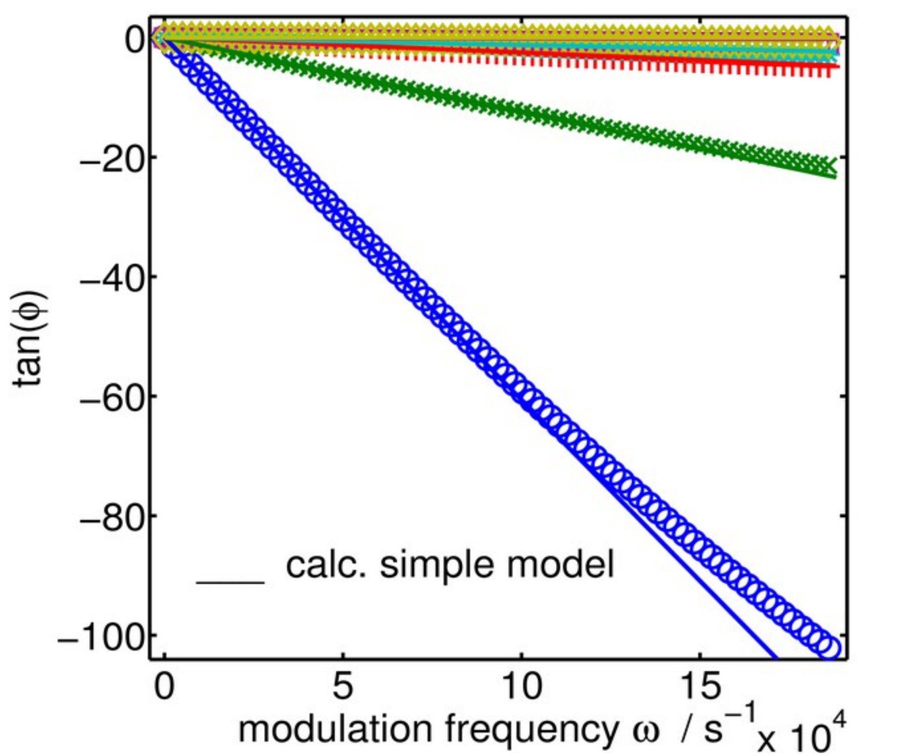

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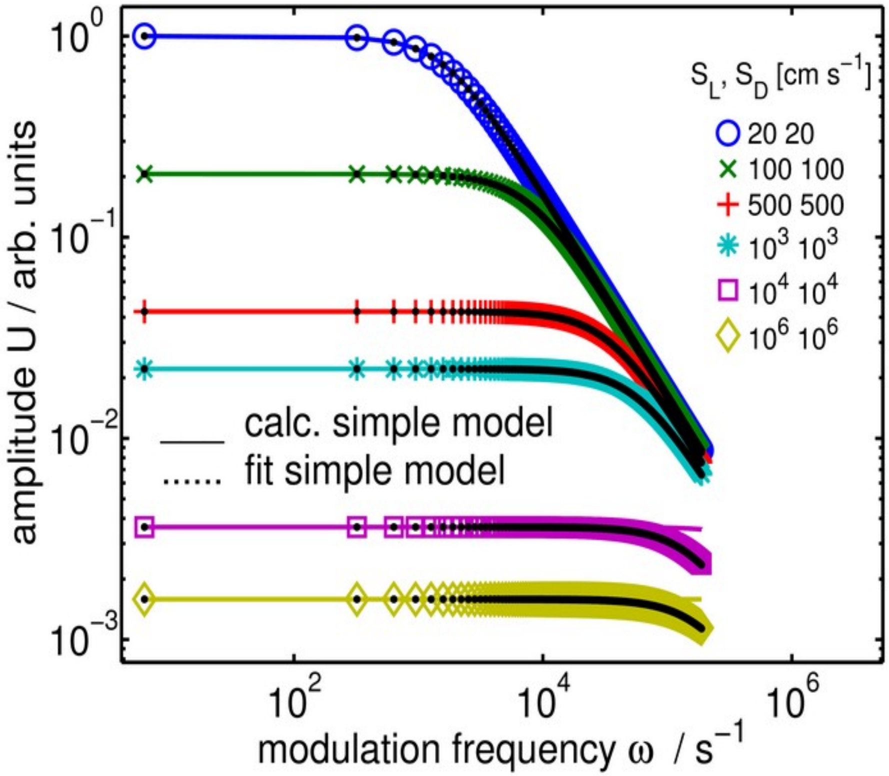

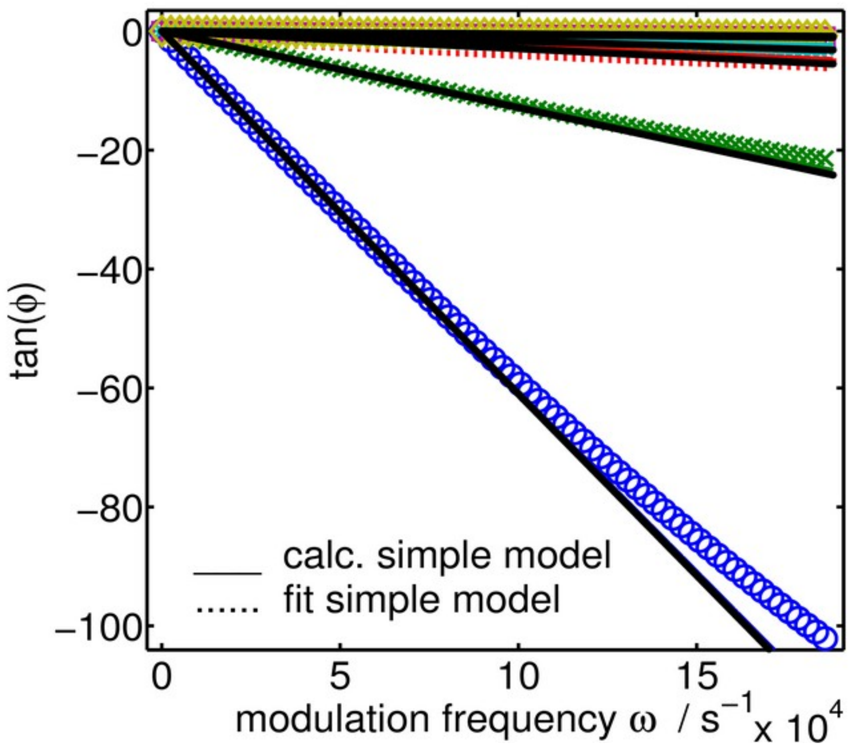

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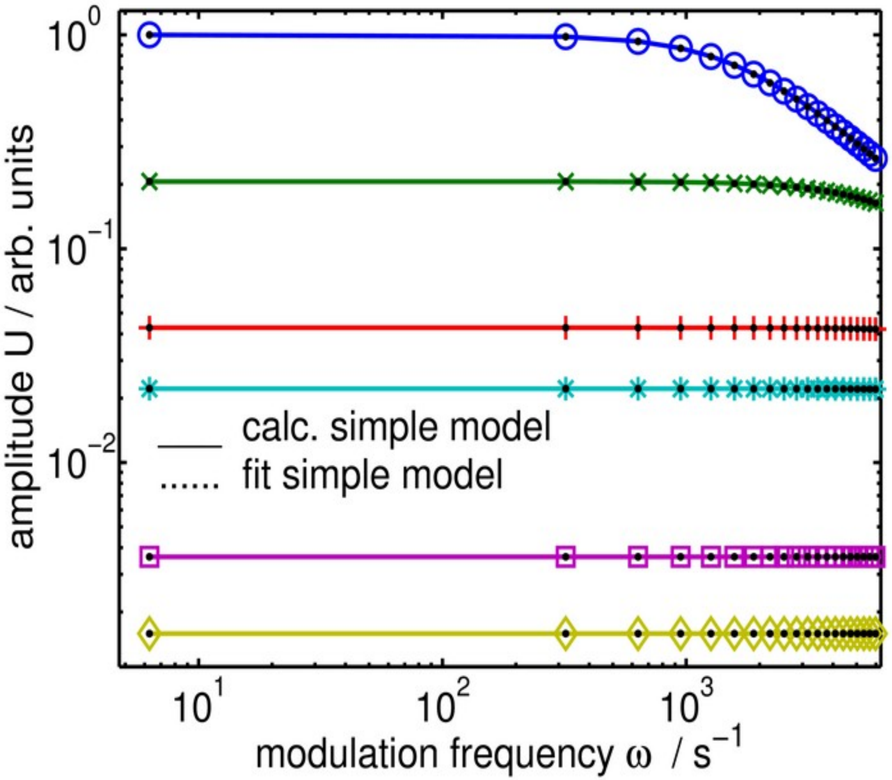
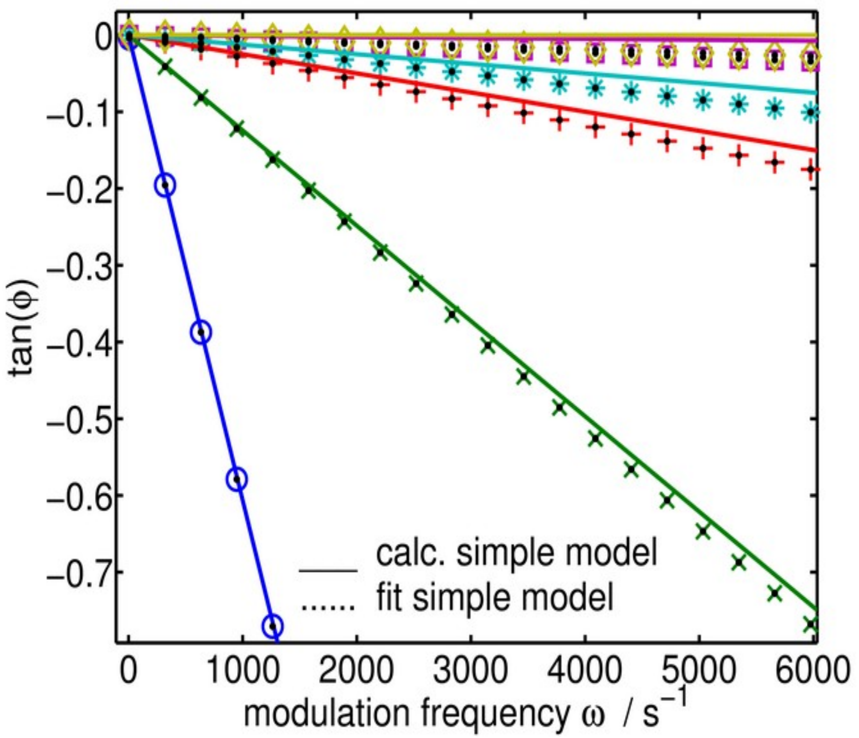
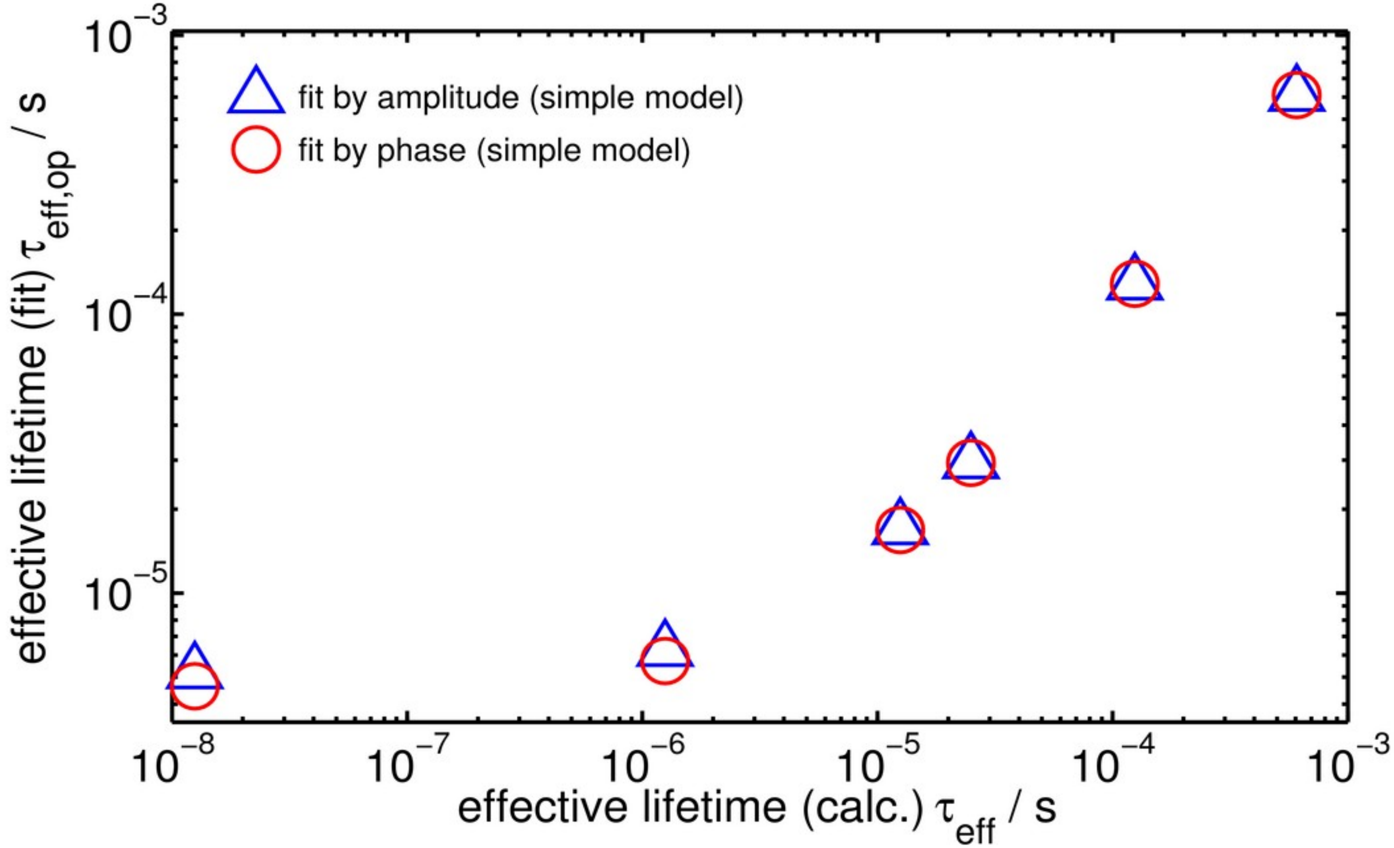




