Low temperature thermally stimulated currents in nanostructured TiO2

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Introduction: Applications

Disordered semiconductors are used in several application fields:

- Radiation theraphy (a-Si, poly-Diamond, etc.)
- Particle detectors (Si, SiC, etc.)
- Solar cells (a-Si, nanostructured TiO2, etc.)

"The theoretical description of electron transport in disordered materials is a challenging issue with implications in the field of dye-sensitized solar cells (DSC), plastic solar cells, organic light emitting diodes and organic electronics."[*]
"Electron transport in porous, nanocrystalline metal oxide electrodes exhibits many features of dispersive transport in disordered semiconductors."[**]

[*]Gonzalez-Vazquez et al., 2009; [**] Nelson and Chandler, 2004.

Introduction: Defects

The defects in such semiconductors have different origin:

- Radiation damage.
- Structure (amorphous).
- Contaminants.

They are classified depending on the structure:

- Physical structure: localized/clusters.
- Energetic structure: single levels/bands.

They act degrading the electrical properties:

- Charge collection (loose of efficiency).
- Dynamical performances (slow transients).
- Polarization effects.

“Energy disorder is usually accompanied by spatial disorder”.[*]
“Therefore, the influence of the traps in the transport must be considered.”[**]

[*] Bisquert et al., 2008; [**] Bisquert et al., 2007.

Introduction:
The study of the defects

To study the defects help in material engineering.

The *Thermally Stimulated Current* (TSC) technique is a powerful tool to investigate the presence of defects in semiconductors.

Shallow (low temperature) to deep (high temperature) levels are evidenced by emissions in the recorded current and the defect characteristics are extracted by fits, according to models.

"The TSC technique has attracted increasing attention over the last years due to the ease with which experiments can be performed and the hope to obtain with its help important information on the energy distribution of the density of states (DOS) in the gap."[*]

[*]Baranovskii et al., 1997.

Theory:
A bit of history of models

- TSC standard models:

    A single level emission.

But we treat distributed levels.

- Simmons, Taylor and Tam model:

    Distributed levels modeled. No recombination.

But we have recombination.

- Fritzsche and Ibaraki model:

    Balance emission-recombination, retrapping neglected.

But we have retrapping.

- Gu et al. Model[*]:

    Conduction by free carriers only. Distributed levels accounting for emission, retrapping, recombination.

But we have hopping.

- Baranovskii model[**]:

    Hopping in a distributed levels, accounting for emission, retrapping, recombination.

But we have degeneration!

"[...] the transport mechanisms at high carrier density is not really known [...]"[*]

$$I \propto \sigma v e^{-\frac{E_{act}}{k_B T}} e^{-\frac{1}{\beta}\int \sigma v e^{-\frac{E_{act}}{k_B T}} dT}$$

$$I \propto \mu_0 \tau_0 g(E_m) f_0(E_m)$$

$$\frac{dn}{dt} = -\frac{n}{\tau} + \int_{E_v}^{E_c} [g[vf - b_t n(1-f)]] dE$$

$$\frac{df}{dt} = b_t n(1-f) - vf$$

$$N_c \rightarrow W * g(E_{tr})$$

[*] Gu et al., 1987; [**] Baranovskii, 1997; [***] Bisquert et al., 2007.

Theory:
A bit of history of models

Basically we have:

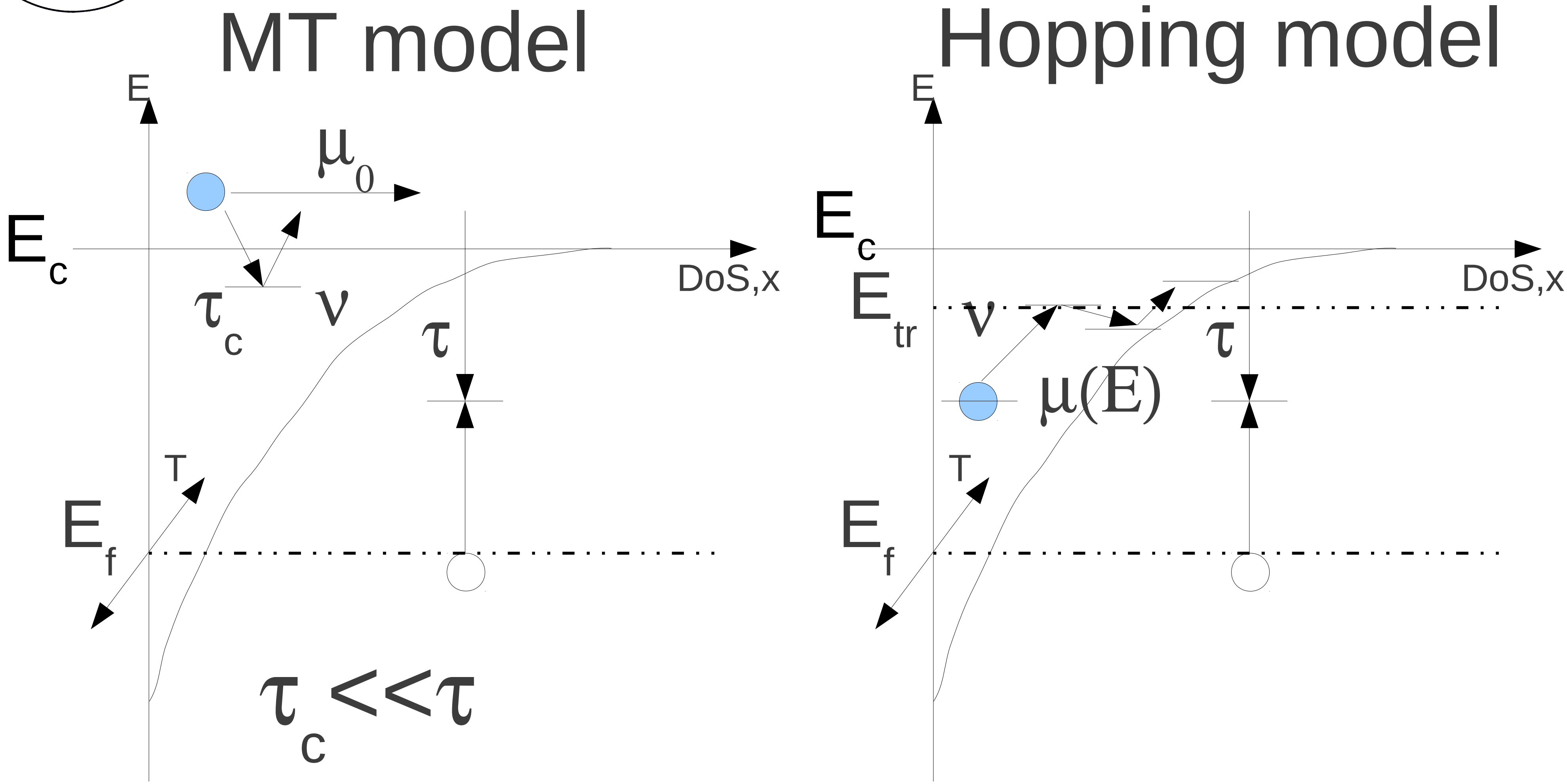
- Because of energetic disorder[*]:
  - Multiple trapping (MT) models.
  - Variable range hopping (VRH) models[**].
- Because of structural disorder:
  - Continuous time random walk (CTRW), percolation[***].
- Because of the ionic nature:
  - Small polaron[****][*****].

