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Potential Fluctuations on CZTSSe Solar Cells Admittance

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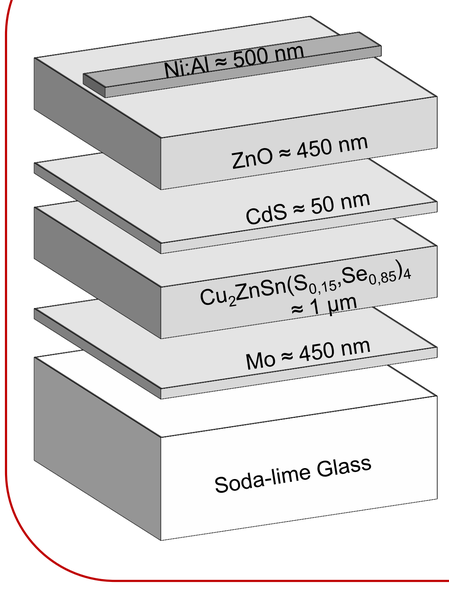
1 – Context

- Low V_{oc} on CZTSSe solar cells ⇨ role of point defects and potential fluctuations suggested but not clearly established
- Density Functional Theory[1] ⇨ V_{Cu} and Cu_{Zn}
  - create acceptor levels
  - are among defects with the lowest formation energy
  - may be stabilized by the formation of neutral defect complexes: [Cu_{Zn}+Zn_{Cu}], [V_{Cu}+Zn_{Cu}], [Cu_{Zn}+Sn_{Zn}]

Objectives:

- Influence of potential fluctuations: - on defect analysis
  - on electrical transport

2 – Solar cell structure



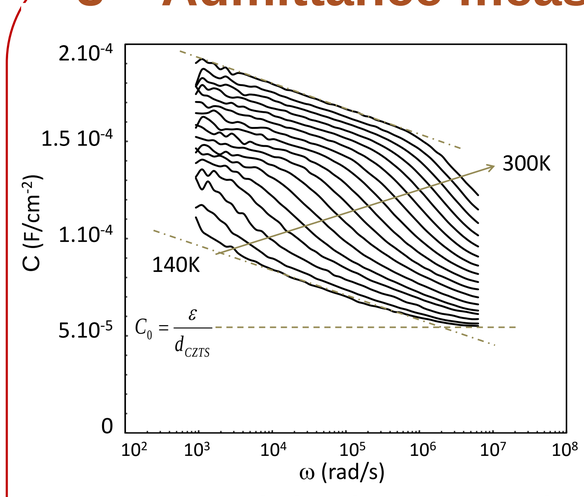
- Two steps process[2]:
  - Precursors deposition: ZnS by sputtering, Cu/Sn by electron beam evaporation
  - Selenization: annealing under Se vapor

V_{oc} (V)	J_{sc} (A.cm^{-2})	FF	η (%)
~ 0.33-0.38	~ 0.03	50	~ 5.3-6.6

Experiment:

Admittance spectroscopy @ 0V from 140K to 300K, 100Hz to 1MHz

3 – Admittance measurement: C(ω)

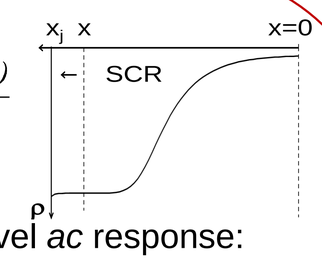


One capacitance step: response of a deep acceptor level at E_{aexp}=E_v+(0.2±0.03)eV not observed on G/ω spectrum

At low temperature, geometrical capacitance value ⇨ CZTSSe absorber fully depleted

⇒ can explain the strong increase of the series resistance at low temperature generally observed on CZTSSe solar cells.