Integrated amplitude and phase spectra

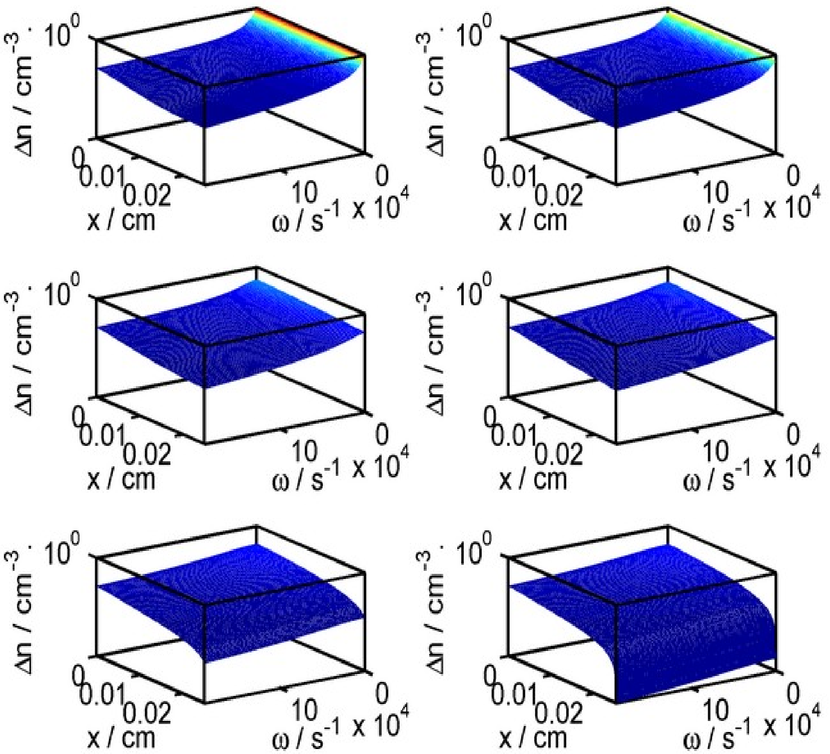
overestimation of real lifetime for high surface recombination rates

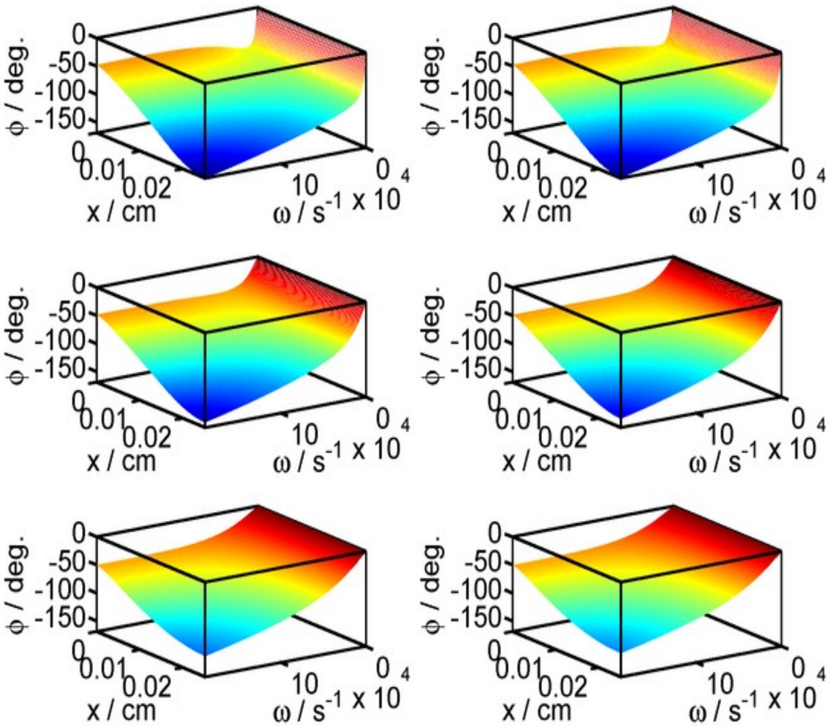


Space depending amplitude and phase spectra

D = 12 cm² s^{-1}; τ_{bulk} = 20 ms; *W*=0.025 cm; α= 1010 cm^{-1};

asymmetrical sample: S_1= 20 cm s^{-1}; S_2= 50, 100, 500, 10³, 10⁴, 10⁶ cm s^{-1}





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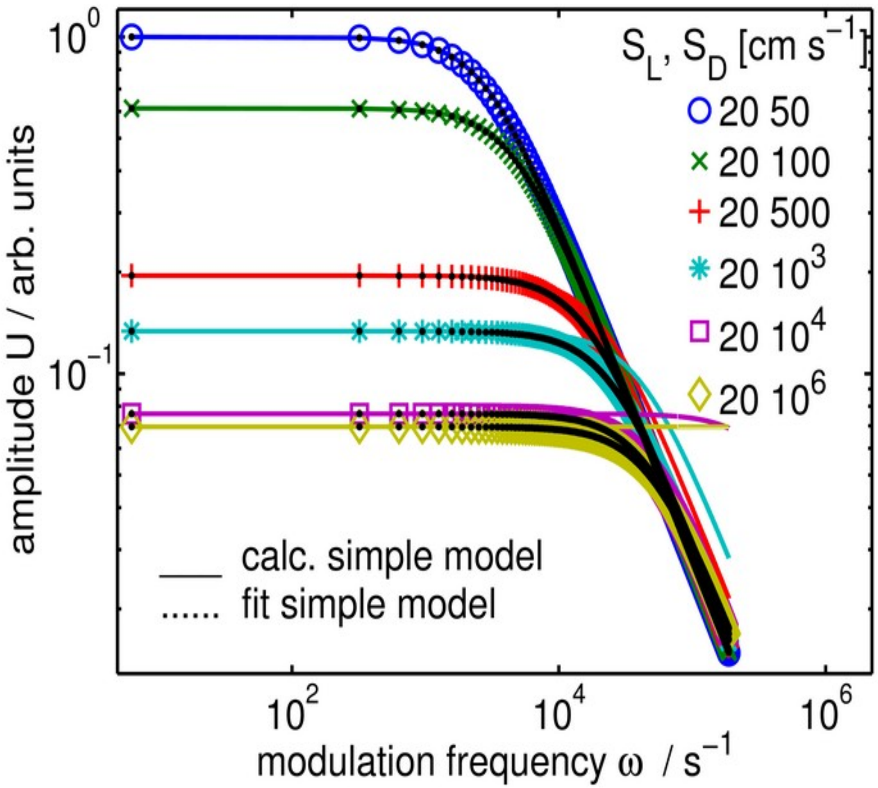