“Carrier transport in these materials usually occurs by transitions in a broad distribution of localized states. As a result the carrier transport is dominated by thermal activation to a band of extended states (multiple trapping), or if these do not exist, by hopping via localized states.”[*]

“An electron in an ionic crystal polarizes the lattice and its neighborhood. This interaction changes the energy of the electron. Furthermore, when the electron moves the polarization state must move with it. An electron moving with its accompanying distortion of the lattice has sometimes been called a polaron.”[******]

[*] Bisquert, 2008; [**] Monroe, 1985; [***] Benkstein, 2003; [****] Yagi, 1996; [*****] Deskin, 2007; [******] Feynman, 1954.

Theory:
MT vs. hopping?



The models coexists, it depend on the temperature!

Theory: The model

- The starting formula:
  - The single hopping frequency (Miller-Abrahams model).
- The basilar equations:
  - The energy of maximum hopping rate.
  - The average distance definition (accounting for degeneration!).

    From which, approximating the Fermi function:

    =>The distance between hopping sites at the transport energy.

    =>The transport energy.
- The definition of the transport quantities:
  - The average hopping rate.

    then
  - The diffusivity coefficient.

    and finally (using the Einstein relation)
  - The conducibility.

$$\nu = \nu_0 e^{-2\frac{r_{ij}}{\alpha} - \frac{E_j - E_i}{k_B T}} \quad , E_j - E_i > 0$$

$$\nu = \nu_0 e^{-2\frac{r_{ij}}{\alpha}} \quad , E_i - E_j > 0$$

$$\frac{\partial \nu}{\partial E} = 0 \quad \Rightarrow E_{tr}$$

$$\frac{1}{r^3} = \frac{4\pi}{3B} \int_{-\infty}^{E} g(1-f)\, dE' \Rightarrow r_{tr}$$

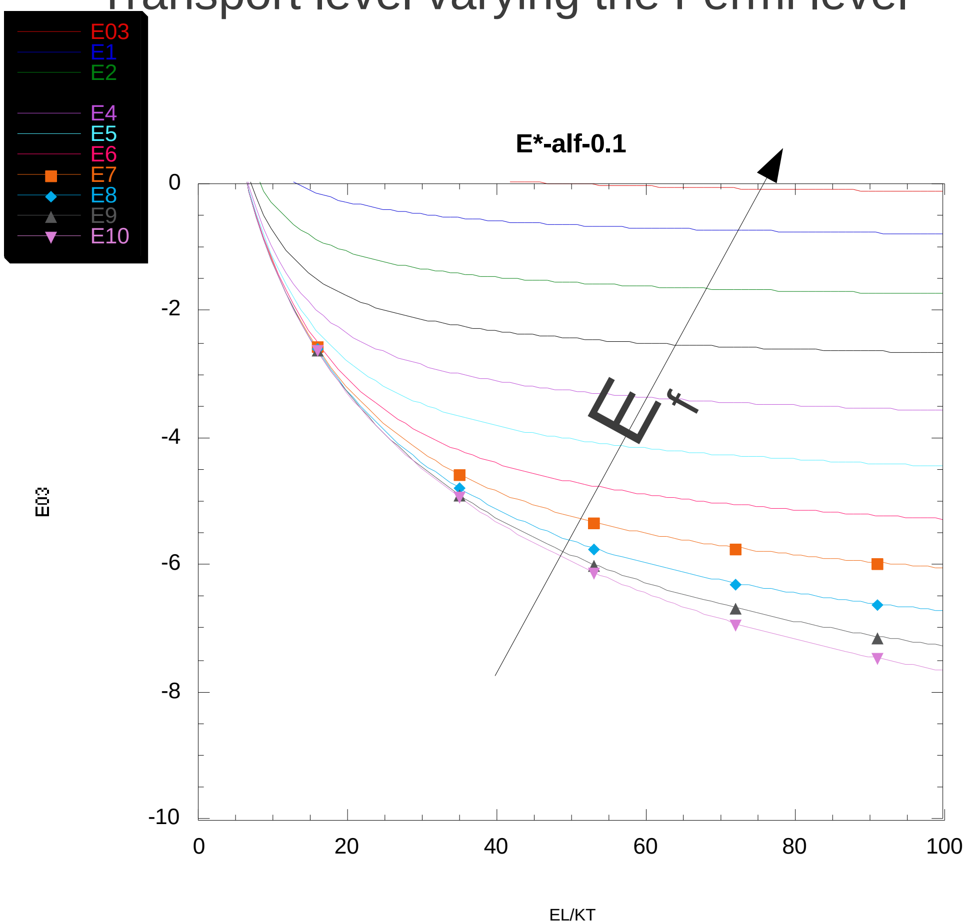
$$<\nu> = \frac{\int_{-\infty}^{E_{tr}} g\nu f(1-f)\, dE}{\int_{-\infty}^{E_{tr}} g f\, dE}$$

