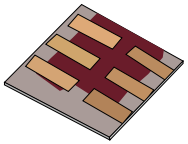
Why do we need trap states when simulating disordered devices?

[alternative title: Please stop simulating disordered semiconductors without trap states]

Dr. Roderick MacKenzie
roderick.mackenzie@oghma-nano.com
Winter 2022

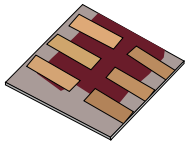
https://www.oghma-nano.com

Overview



- **Introduction**
- Standard drift diffusion models for ordered materials such as GaAs
- Comparison of disordered and ordered semiconductors
- Why is having the correct distribution of trap states important?
- Furthermore… mobility…
- Simulating disordered devices with traps
- Including the SRH equation is not enough esp in time domain.
- Demos

Why am writing this slide deck on a weekend?



- Recently I've noticed a few 'drift diffusion' models being applied to disordered materials without trap states.

- Broadly speaking this ***should not be done***, so I thought I would make some comments as to why this should not be done.

Some examples

Jesús Capistrán @capis · Dec 17

🌅If you are working on the design of novel solar cells. do not forget to explore the ∂PV simulator by Sean Mann and @_romanog_

∂PV: An end-to-end differentiable solar-cell simulator

sciencedirect.com
∂PV: An end-to-end differentiable solar-cell simula...
We introduce ∂PV, an end-to-end differentiable photovoltaic (PV) cell simulator based on the drift-...

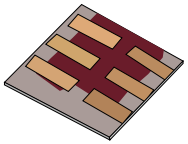
3 3

Photovoltaic Device Model (gpvdm) @gpvdm_info · Dec 17

Does it have trap states? I can't see form the docs it does... if not it won't be valid for OPV or anything which is not super ordered. (Perovskites are prob also out..)

2 2

Some examples



Giuseppe Romano @_romanog_ · Dec 20

@gpvdm_info , we have the SRH recombination model. Is this what you meant? github.com/romanodev/delt... We just overlooked adding it to the doc (will do!).

Photovoltaic Device Model (gpvdm)
@gpvdm_info

Replying to @_romanog_ and @capis

1: Sort of but not really. So from reading the script it looks as if you are using the standard SRH equation describing recombination. This will give you free->trap recombination via a single trap state. However the actual charge trapped in this state...

7:56 AM · Dec 20, 2021 · Twitter Web App

View Tweet activity

$$R^{SRH} = \frac{np - n_0 * p_0}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

Photovoltaic Device Model (gpvdm) @gpvdm_info · Dec 20
Replying to @gpvdm_info @_romanog_ and @capis
3: You need to explicitly include trap states whereby carriers can get captured and then at a later time escape. You will need this to get the correct carrier density v.s. average charge carrier mobility i.e. mu=mu_0*n_free/(n_free+n_trap) relations.

Photovoltaic Device Model (gpvdm) @gpvdm_info · Dec 20
Replying to @gpvdm_info @_romanog_ and @capis
4: Also a single SRH trap state will not describe the Urbach tail descending into the band.

Photovoltaic Device Model (gpvdm) @gpvdm_info · Dec 20
Replying to @gpvdm_info @_romanog_ and @capis
2: will not be accounted for in your Poisson equation, and as the majority of charge in disordered devices exists in trap states your potential dist across the device will be wrong.

Photovoltaic Device Model (gpvdm) @gpvdm_info · Dec 20
Replying to @gpvdm_info @_romanog_ and @capis
5: I try to explain this here gpvdm.com/physical.html#... but the origonal SRH papers are prob better to read.

Photovoltaic Device Model (gpvdm)
@gpvdm_info

Replying to @gpvdm_info @_romanog_ and @capis

6: Happy to zoom - kind of hard to do physics in 280 chars.. I've also not picked through the code base in detail so you may be doing this but I don't think so. Will all still be totally valid for ordered materials just not for anything disordered.

8:10 AM · Dec 20, 2021 · Twitter Web App

THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

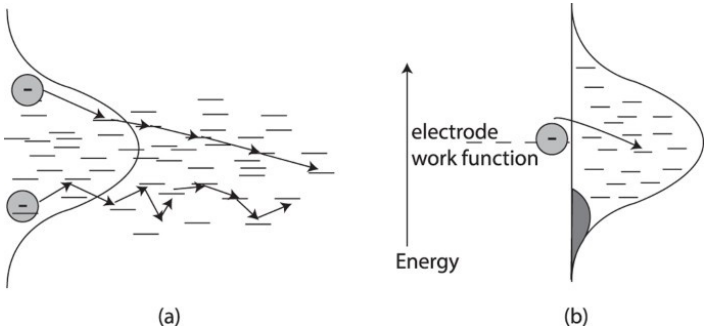
pubs.acs.org/JPCL Letter

Slow Relaxation of Photogenerated Charge Carriers Boosts Open-Circuit Voltage of Organic Solar Cells

Tanvi Upreti, Sebastian Wilken, Huotian Zhang, and Martijn Kemerink*

Cite This: J. Phys. Chem. Lett. 2021, 12, 9874–9881 Read Online

Monte-Carlo hopping with traps



Picture from:10.1038/srep19794

Drift diffusion model with no traps

$$\nabla \epsilon_o \epsilon_r \cdot \nabla \phi = q \cdot (n - p)$$

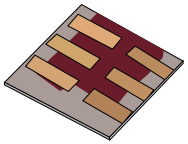
$$J_n = q \mu_e n \nabla E_c + q D_n \nabla n$$

$$J_p = q \mu_h p \nabla E_v - q D_p \nabla p$$

They concluded that you need traps and their DD model did not work as it had no traps.