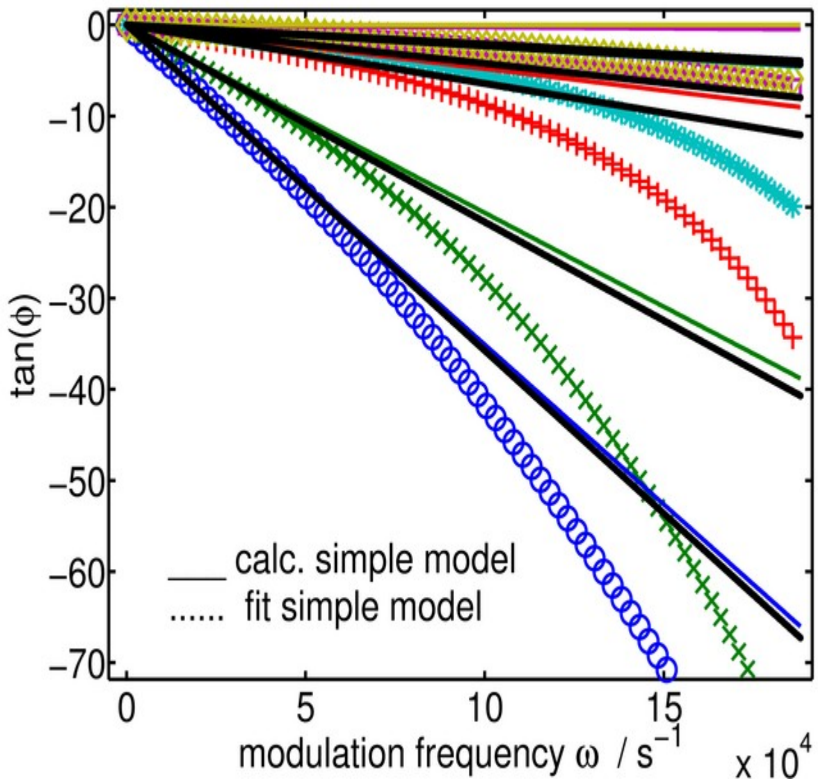

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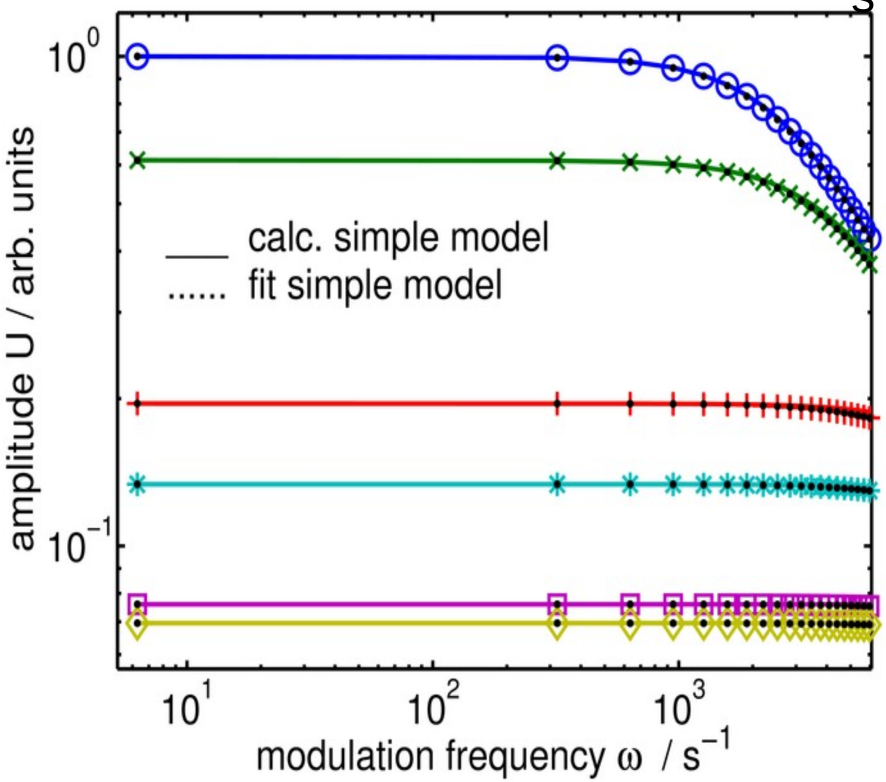

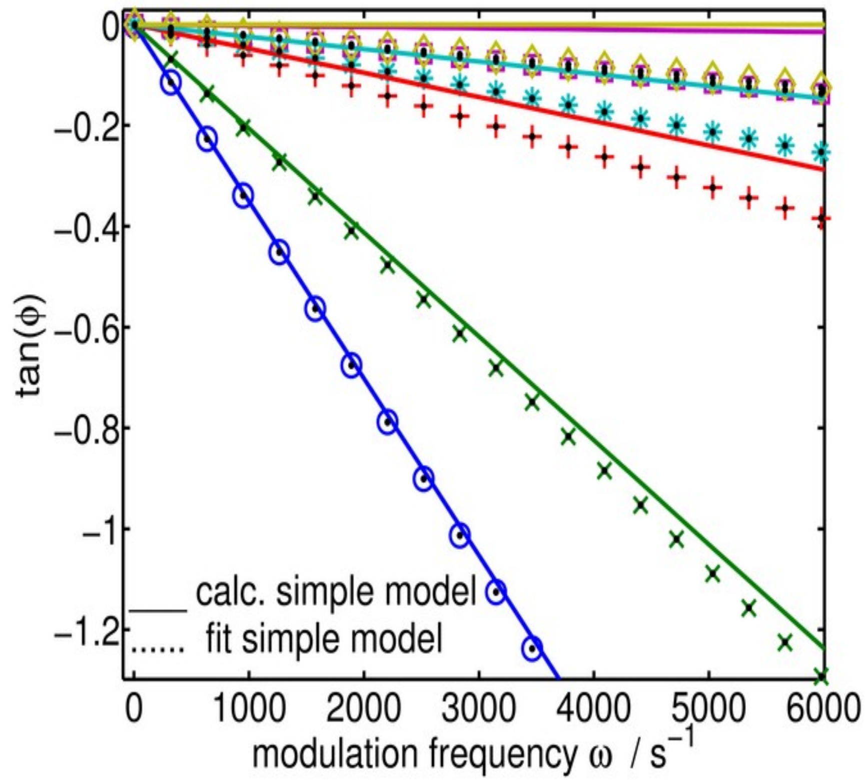

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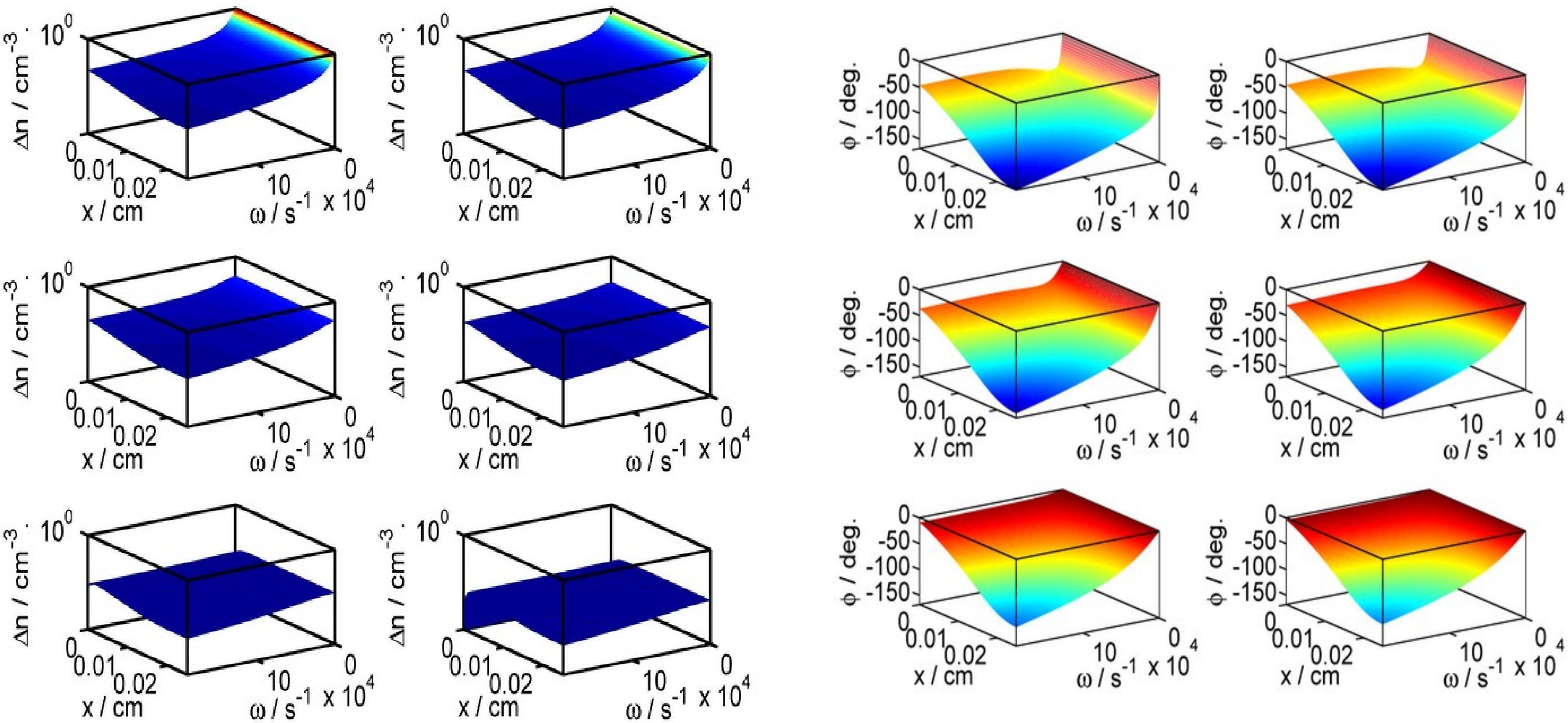
D = 12 cm² s⁻¹; τ_{bulk} = 20 ms; W=0.025 cm; α= 1010 cm⁻¹;