$$D = r_{tr}^2 <\nu>$$

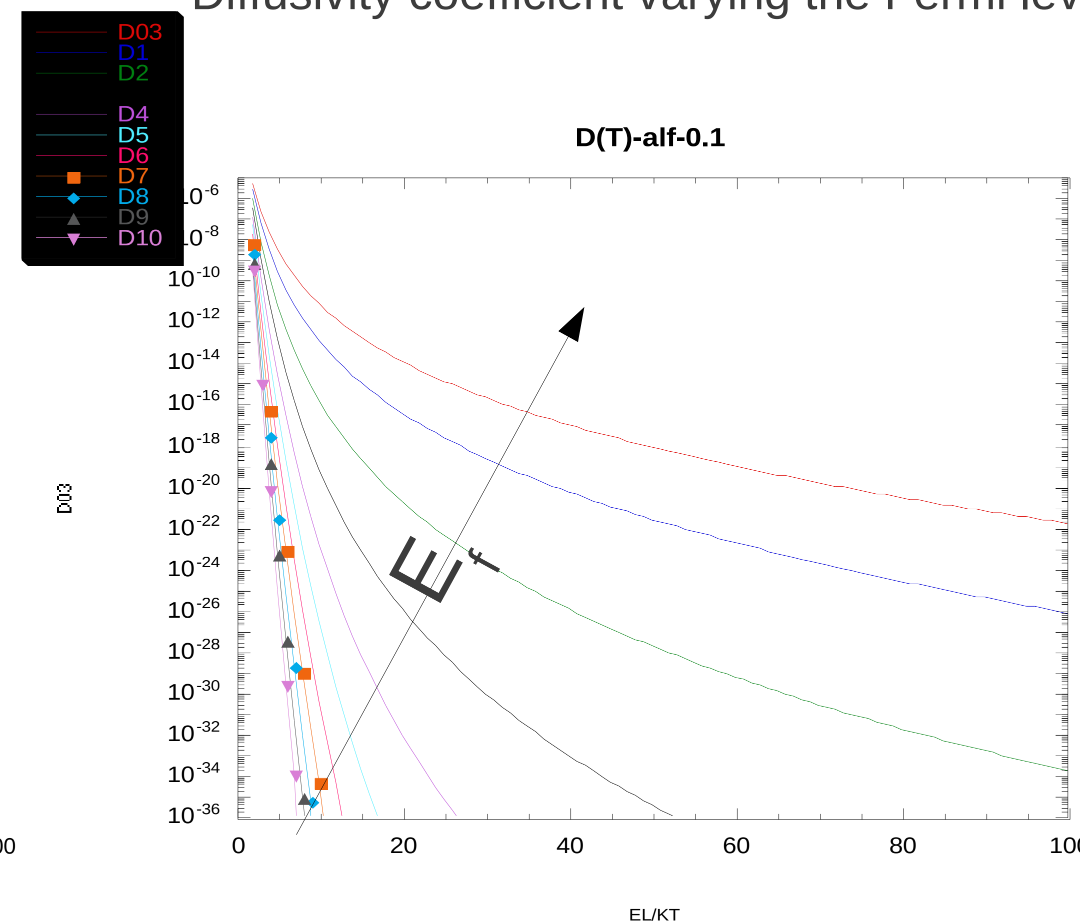
$$\sigma = \frac{q^2}{k_B T} r_{tr}^2 <\nu> n_{tr}$$

Theory: The model

Transport level varying the Fermi level



Diffusivity coefficient varying the Fermi level



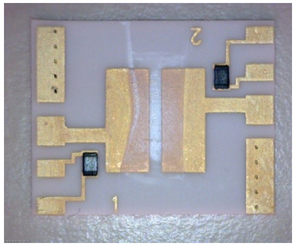
- The equation evolving the Fermi level:
  - The rate equation (with recombination time from Baranovskii).

$$\frac{d(n+n_L)}{dT} = -\frac{n}{\beta\tau} \Rightarrow \frac{dE_F}{dT}$$

Materials: Samples and set-up

• Samples

Samples are made with Ti-nanoxide D produced by Solaronix, containing about 11% wt nanocrystalline TiO_2 anatase particles (mixed dimensions 13/400 nm, Ti-nanoxide D).



Use: Dye Sensitized Solar Cells.

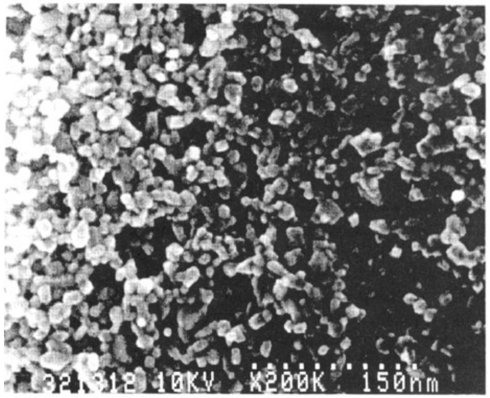
We use two step heating process for sinterization: 30' @280°C+30'@450°C.

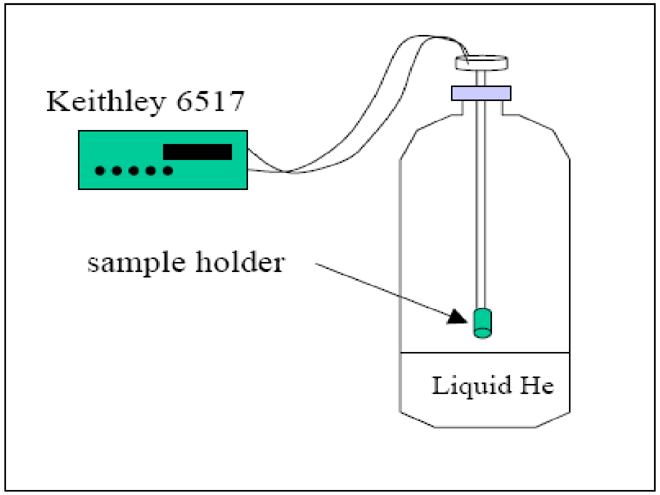
• Set-up

For cooling, we use liquid He vapours in a dewar.

The priming sources are:

- NUV (400nm) LED;
- FUV (355nm) LED.