I broadly agreed with their conclusion but I think they should not have been modeling disordered devices without traps in the first place.

Overview



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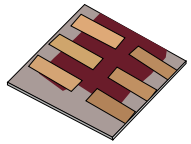
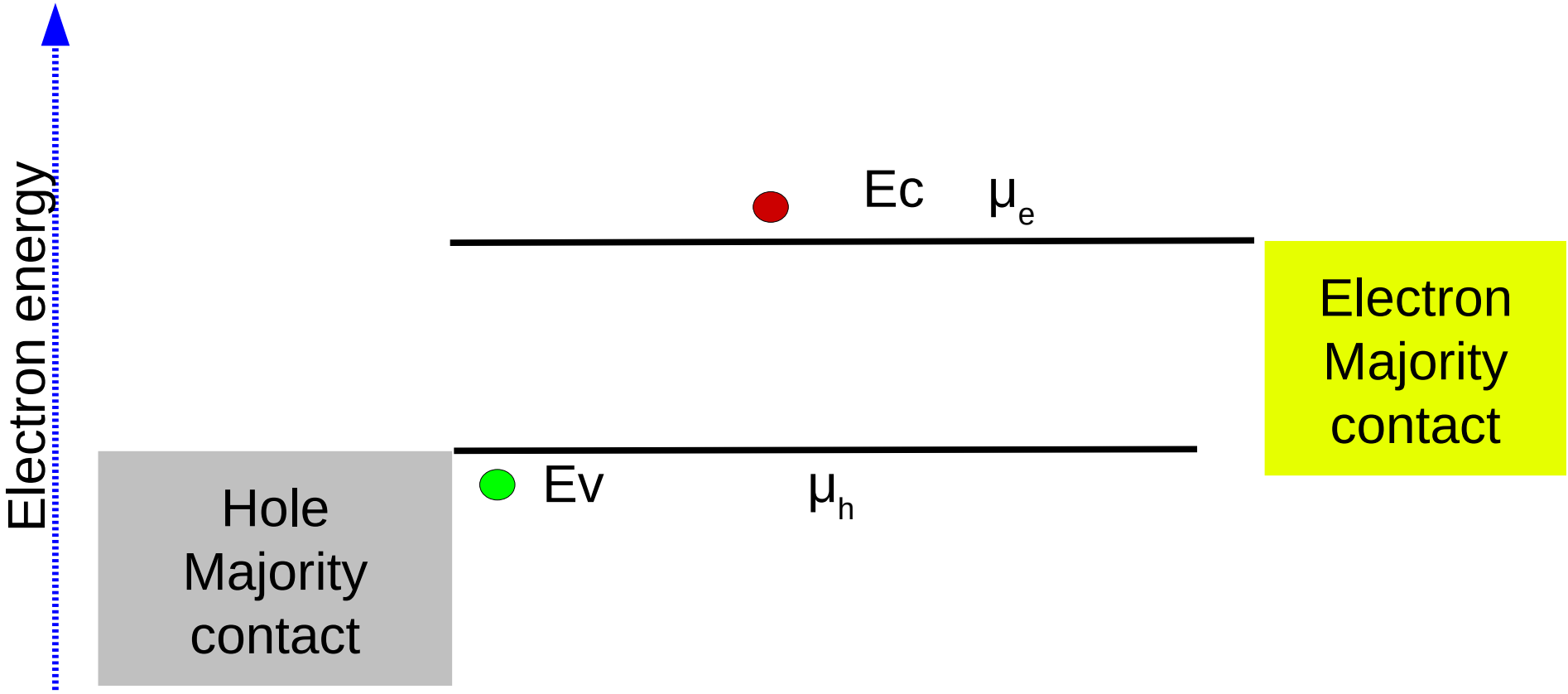
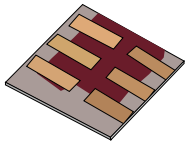
An ordered semiconductor such as GaAs





Simulating charge transport for ordered semiconductors.