4 – Admittance modelling



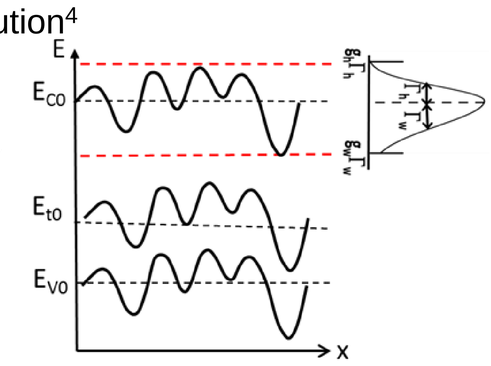
- **plane capacitor:**[3] $C_{ac}(x,\omega)=\frac{\delta\sigma(x,\omega)}{\delta\psi(x,\omega)}==\frac{\varepsilon\,\delta\mathcal{E}(x,\omega)}{\delta\psi(x,\omega)}$
- **one deep acceptor level:**

small signal Poisson equation including the deep level *ac* response:

$$\frac{d^2\delta\psi}{dx^2}=-\frac{\delta\rho(x)}{\varepsilon}=-q\frac{\delta p(x)-\delta n(x)-N_{Ta}(x)\delta f(x)}{\varepsilon}$$

- **potential fluctuations:**

Truncated and asymmetric Gaussian distribution[4]



Hole concentration in valence band:

$$p=cste\int_{E_{v0}-g_w\Gamma_w}^{E_{v0}+g_h\Gamma h}\int_{-\infty}^{E_v}\sqrt{E_v-E}\,[1-f(E)]dE\,\exp-\frac{(E_v-E_{v0})^2}{\Gamma^2}dE_v$$

Ionized defect concentration:

$$N_{ta}^{-}=cste\int_{E_{ta0}-g_w\Gamma_w}^{E_{vta}+g_h\Gamma h}\left[\frac{1}{1+g\exp\left(\frac{E_{ta}-E_F}{kT}\right)}\right]\exp-\frac{(E_{ta}-E_{ta0})^2}{\Gamma^2}dE_{ta}$$

Complex occupation function defined for each elemental energy ζ :

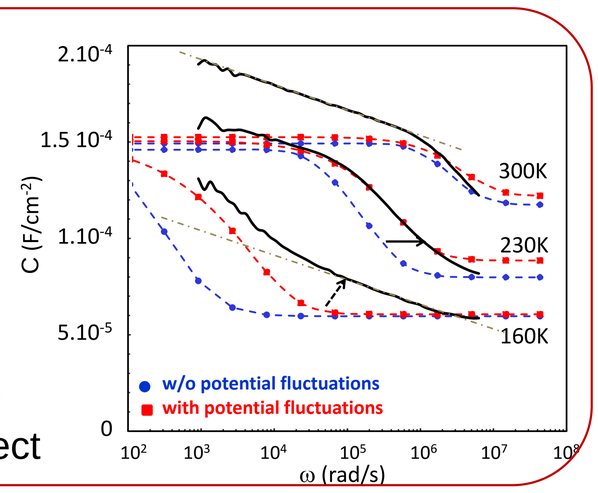
$$\delta f(x,\zeta)=\tau(x,\zeta)\frac{c_n(\zeta)[1-f(x,\zeta)]\delta n(x)-c_p(\zeta)\,f(x,\zeta)\,\delta p(x)}{1+j\omega\tau(x,\zeta)}$$

Admittance expression:

$$\tilde{Y}=G+j\omega C\equiv j\omega\tilde{C}_{\psi_0}(x,\omega)=j\omega\frac{\delta\tilde{Q}_T(x,\omega)+\varepsilon\,\delta\tilde{E}(x_{bulk},\omega)}{\delta\tilde{\psi}(x,\omega)-\delta\tilde{\psi}(x_{bulk},\omega)}$$