Methods: Objectives and procedures

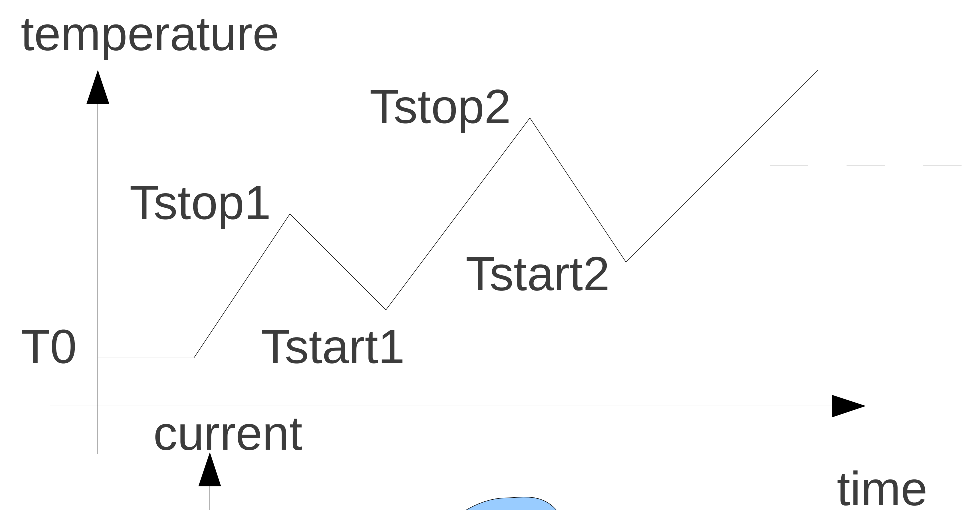
- **Objectives:**

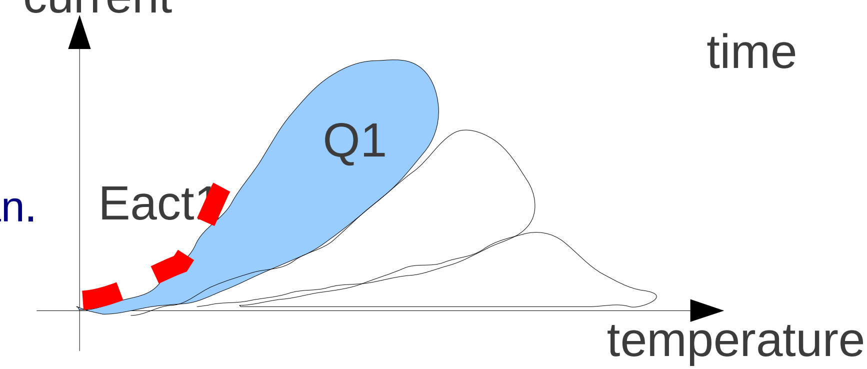
  To verify the Density of State (DoS).

- **Measurements:**

  Fractional TSC:

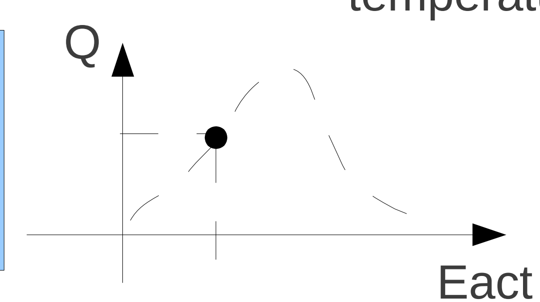
  - Priming at low temperature T0=Tstart0: ONLINE
  - Heating with bias to Tstop1
  - Cooling with bias to Tstart1
  - Heating with bias to Tstop2
  - Etc.





- **Analysis:**

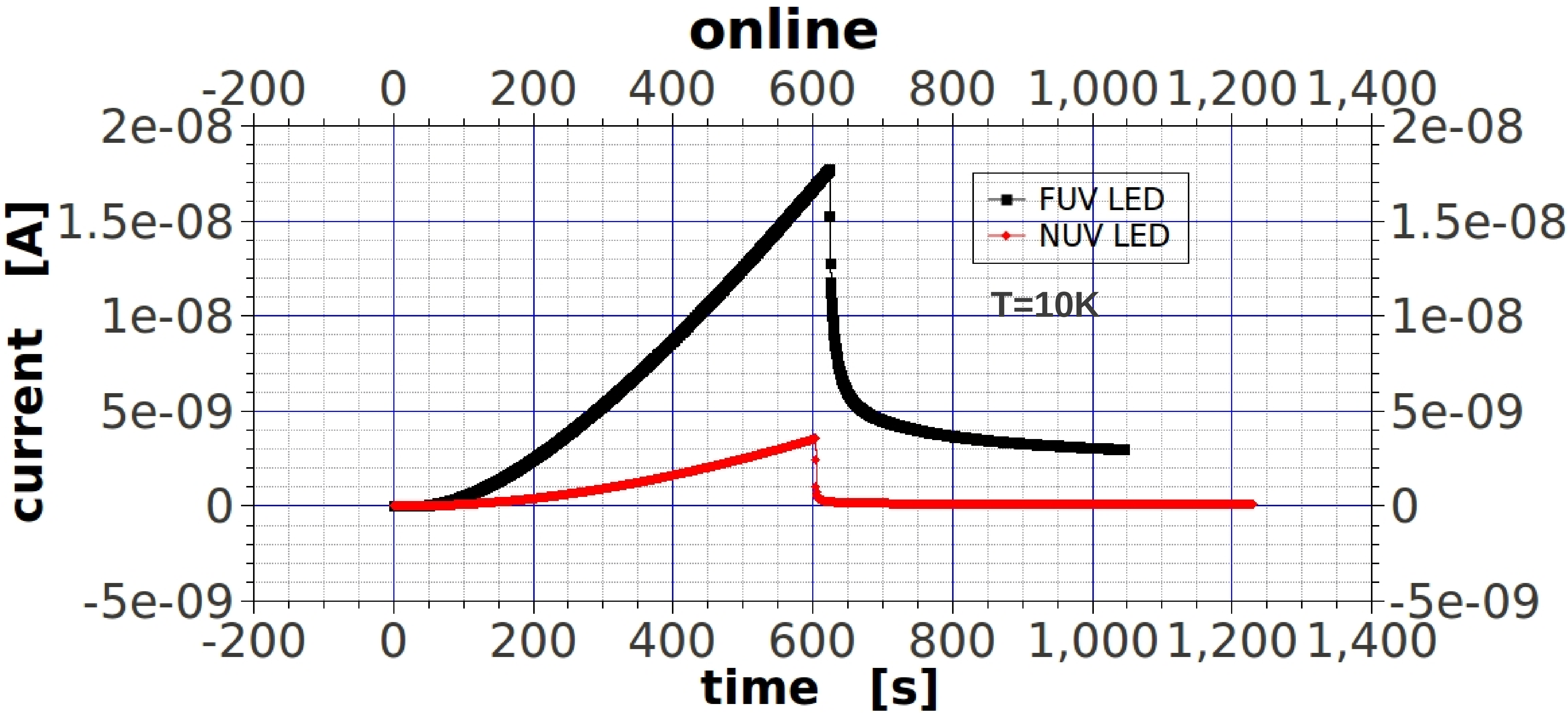
  - Computation of the initial rise activation energy at each scan.
  - Computation of the emitted charge at each scan.
    - Association=>DoS[*]



"in order to obtain the energetic trap distribution the released charge is calculated from the difference of two successive residual TSC scans and correlated to the activation energy obtained from the slope of the first of those residual scans."[*]