Gauss's Law

$$\nabla \epsilon_o \epsilon_r \cdot \nabla \phi = q \cdot (n - p)$$

Electron driving terms

$$J_n = q \mu_e n \nabla E_c + q D_n \nabla n$$

Hole driving terms

$$J_p = q \mu_h p \nabla E_v - q D_p \nabla p$$

Electron continuity

$$\nabla \cdot \boldsymbol{J}_n = q \left(R_n + T_n + \frac{\partial n_{free}}{\partial t} \right)$$

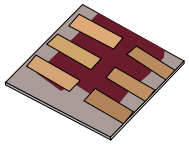
Hole continuity

$$\nabla \cdot \boldsymbol{J}_p = -q \left(R_p + T_p + \frac{\partial p_{free}}{\partial t} \right)$$

Demo

MacKenzie , Shuttle, Adv. Energy Mater. 2012, 2 (6), 662-669

Overview



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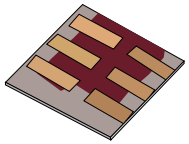
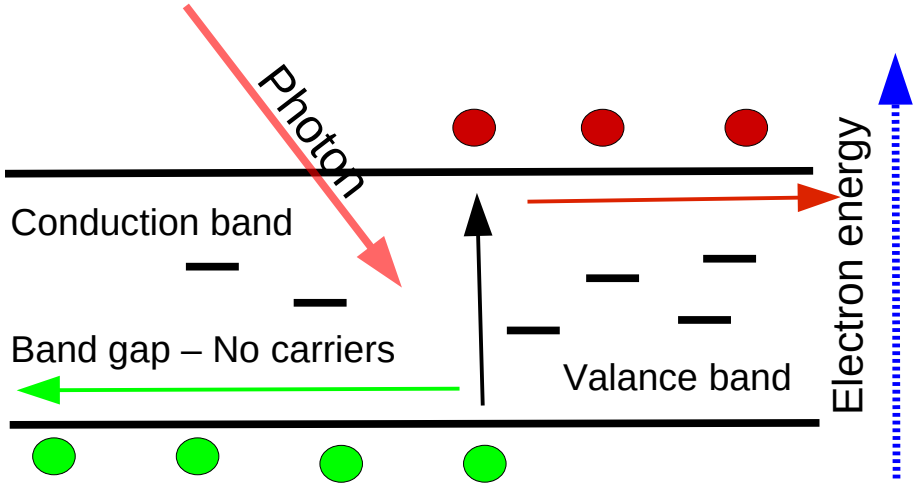
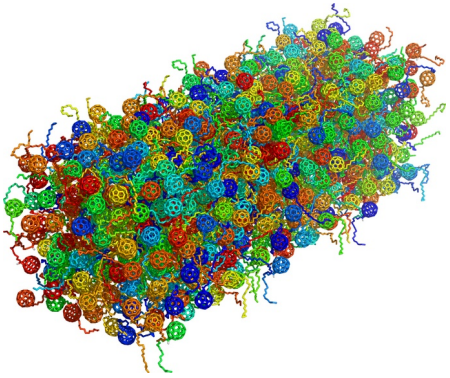
Compare band structure of silicon and an organic semiconductor

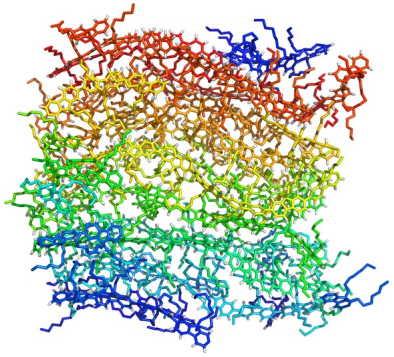


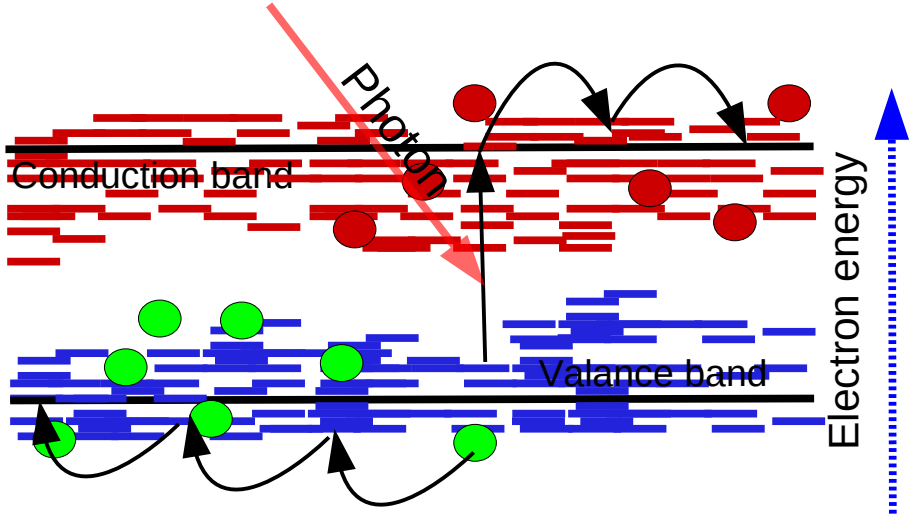
- Inorganic semiconductors are crystalline and have a well defined bandgap and few traps.

- Inorganic semiconductors are very disordered and have a distribution of trap states.