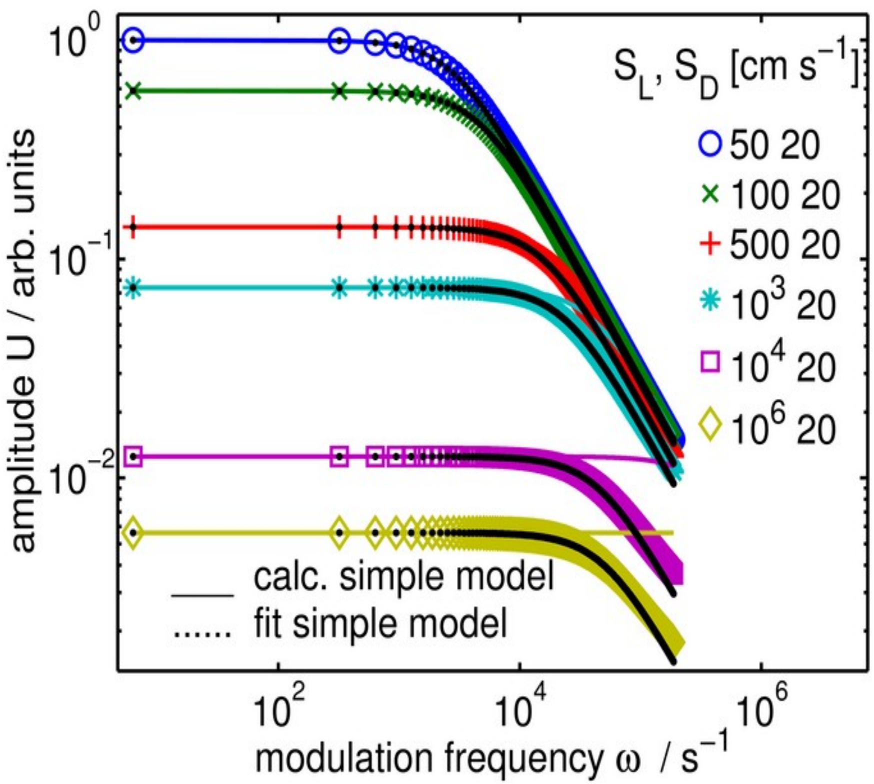
asymmetrical sample: S_1= 50, 100, 500, 10^3, 10^4, 10^6 cm s^{-1}; S_2= 20 cm s^{-1}

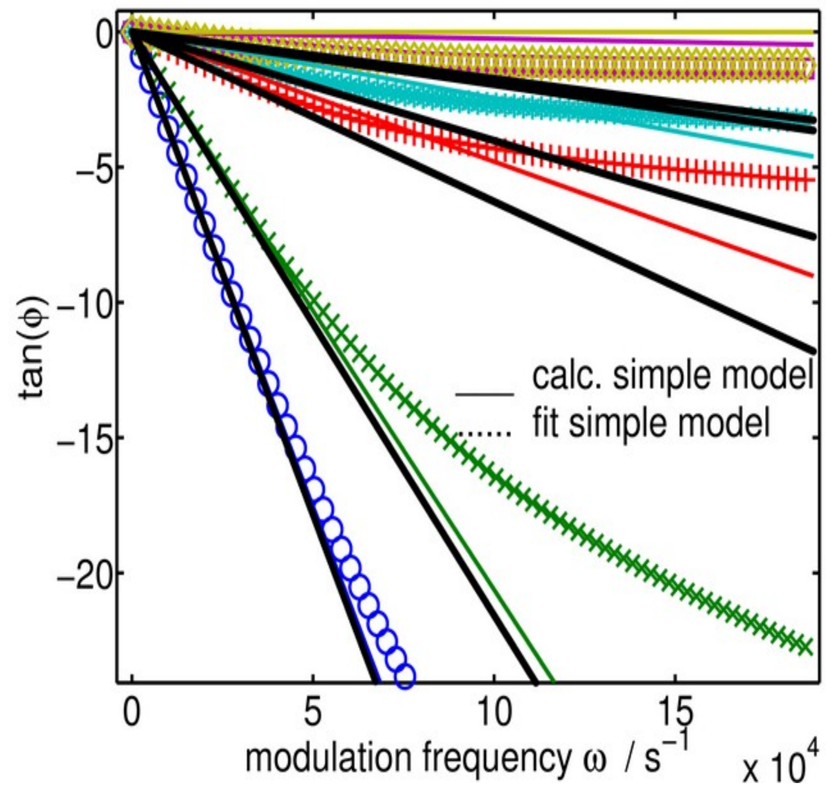


Integrated amplitude and phase spectra

D = 12 cm² s⁻¹; τ_{bulk} = 20 ms; W=0.025 cm; α= 1010 cm⁻¹;

asymmetrical sample: S_1= 50, 100, 500, 10^3, 10^4, 10^6 cm s^{-1}; S_2= 20 cm s^{-1}





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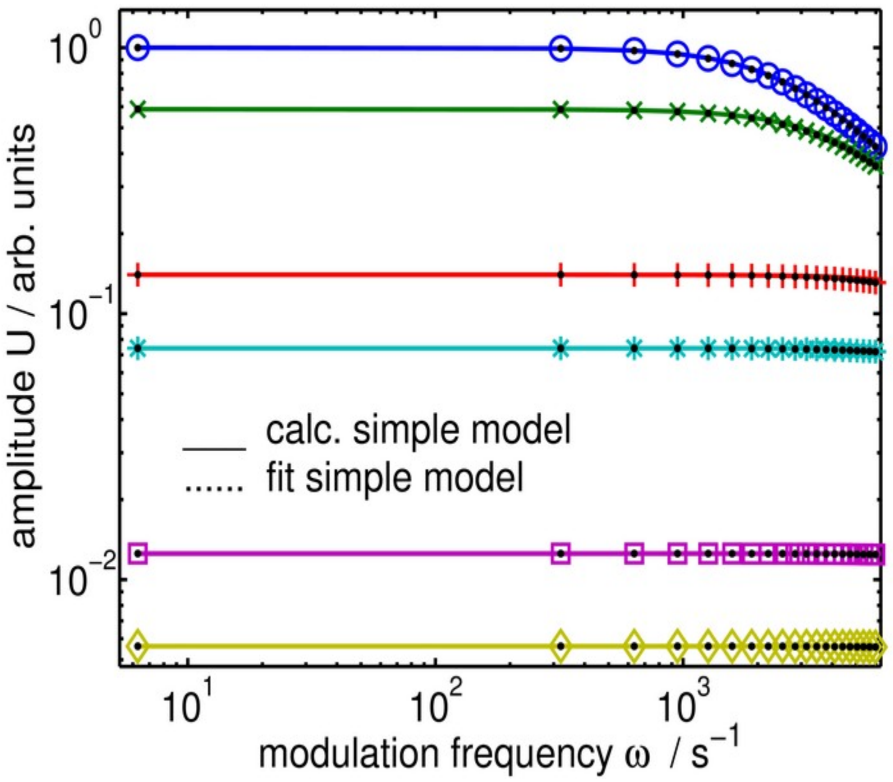
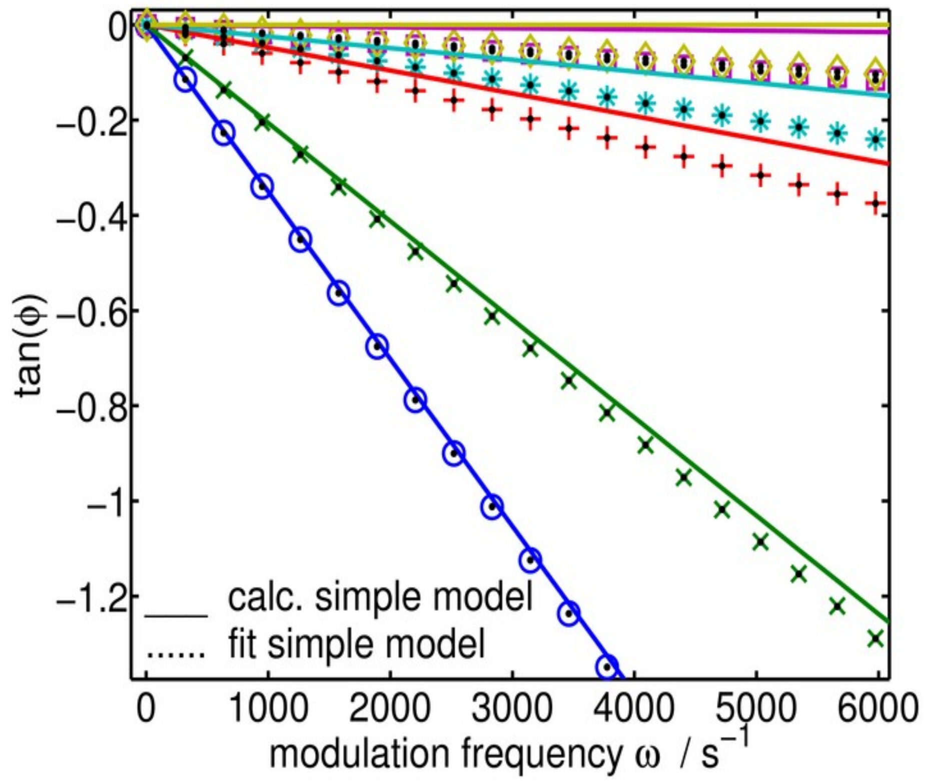
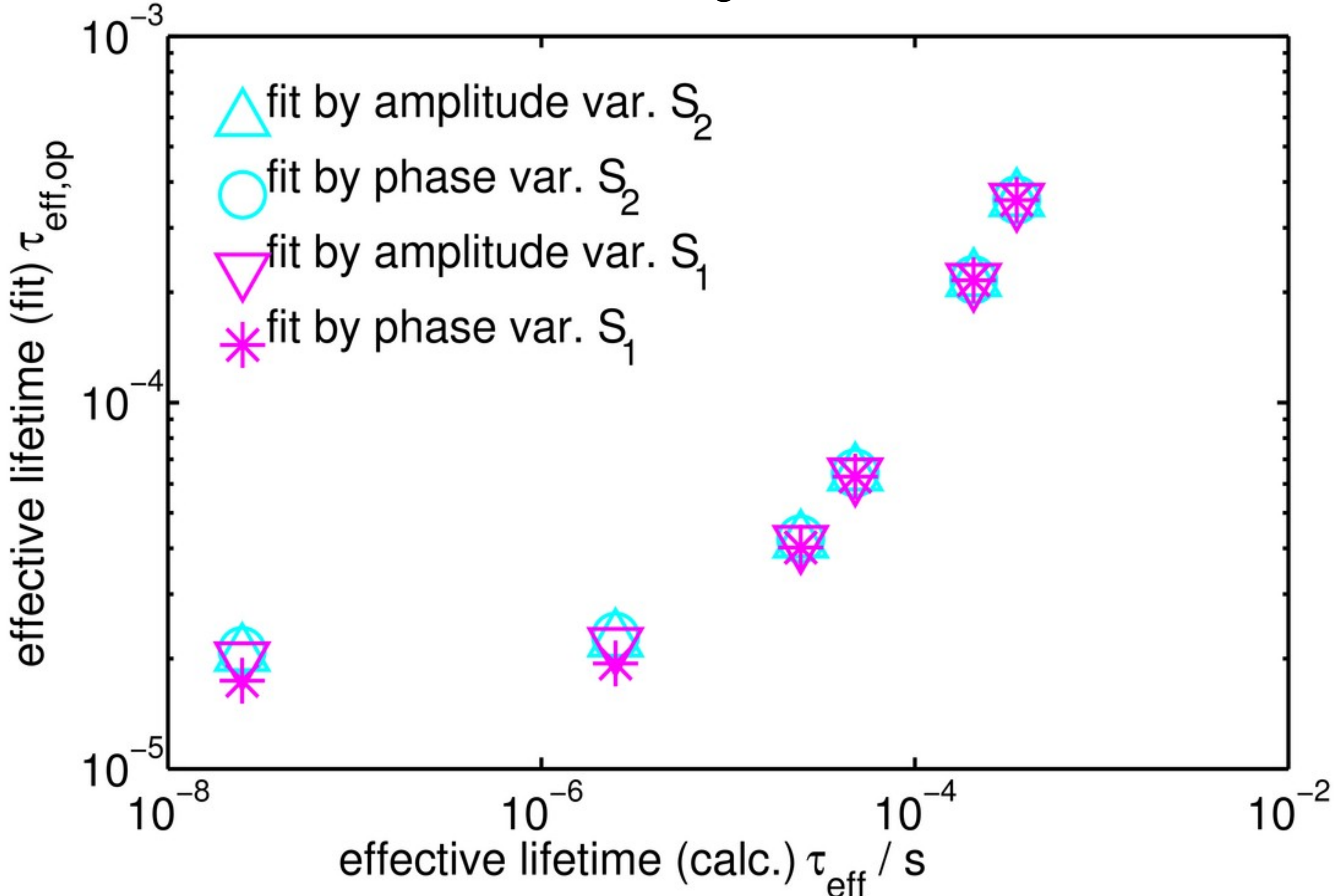