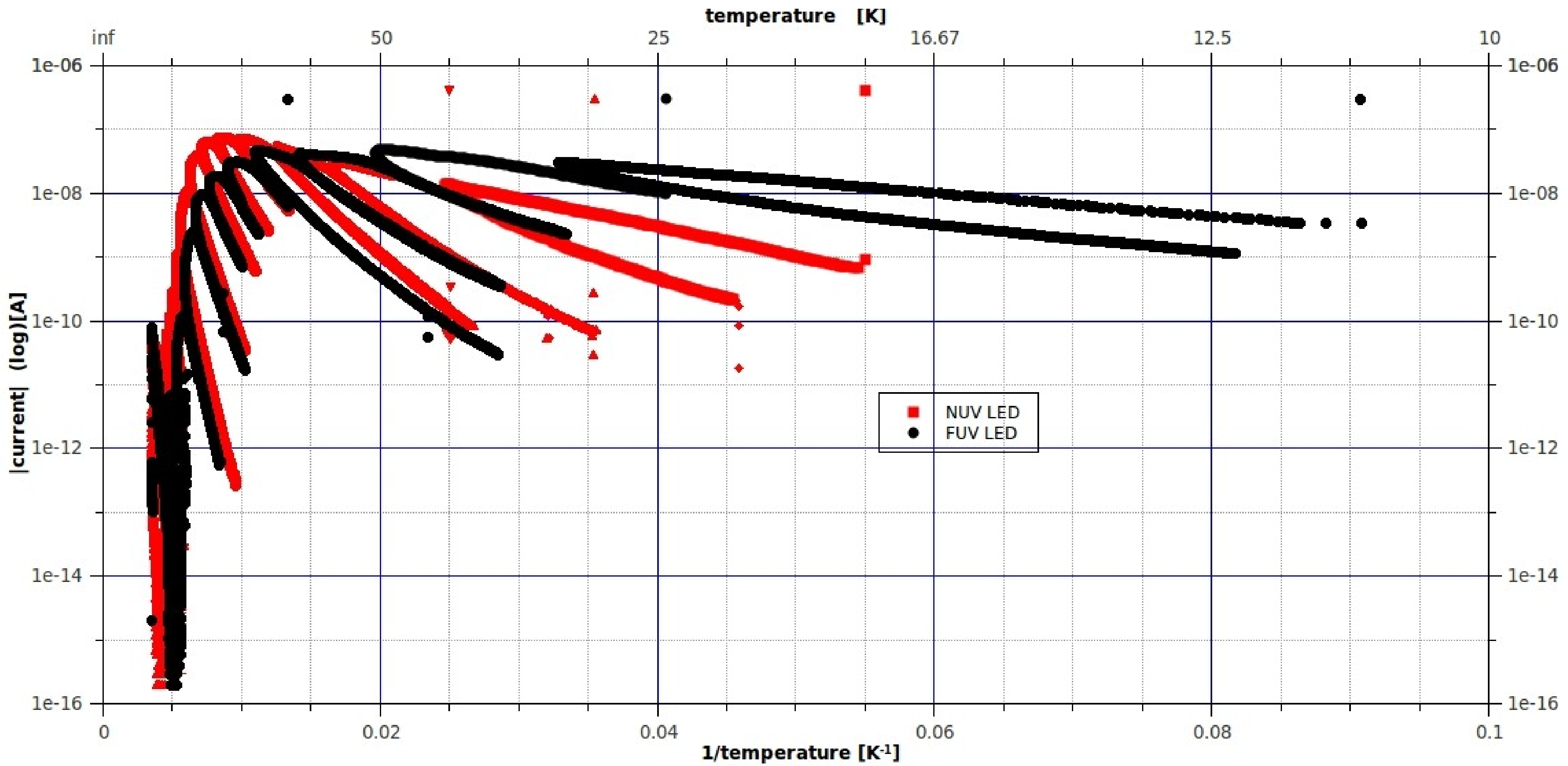
[*] Steiger, 2002

Experimental results: Onlines (photocurrent transients)



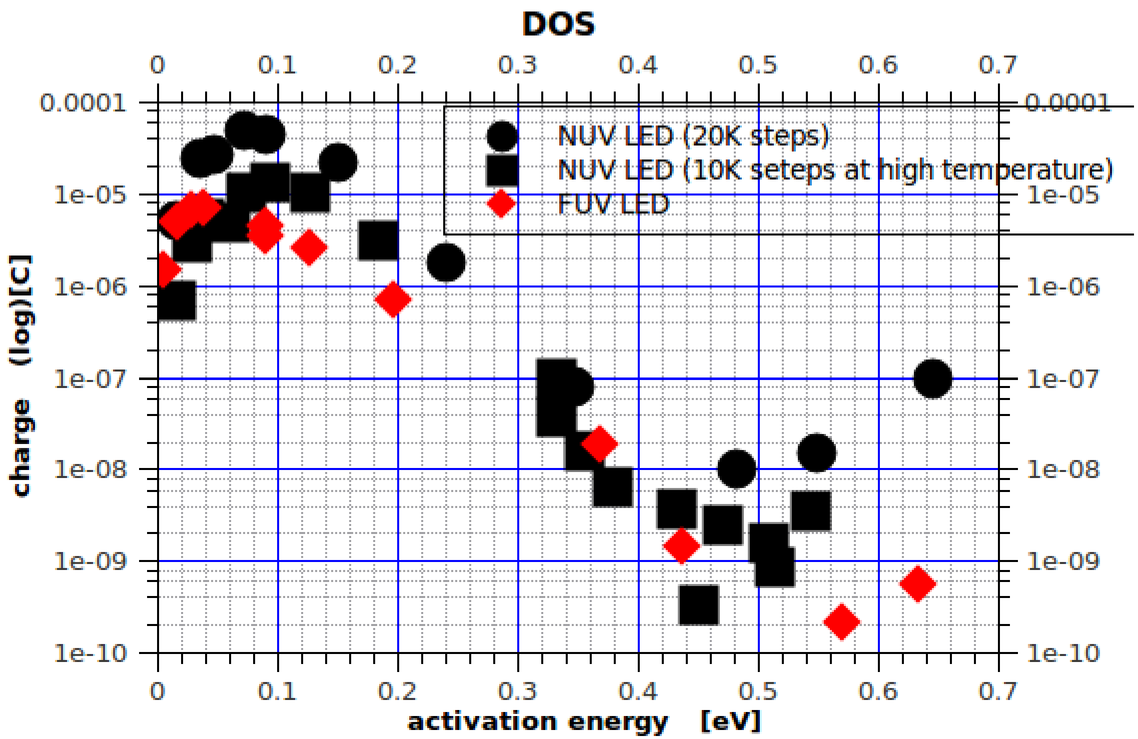
- Very slow time constants: high disorder.
- Multiple time constants: dispersion.