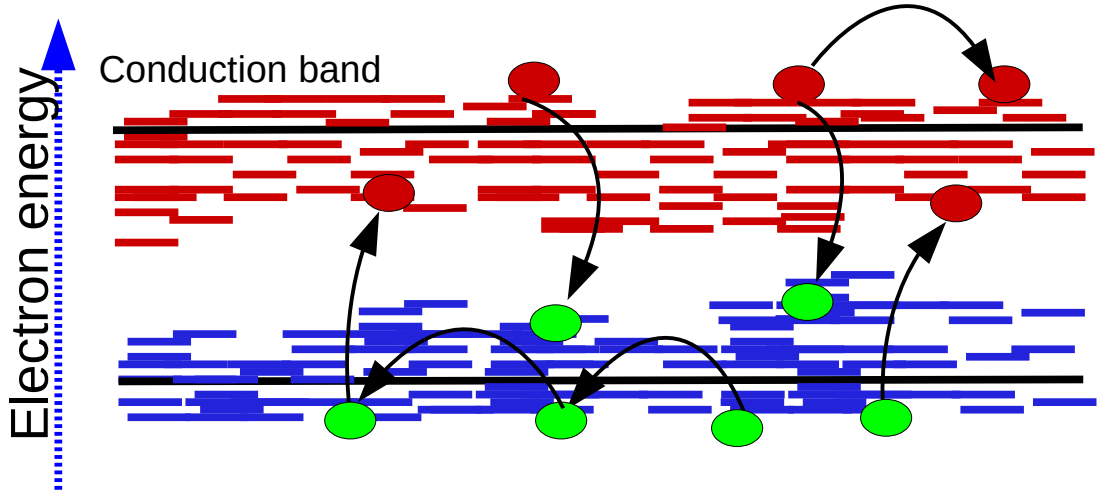




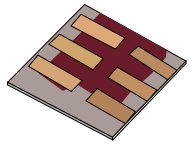


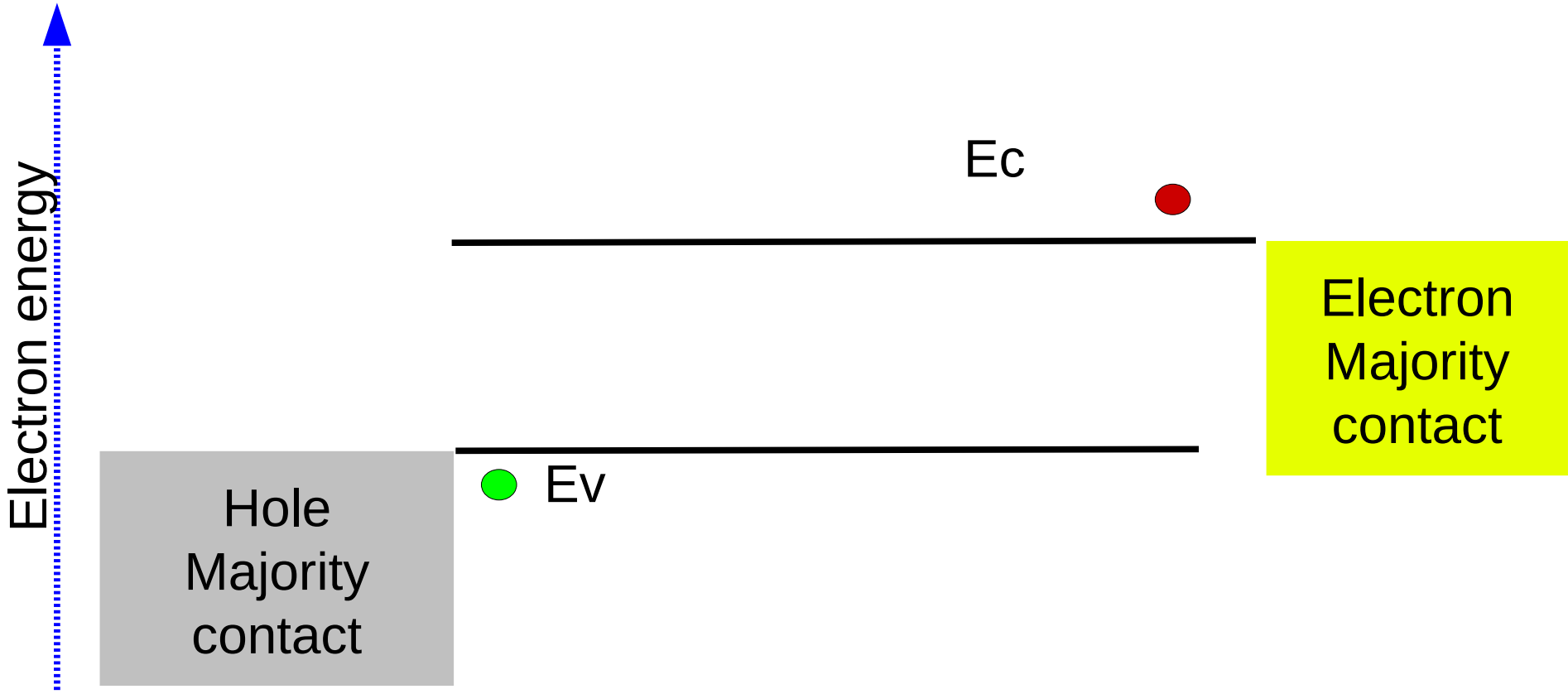


The majority of charge is stored in these trap states

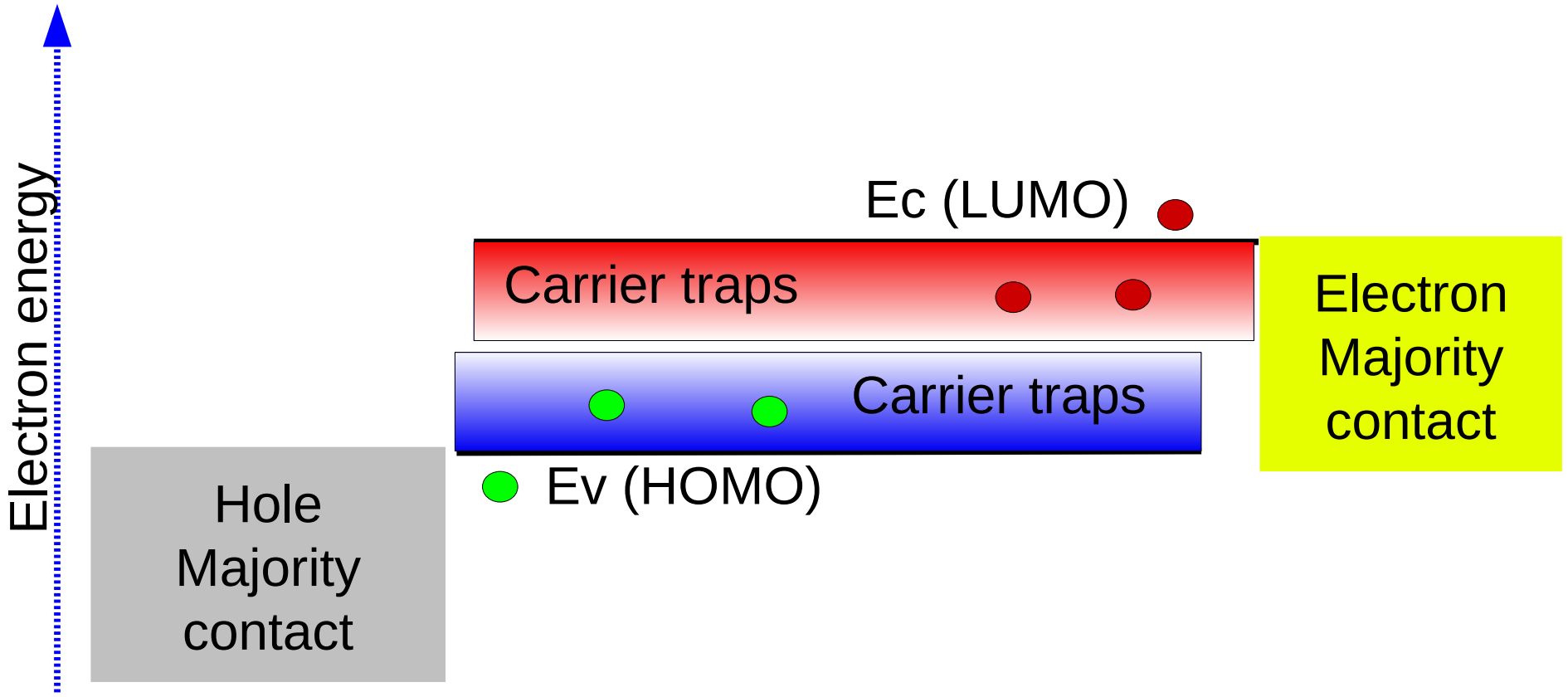