Integrated amplitude and phase spectra

overestimation of real lifetime for high surface recombination rates



Simple model vs. exact solution of diffusion equation

- good agreement of spectra for low frequencies
- good agreement of lifetimes for $S_i < 200$ cm s^{-1}
- simple model overestimates the effective lifetime for high surface recombination velocities
- exact solution of the diffusion equation does not explain nonlinear deviations in the spectra in low frequency range

Dispersive model [3]

Approach: effective lifetime depends on frequency ⟶ lifetime distribution

$$\Delta n_1^*(\omega) = \frac{G_1 \tau_0}{1 + (i\omega\tau_0)^{\delta_{disp}}}$$

U(ω) ~ $\left\| \Delta n_1^*(\omega) \right\|$

$$\phi(\omega) = -\tan^{-1}\left(\frac{\Im(\Delta n_1^*(\omega))}{\Re(\Delta n_1^*(\omega))}\right)$$

Stieltjes transformation:

$$G(\ln(\tau)) = \frac{1}{2\pi i G_1 \tau_0}\left(\Delta n\left(\frac{e^{-i\pi}}{\tau}\right) - \Delta n\left(\frac{e^{i\pi}}{\tau}\right)\right)$$

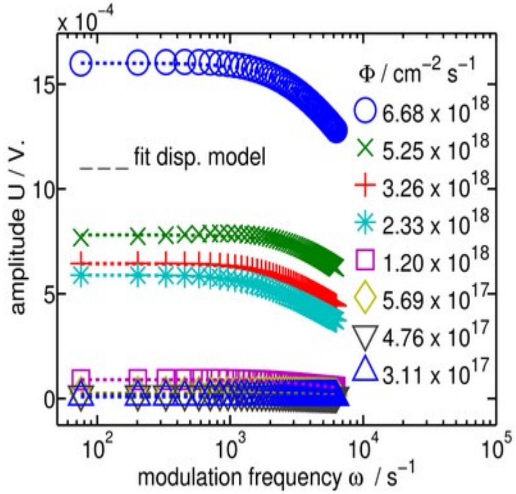
$$\Rightarrow$$

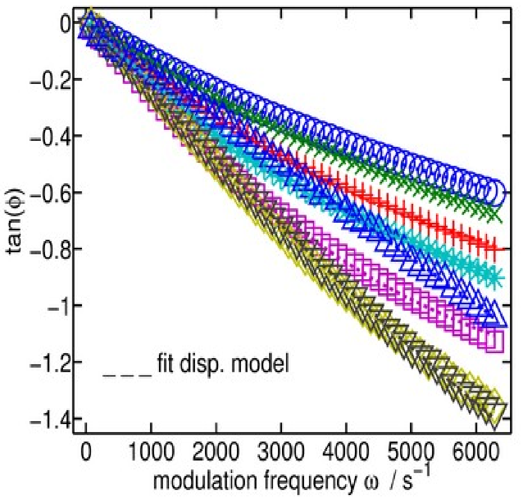
$$G(\ln(\tau)) = \frac{1}{2\pi}\frac{\sin(\delta_{disp}\pi)}{\cosh\left(\delta_{disp}\ln\left(\frac{\tau}{\tau_0}\right)\right) + \cos\left(\pi\delta_{disp}\right)}$$

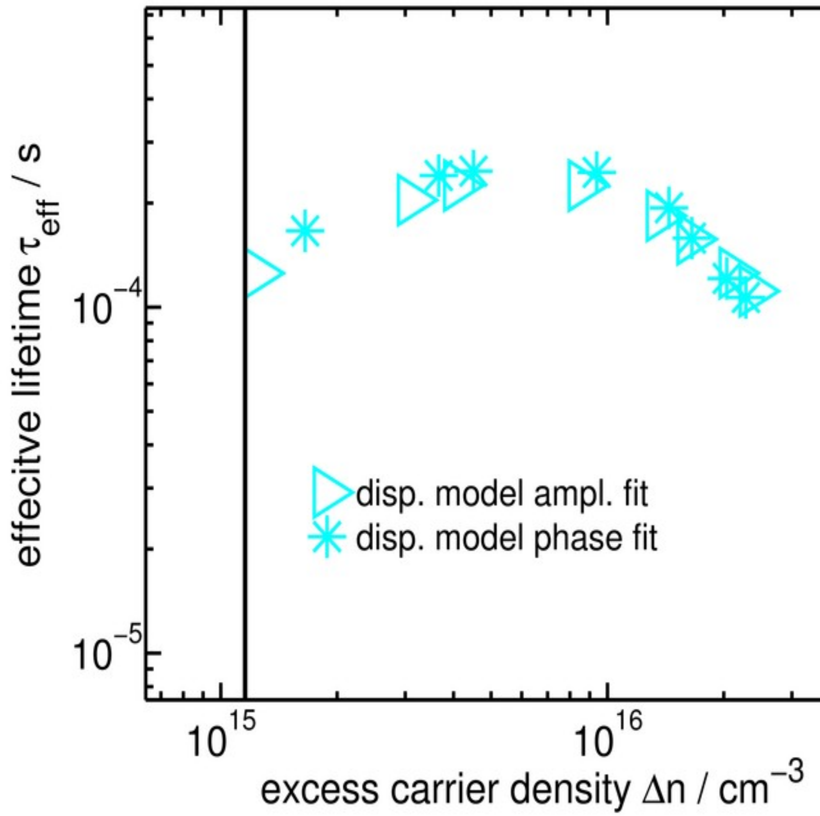
[3] D. W. Davidson, R. H. Cole, J. Chem. Phys 19(12), 1484-1490 (1951)
[4] R. Fuoss, J.G. Kirkwood, J. Am- Chem. Soc. 63(2), 385-394 (1941)

Dispersive model

(i)pm-Si:H/(n)a-Si:H (14 Ωcm)



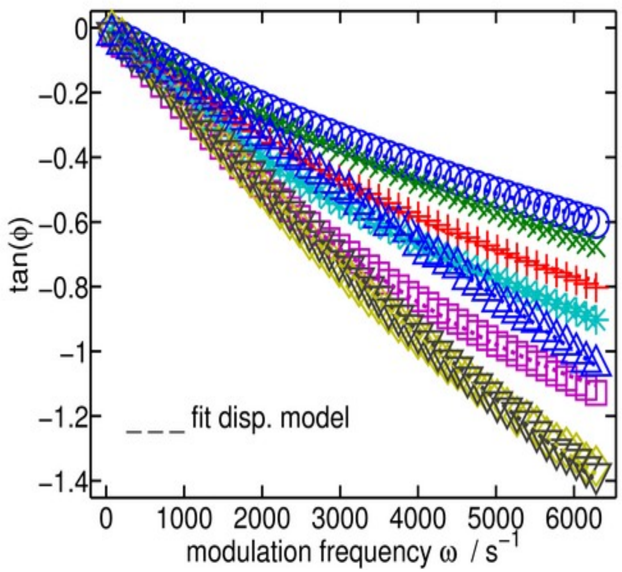


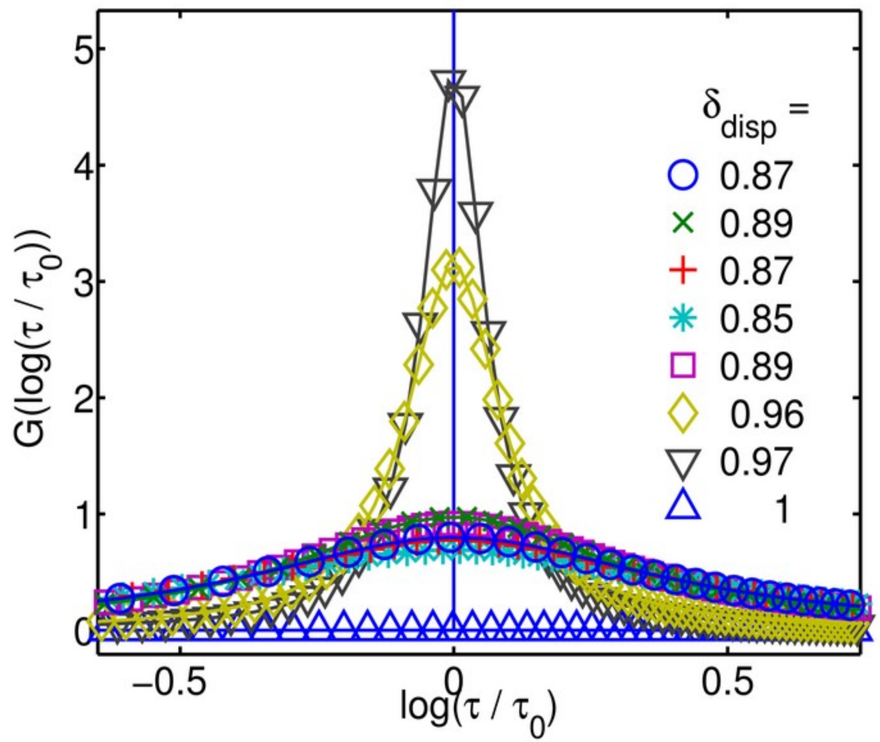


Dispersive model

(i)pm-Si:H/(n)a-Si:H (14 Ωcm)

shape/wide distribution in low/high excitation range





Nonlinear approach

linear-to-quadratic recombination regime [5]: **bimolecular model**

solve spherical diffusion equation:

$$\Delta n(r,t) = \frac{G_0 e^{-Lr}}{8\pi D r} + \frac{G_1 \cos(r \sin(\frac{1}{2}\theta) L \Lambda^{\frac{1}{4}} - \omega t) e^{-L\Lambda^{\frac{1}{4}}\cos(\frac{1}{2}\theta) r}}{8\pi D r}$$