Experimental results: Fractional TSC



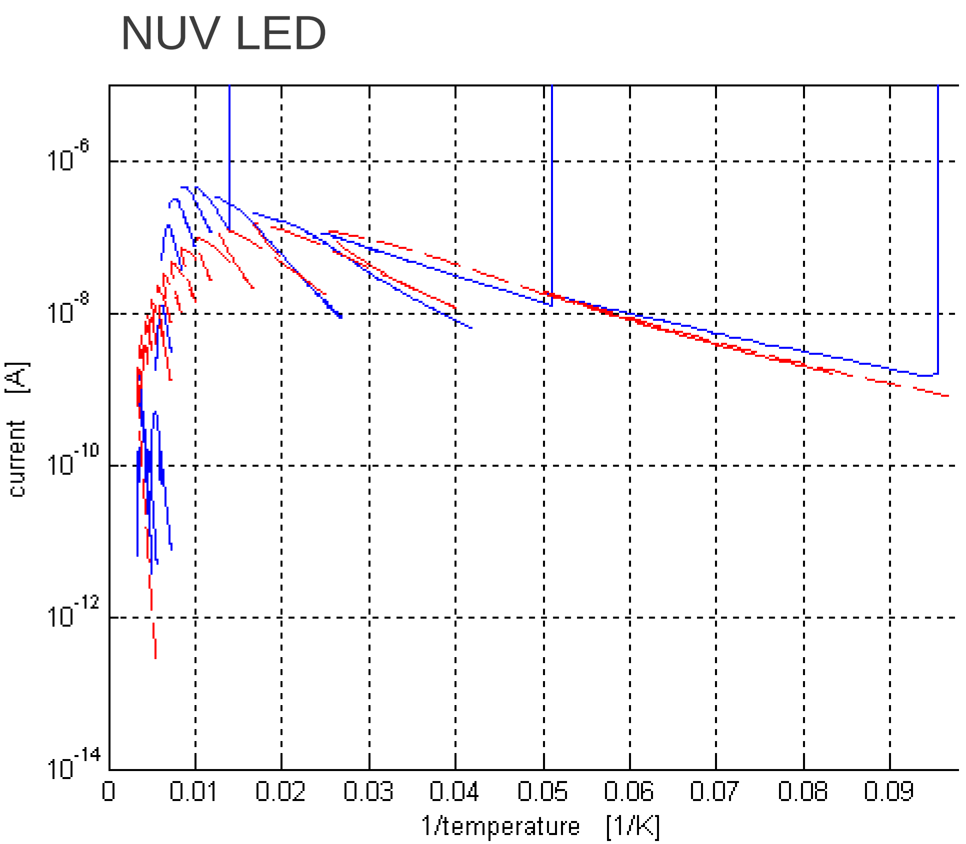
- Broad emission: distributed levels.
- Lower slope from the FUV LED: larger priming.

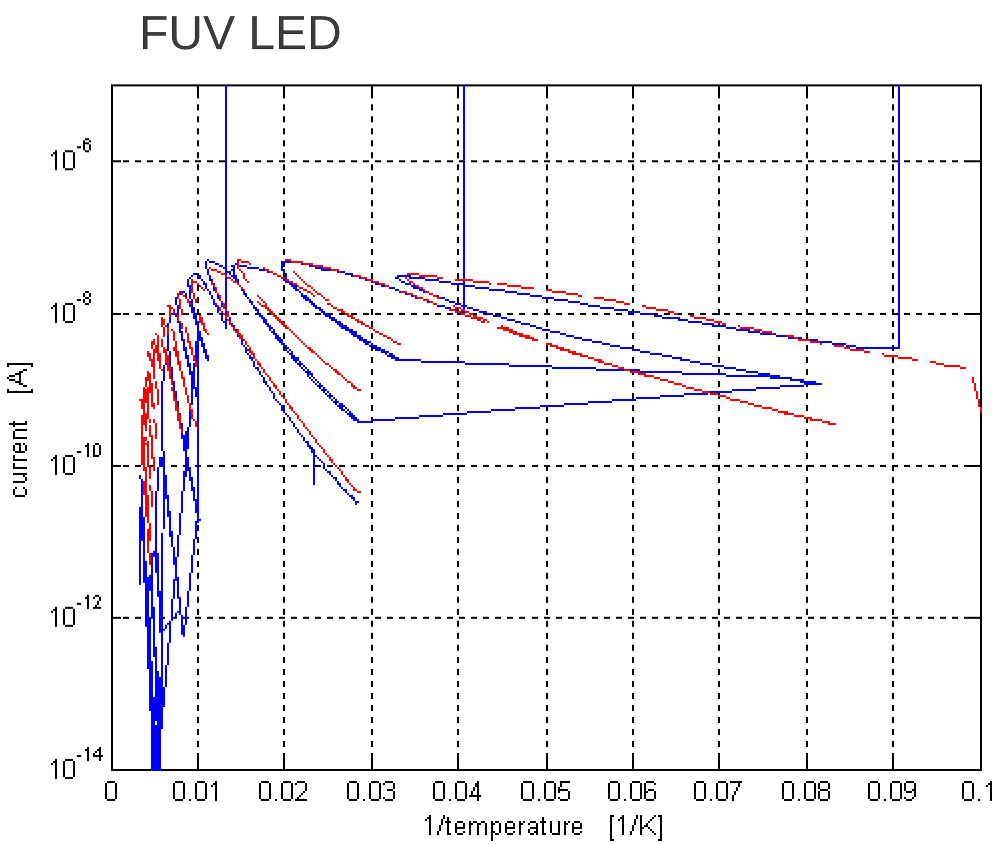
Experimental results: DoS



- Exponential DoS up to a shallow level
- FUV LED prime up to a shallower level.
- Priming up to 0.1 eV from conduction band.

Experimental results: Fits





- Good agreement for each scan.
- Lower agreement at the high temperature decay.
- Parameters in the range of expectation.

Work in progress: Theoretical works

- Accounting for free carrier density (MT model):
  - The free carrier conducibility added to the total.
  - Recombination of free carrier added to the rate equation.
- Transients modeling:
  - Rate equation during priming: adding the source term, at a fixed temperature.

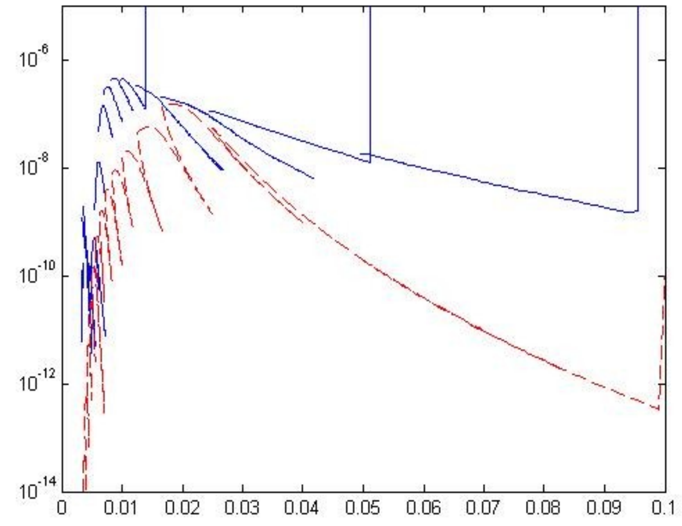
$$\sigma_c = q \mu_{c0} N_{c0} e^{\frac{E_F}{k_B T}}$$