So this type of model is not valid as there are no traps

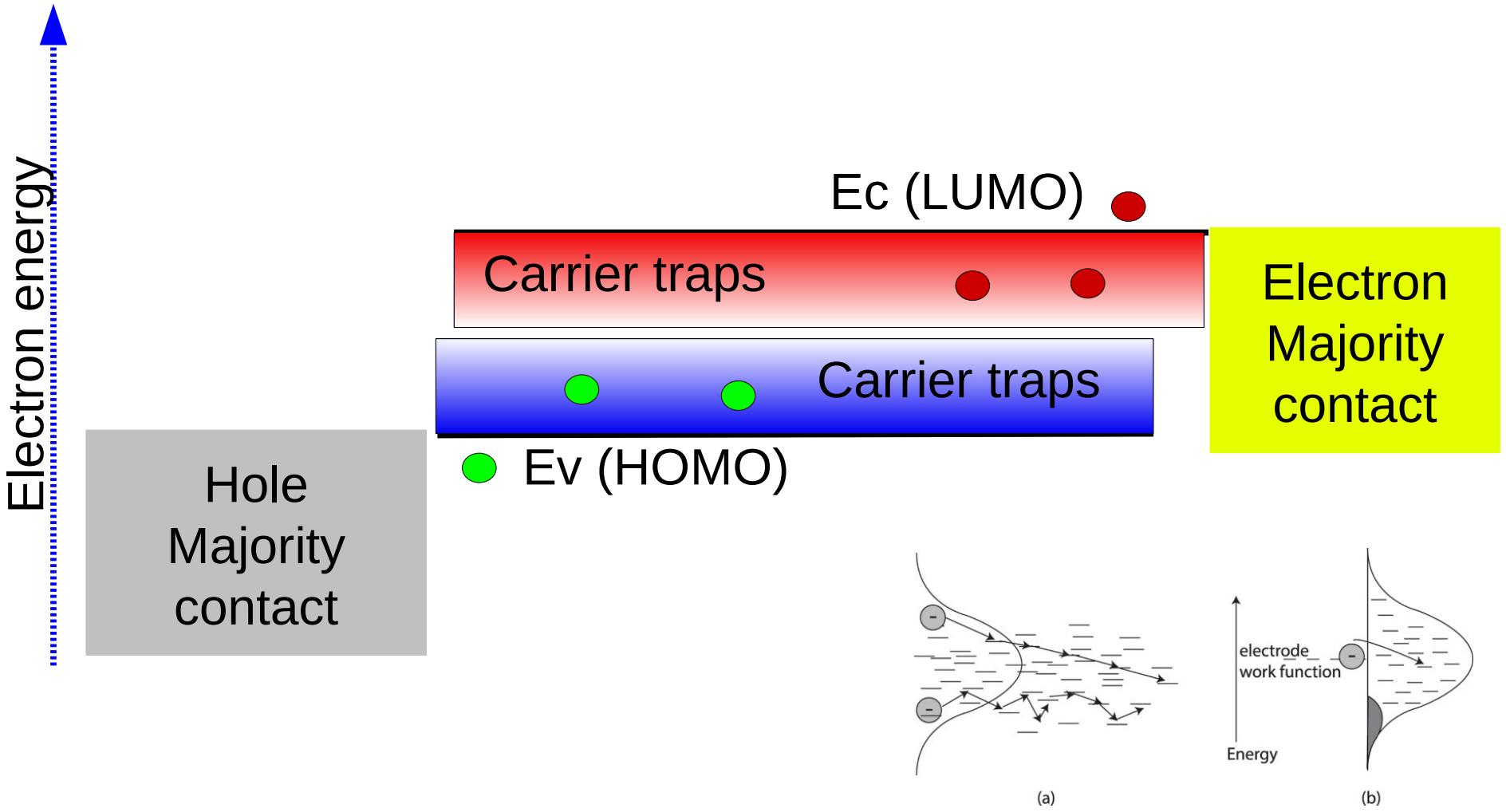




We need to add carrier traps to our model

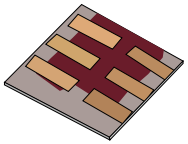


Then it starts to look a lot more like the traditional Monte-Carlo hopping models.