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}$$

$$\Lambda(\omega) := (1 + (\omega\tau_{eff})^2)$$

$$L := \sqrt{D\tau_{eff}}$$

$$\theta(\omega) := \arctan(\omega\tau_{eff})$$

calculate total recombination rate:

$$R(t) = \int_0^\infty \left(\frac{\Delta n(r,t)}{\tau_R} + B\Delta n(r,t)^2 \right) 4\pi r^2 dr$$

$$\longrightarrow \quad S_{IP} = \frac{2}{T}\int_0^T R(t)\cos(\omega t)dt, \quad S_{OP} = \frac{2}{T}\int_0^T R(t)\sin(\omega t)dt \quad \longrightarrow$$

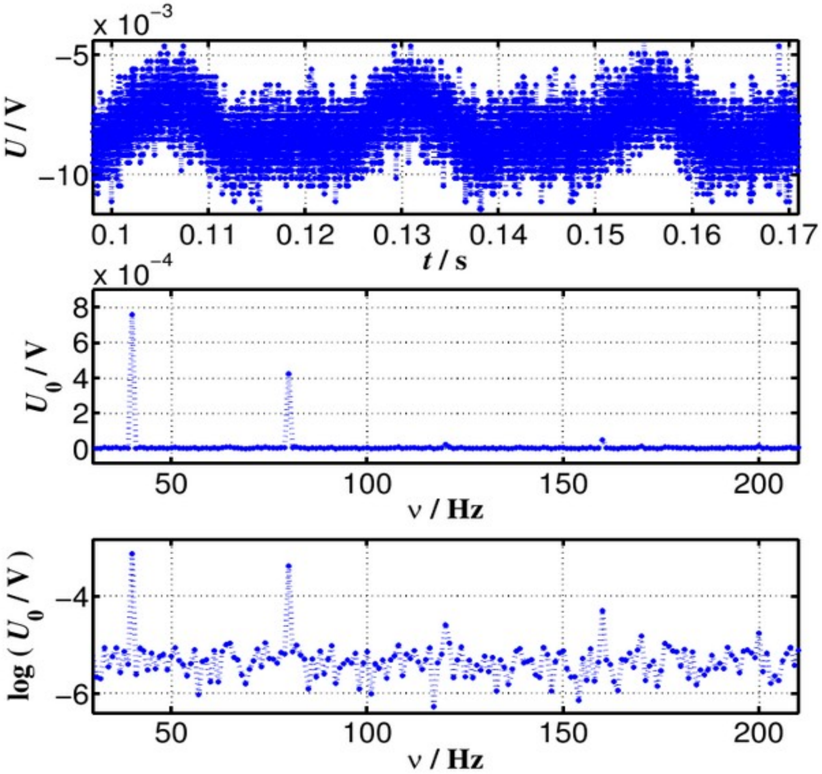
amplitude and phase spectra

[5] D. Guidotti, J. S. Batchelder, A. Finkel, Phys. Rev. B, 38(2), 1569-1572 (1988)

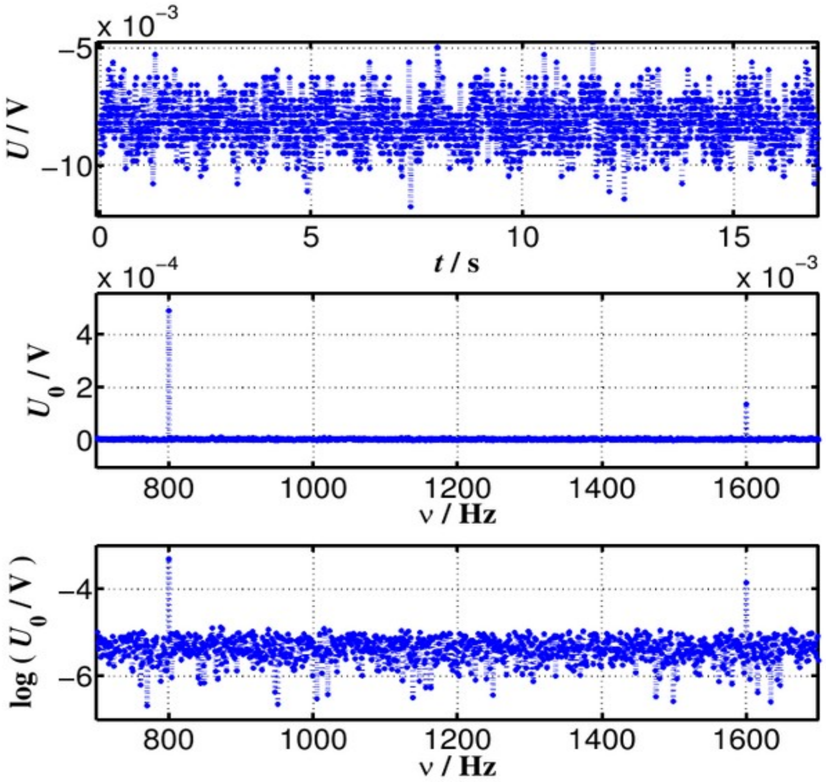
Influence of first-overtone (2ω)

Δn >> N_A

@ 40 Hz:



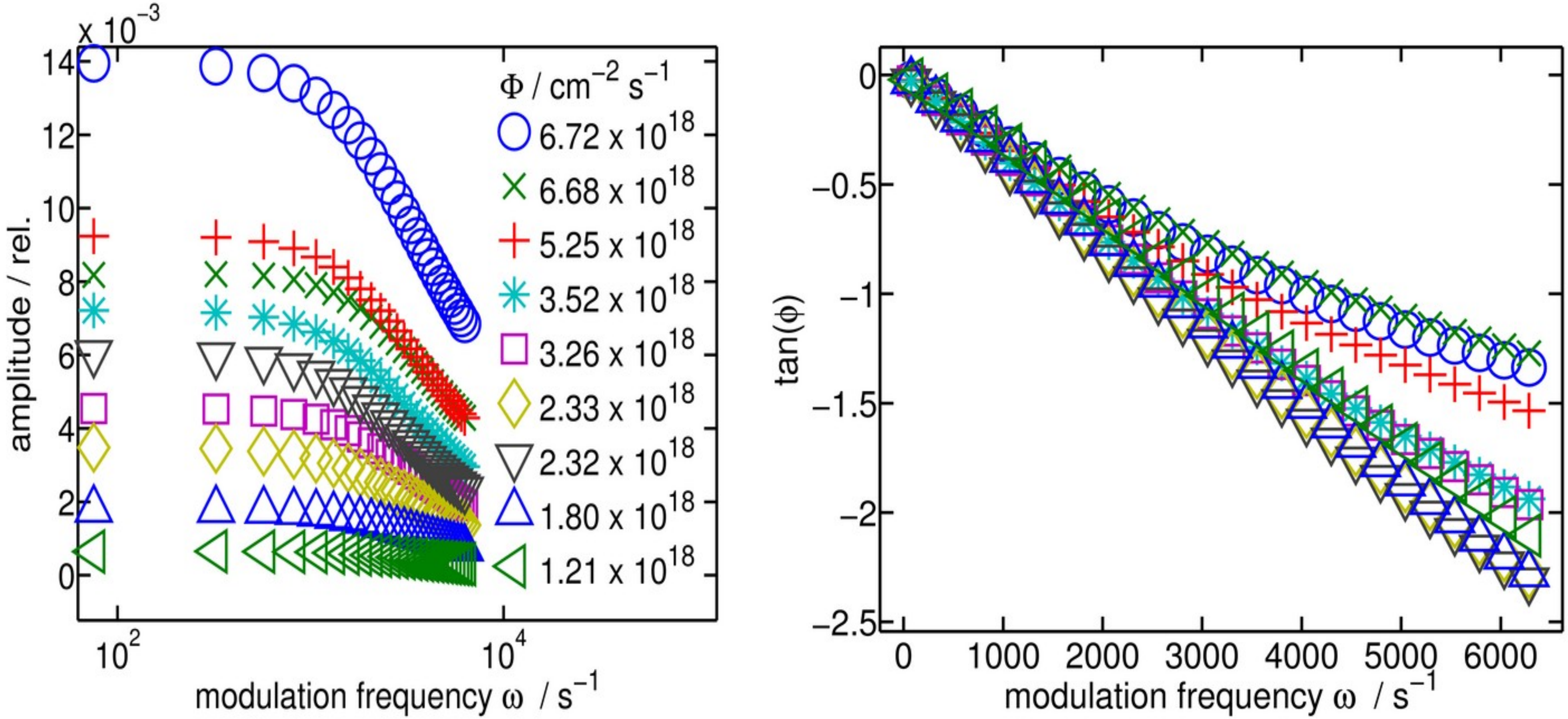
@ 800 Hz:



Bimolecular model

SiN passivation (1 Ωcm)