$$\frac{d(n+n_L+n_c)}{dT} = -\frac{n}{\beta \tau} - \frac{n_c}{\beta \tau_c}$$

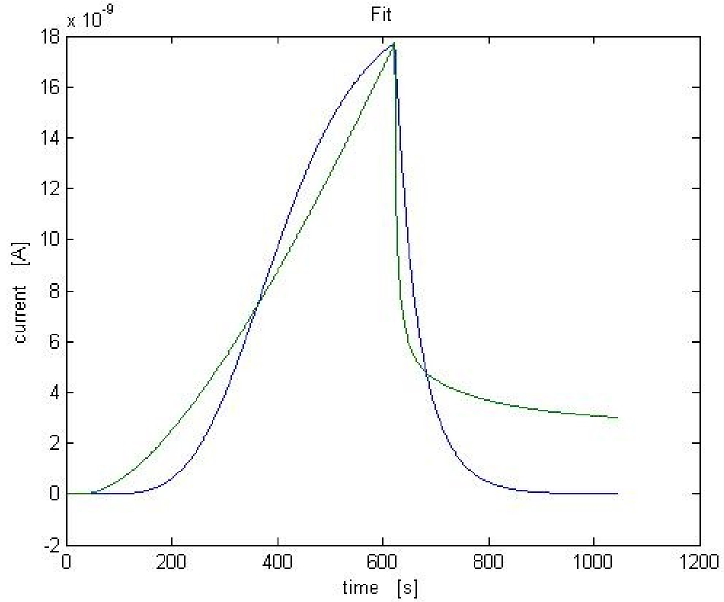
$$\frac{d(n+n_L+n_c)}{dt} = -\frac{n}{\tau} - \frac{n_c}{\tau_c} + S$$

Work in progress: Expected results

- Fractional TSC fits:
  - More rapid decay, as the Fermi level should decrease faster.



- Onlines fits:
  - The fit of the transients help the resolution of the parameters.



Discussion

- On the model:
  - The conducibility is determined by the distance between the Fermi level and the transport level.
  - Taking into account of the degeneration is essential at low temperature. The model should account for degeneration in all the steps.
- On the method:
  - The priming is not much deep.
  - The TSC usually suffer of resolution in energy but with a distributed level the fractional TSC work well to resolving the DoS.
- On the results:
  - The onlines reveal dispersion of the parameters as expected in disordered systems.
  - The fractional TSC reveal an exponential DoS, expected from literature on TiO_2 and for such a disordered system.
  - The model agree with the experimental results but it should be improved accounting for multi trapping (MT).

Conclusions

- Disordered semiconductors are actually of great interests for clinical radiotherapy, particle detectors, solar cells.
- We have improved the existing models of the TSC in disordered semiconductors.

  We have investigated the DoS of nanocrystalline TiO2 and verified the consistency of the model.
- The model should work for interesting materials such a-Si, poly-diamond, SiC.
- In the future we will improve the model, we will perform new measurements varying the experimental settings and verifying the model in such cases.

Thank you!!!

- Multiple trapping or hopping?

- Both!!!

Spares

- Introduction
  - References
  - TiO2
- Theory
  - MT vs. hopping
- Materials
  - Chemical results
  - High temperature set-up
- Results
  - I-V
  - Quantities of fit in temperature

Spares: Introduction: References(1)

"In the polaron model, a conduction electron localized at a site, or atom, in the system and causes a lattice distortion which stabilizes (traps) the localized electron. This electron migrates from site to site via hopping mechanism, primarily through thermal motion. In the case of TiO2, electrons localized at Ti4+ sites from Ti3+."[Deskin et al., 2007]

"Transport in random particle network could be described by percolation theory."[Benkstein et al., 2003]

"Multiple trapping, in which transport occurs in the conduction band, punctuated by a series of trapping and detrapping events, and hopping models in which electron hop between traps and any detrapping is ignored are commonly used to explain carrier transport in amorphous materials."[Cass et al., 2003]

Spares: Introduction: References(2)

“CTRW model describe electronic transport in a wide variety of disordered materials. It is based on the idea that the length of jumps as well as the waiting time between two jumps are broadly distributed quantities. MT model describe the transport by the displacement of conduction band electrons limited by the rate of trapping and release from the broad ususally exponential distribution of localized states.” [Bisquert et al., 2007]

“Percolation apply when porosity has an atomic length scale.”[Kopidakis et al., 2006]

“TSC were considered to arise from the balance between thermal emission and recombination. In reality it arise from the interplay between thermal emission and retrapping.”[Baranovskii etal., 1997]

“A theory taking into account emission, retrapping, recombination, has been suggested by Gu et al.. It treat free carriers, above the mobility edge, but at low temperature hopping is important. At T<~120K hopping will probably dominate.”[Baranovskii et al., 1997]

Spares: Introduction: References(3)

“The main feature of hopping is at follows: at very low temperatures, the transport path of electrons lies deep in the band tail and the hopping mobility of carriers is low due to the large distances between the localized states involved in the hopping processes. When raising the temperature progressively, more shallow state are used by electrons in their hopping and the carrier mobility increases drastically because localized states involved become closer in space and tunneling between them becomes exponentially easier. At some particular temperature Tcrit the transport path emerges into the mobility edge and the mobility achieves its value for free carrier μ0. At T>T0 movement of electrons in the extended states above the mobility edge determines the transport properties.” [Baranovskii et al., 1997]

“The main feature of our model of the low temperature TSC is that is determined by the interplay between the hopping mobility μ(T) increasing with T and the concentration of carriers in the system, decreasing in the course of time due to recombination.”[Baranovskii et al., 1997]

Spares: Introduction: TiO2

- Applications:

  Nanocristalline TiO2 is mainly used as electrode in dye-sensitized solar cells.