Picture from:10.1038/srep19794

Overview



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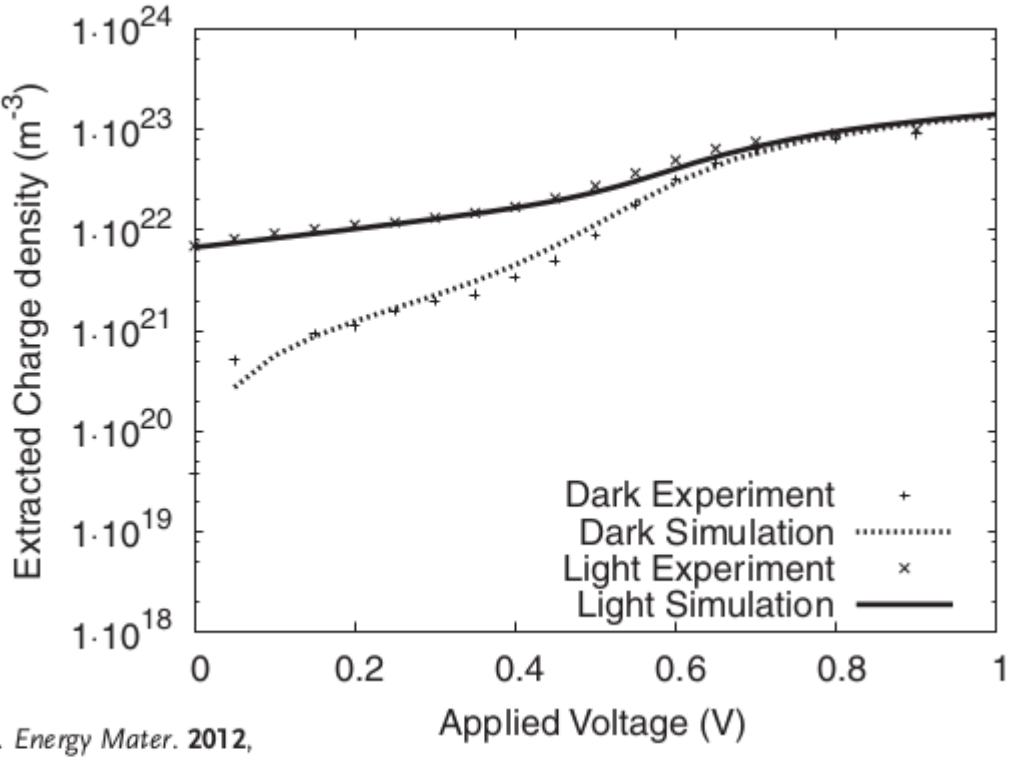
The trap distribution determines the voltage and light dependence of carrier density.