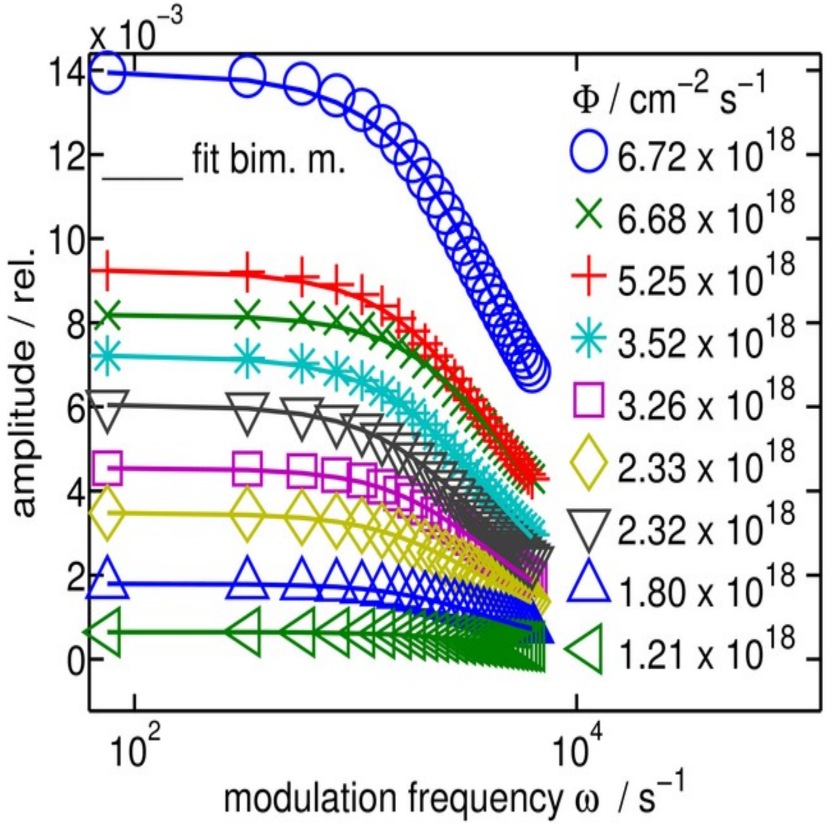
high injection regime: $\Delta n > N_A$

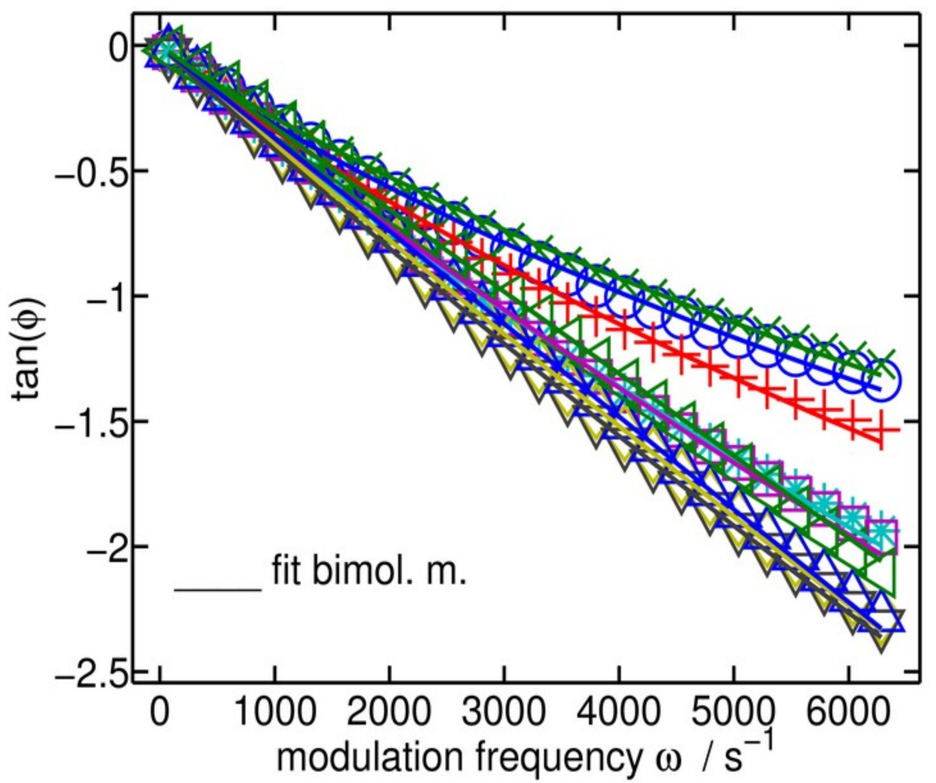


Bimolecular model

SiN passivation (1 Ωcm)

high injection regime: $\Delta n > N_A$



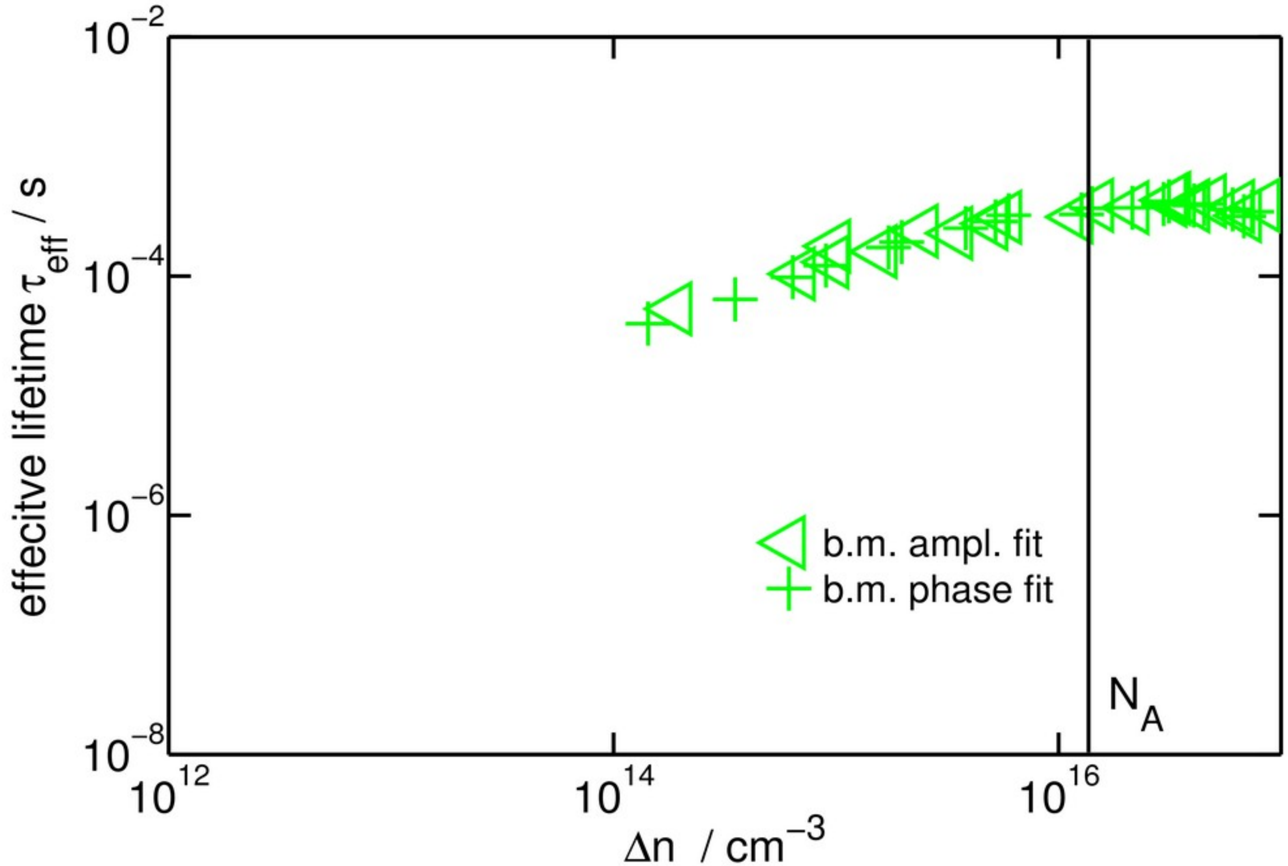


Bimolecular model

SiN passivation (1 Ωcm)