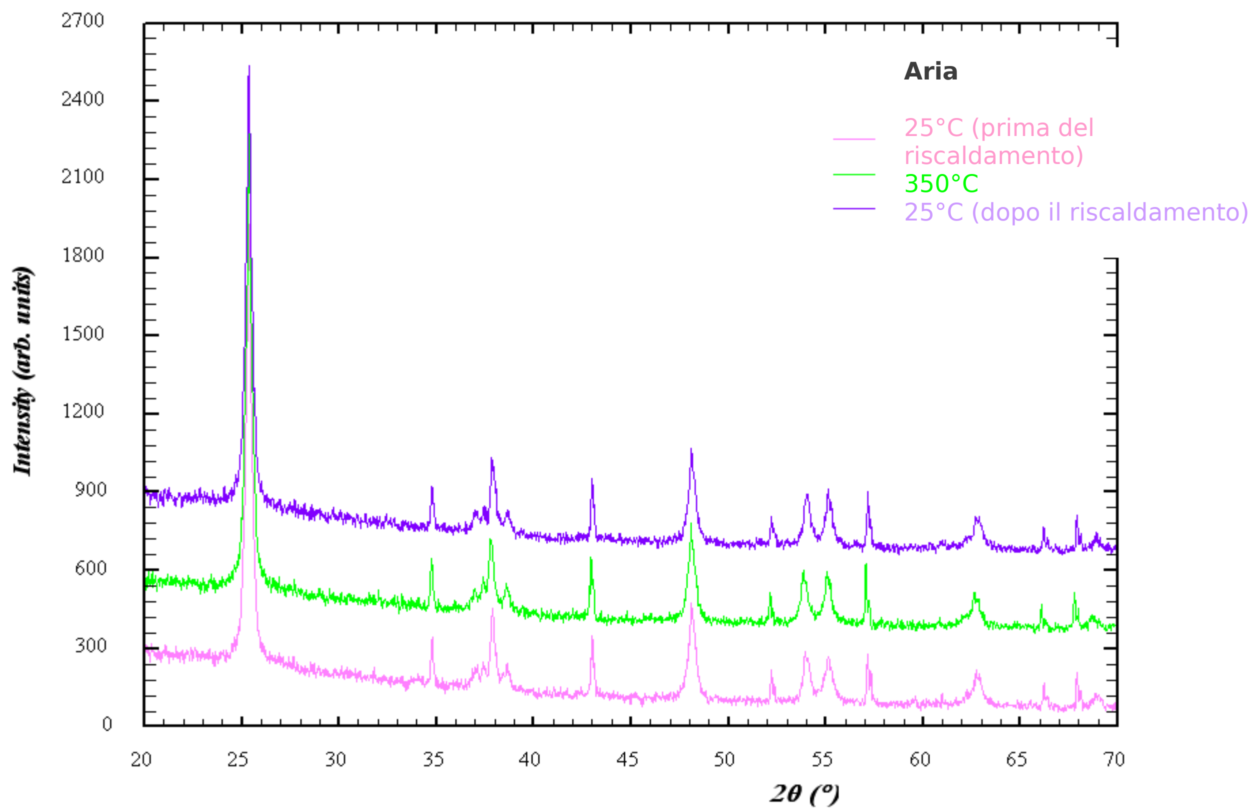
- Defects:

  The main defects in TiO2 are Ti cations and interstitials (which emitt at low temperature). Oxygen act as a scavenger for the electrons. The nanoparticulate structure add a lot of energetic disorders.

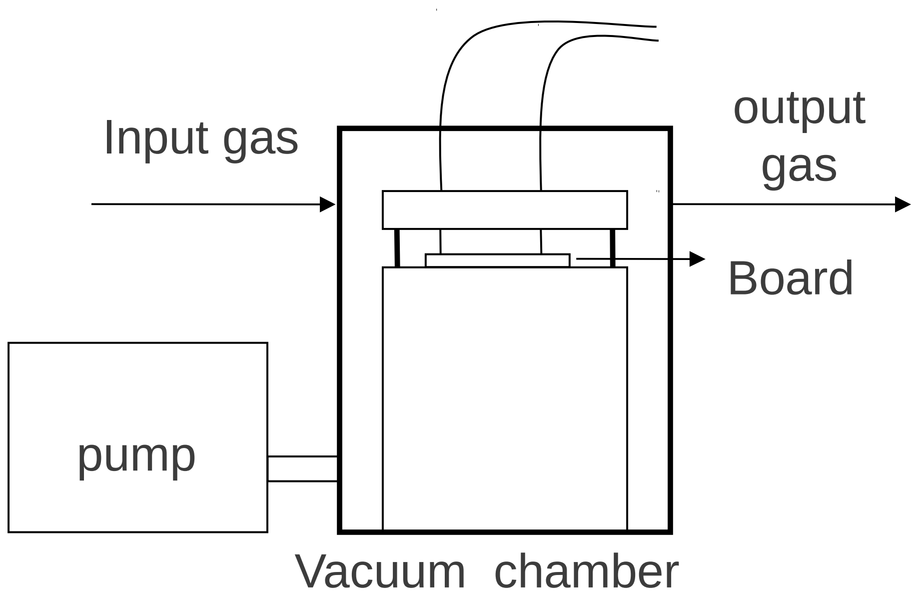
- Studies:

  TiO2 is actually studied with *Intensity Modulated Photocurrent Spectroscopy* (IMPS), with *Electrical Impedance Spectroscopy* (EIS), transient tecniques, but there is still a lack of studies of the properties in temperature.

Spares: Materials: Chemical results

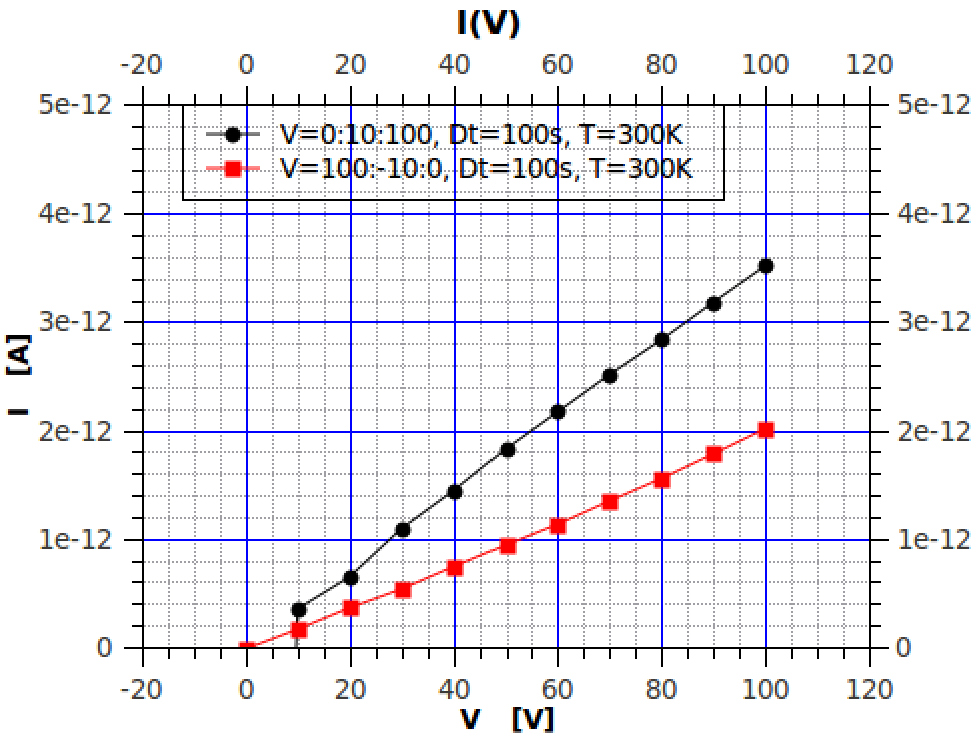


Spares: Materials: High temperature set-up



Spares: Results:

I-V



Spares: Results:
Quantities of fit in temperature