Adv. Energy Mater. **2012**,
DOI: 10.1002/aenm.201100709

- In disordered devices because all the charge is stored in trap states, carrier density in the device varies strongly as a function of applied voltage and light intensity

n(V,light), p(V,light)

The trap distribution determines the voltage and light dependence of carrier density.

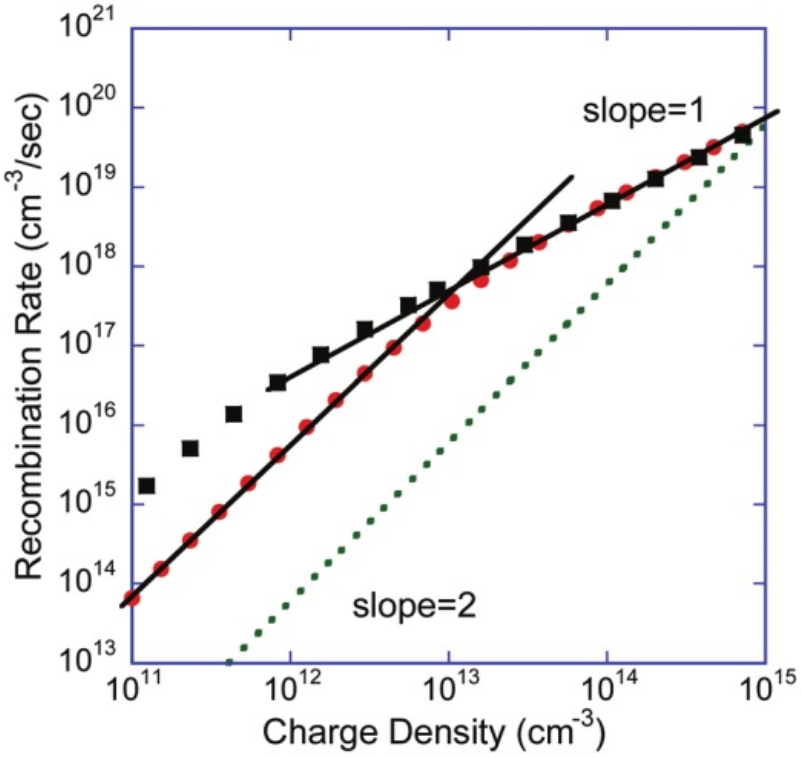
- Or said in another way rho (the DoS) multiplied by the fermi level determines charge density.

$$n = \int_{E_{min}}^{\infty} \rho(E) f(E, E_f, T) dE$$

$$p = \int_{E_{min}}^{\infty} \rho(E) f(E, E_f, T) dE$$

- OK so what you might ask?

Recombination is a strong function of carrier density.



L. Tzabari and N. Tessler

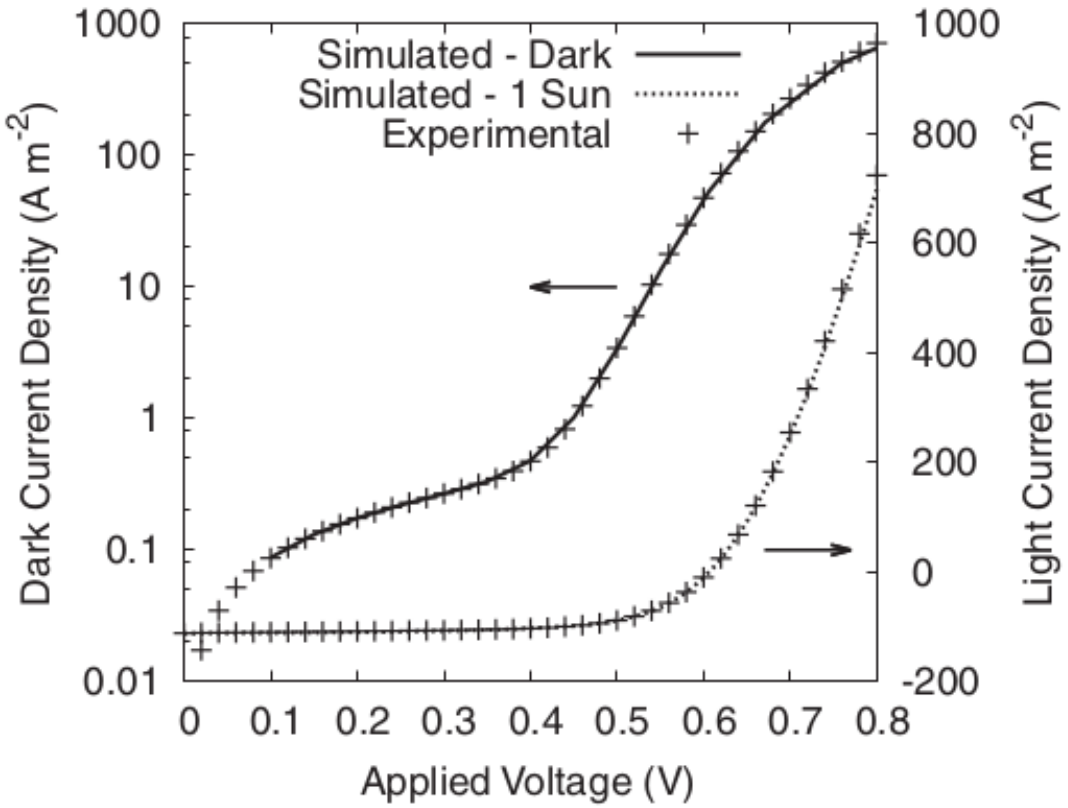
J. Appl. Phys. **109**, 064501 (2011)