<u>low injection</u>: $\Delta n \ll N_A$

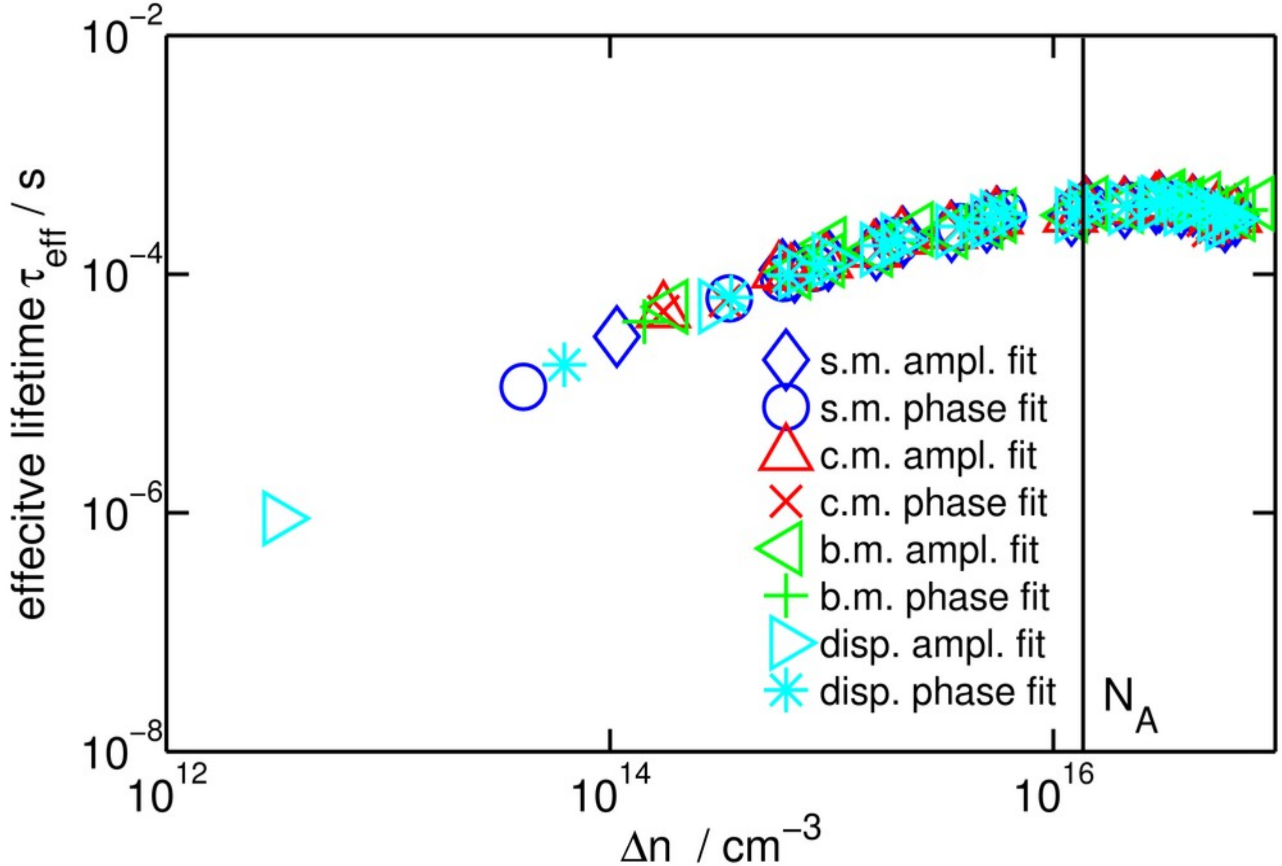
high injection: $\Delta n \gg N_A$



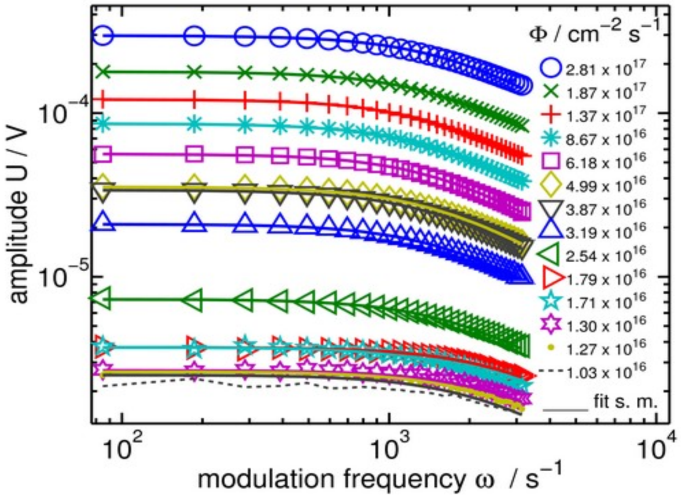
Linear and nonlinear models

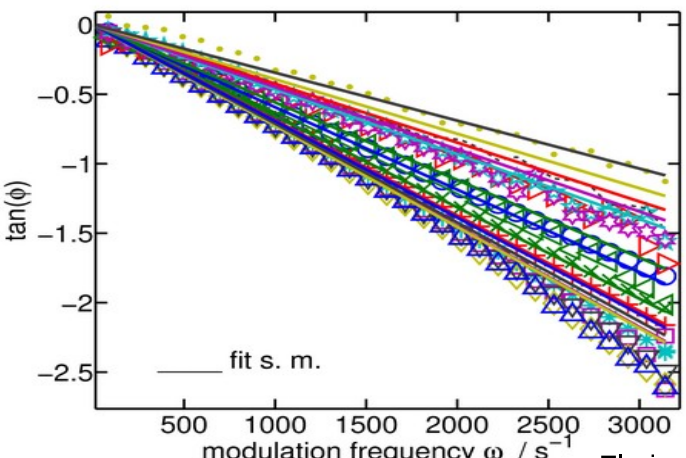
SiN passivation (1 Ωcm)

low injection: $\Delta n << N_A$ **high injection**: $\Delta n >> N_A$



MPL and measurement of V_{oc}





measurement of V_{oc} by multimeter and MPL

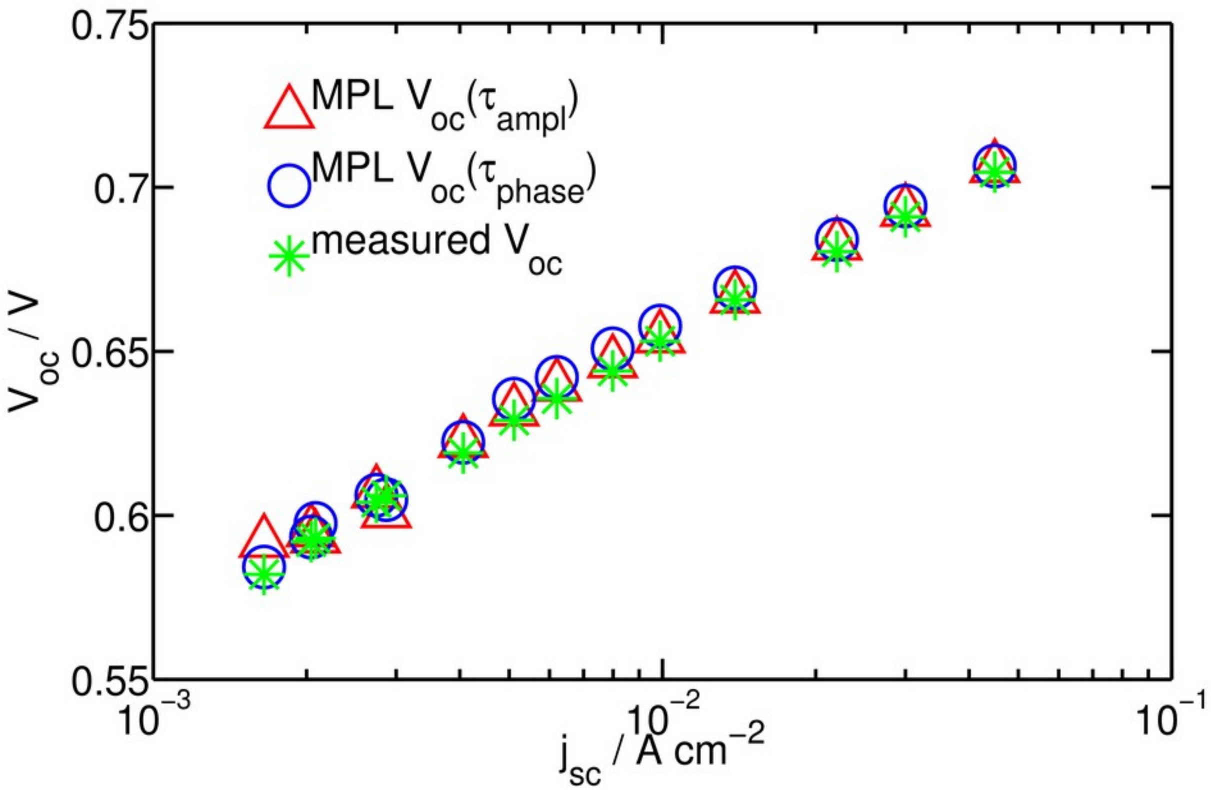
τ_{amp} by MPL

$$V_{oc} \approx \frac{k_B T}{q} \ln\left(\frac{N_A \Delta n + \Delta n^2}{n_0 N_A}\right)$$

$$\Delta n = \Delta p = G\tau_{eff}$$

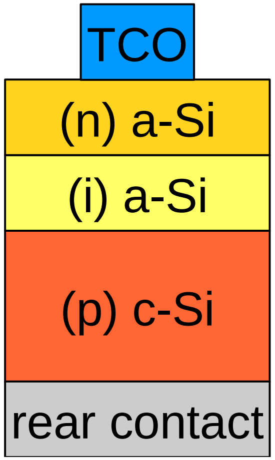
τ_{ϕ} by MPL

MPL and measurement of V_{oc}



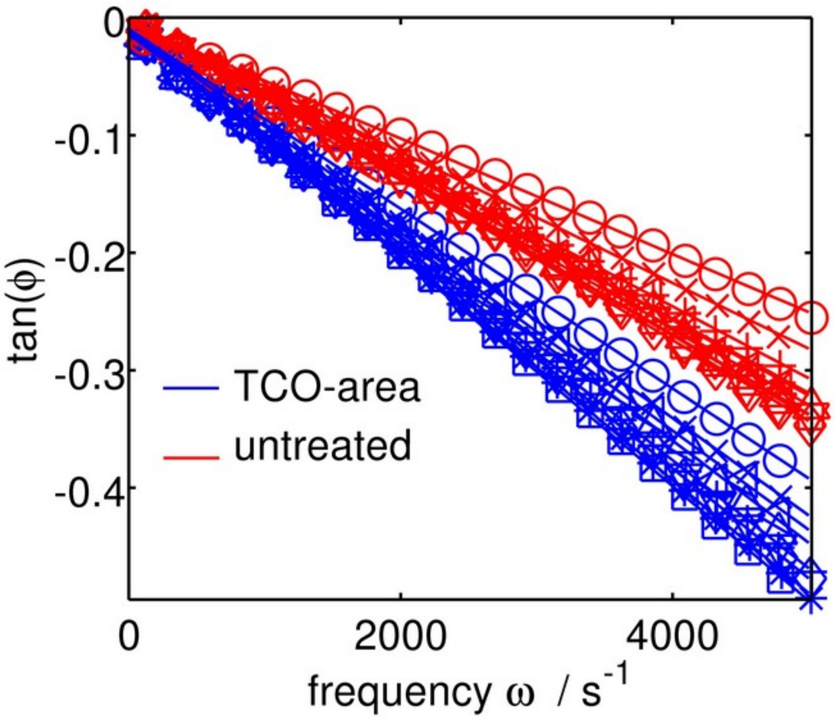
→ Good agreement between measured V_{oc} and $V_{oc}(\tau_{eff})$ by MPL

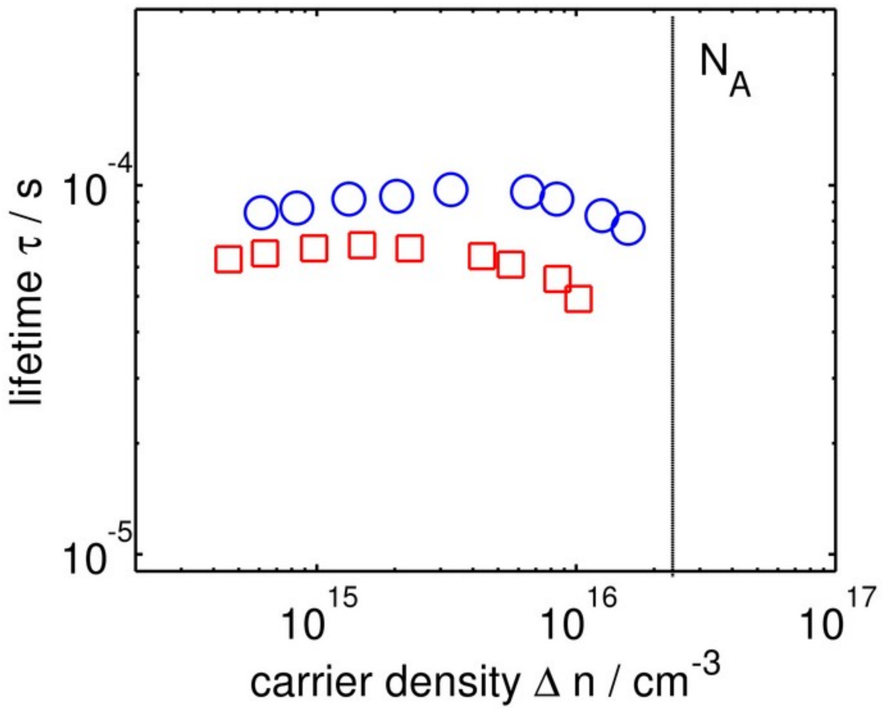
Results: Cell



a-Si passivated p-type wafer (1 Ωcm, $N_A = 10^{16}$ cm^{-3}) with TCO

MPL allows measurement on bare wafer and TCO-texture (via small excitation spot)





Summary

- Modulated photoluminescence promises an efficient method for effective lifetime measurement

- Simple model allows approximation of effective lifetime for low surface recombination and symmetrical samples in low frequency range

- In the case of asymmetrical samples and high surface recombination the exact solution of the diffusion equation leeds to a more detailed model

- In case of high excitation (quadratic recombination) modified nonlinear approaches offer a qualitatively better description of spectra

- MPL determinated lifetime allows a reliable approximation of V_{oc}

- Advantage of MPL to other lifetime measurements: local investigation of wafers and cells with high doping and backcontacts