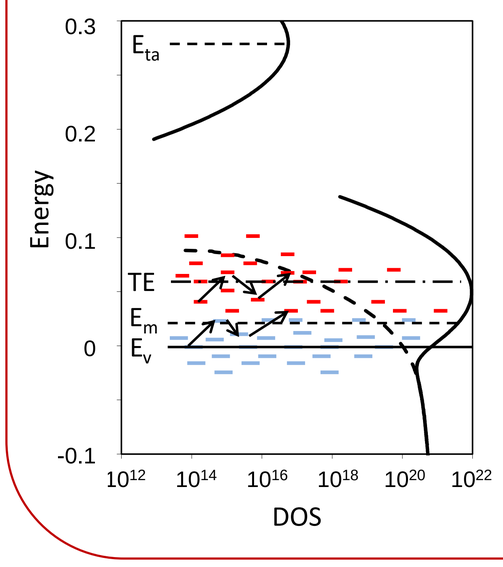
5 – C(ω) fit

- Potential fluctuations explain the stretching of the capacitance step
- E_{afit} (0.28eV) > E_{aexp} due to PF
- Continuous capacitance variation superimposed to the defect related step not reproduced by the model ⇨ associated with ω^s conductance increase ⇨ dielectric relaxation effect



6 – localized states transport

Conduction in disordered materials:[5]

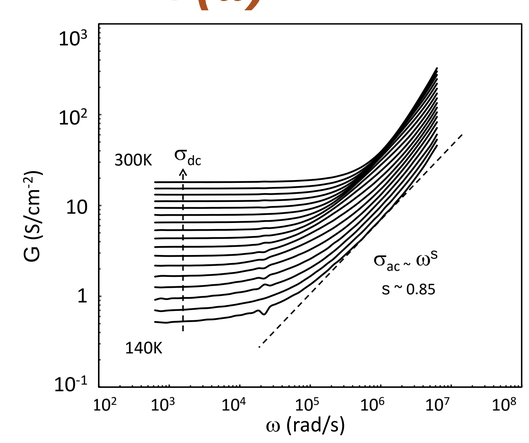


⇒ At moderate temperatures, multi-trapping relaxation process dominates: hole transition between extended states below the mobility edge E_m and localized states in band tail

⇒ neutral complex defects can introduce a high density of states in the band tail: hopping transport near TE, the Transport Energy, can occur at low temperature:

$$\sigma_{dc}\approx\sigma_0\exp\left(-\frac{2r(TE)}{B^{-1/3}\alpha}-\frac{E_F-TE}{kT}\right)$$

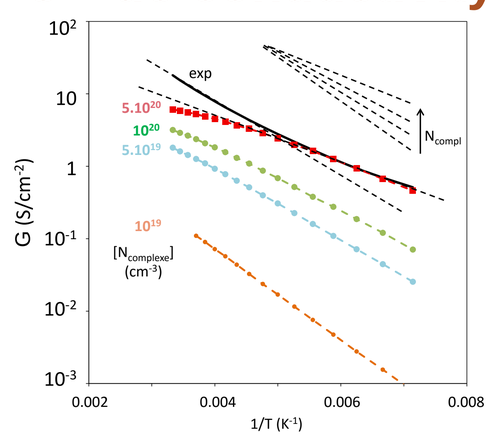
7 – G(ω)



⇒ low frequency: *dc* conductivity

⇒ high frequency/low temperature: universal power-law frequency response

8 – *dc* conductivity



⇒ hopping through localized states in band tail due to high concentration of neutral complexes

9 – Conclusions

- At low temperature, potential fluctuations effects are enhanced in CZTSSe bulk due to free carrier compensation mechanism.
- High density of neutral complexes can favor the *dc* charge carrier transport due to hopping process in the band tails

10 – Perspectives

- Hopping process in the band tails has to be taken into account to model the *ac* transport properties
- Effect of the potential fluctuations on V_{oc}
- Benefit of an additional shallow doping level

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Refs: (1): S. Chen et al, Adv. Mat., 25(11), 1522-1539 (2013) , (2) L. Grenet et al. Solar Energy Mat. Solar Cells, 126:135–142, (3) M. Begulawa et C.R. Crowell, Solid-State Electron. 17, 203 (1974), (4) B. Pistoulet et al, Phys. Rev. B, 30 5987 (1984), (5) D. Monroe, Phys. Rev. Lett. 54, 146 (1985).