R=f(n(V,light),p(V,light))

- So to get recombination correct we need to get n(V,light) and p(V,light) correct.

- Note the very simplified recombination model, don't assume your material is bi-molecular but that is another story.

Getting recombination correct is key to getting Jsc, Voc, and FF correct.



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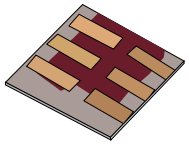

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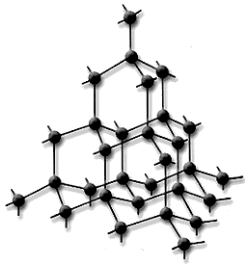
Mobility in ordered materials is constant



$$J_n = q\mu_e n \nabla E_c + q D_n \nabla n$$

Electron energy

Ec μ_e

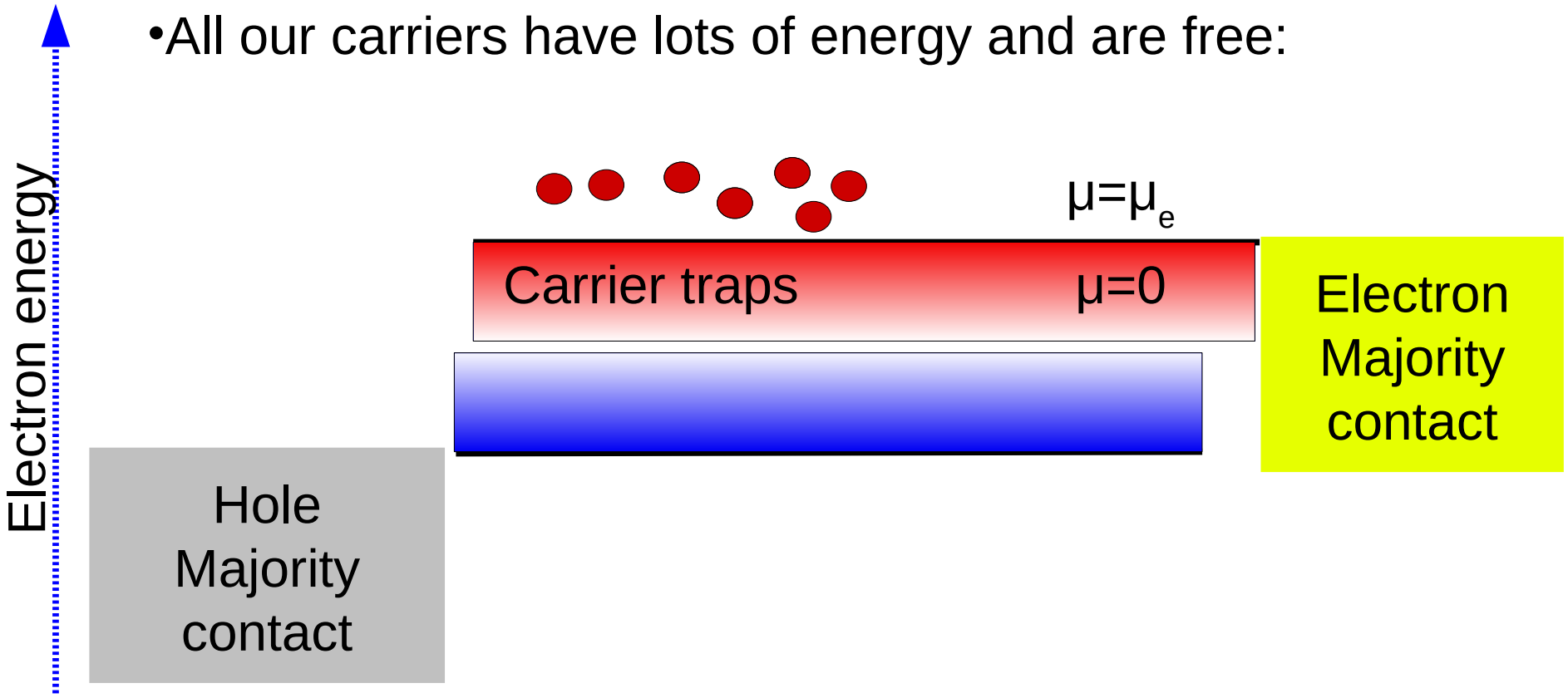
Electron Majority contact

Ev μ_h

Hole Majority contact

$$J_p = q\mu_h p \nabla E_v - q D_p \nabla p$$

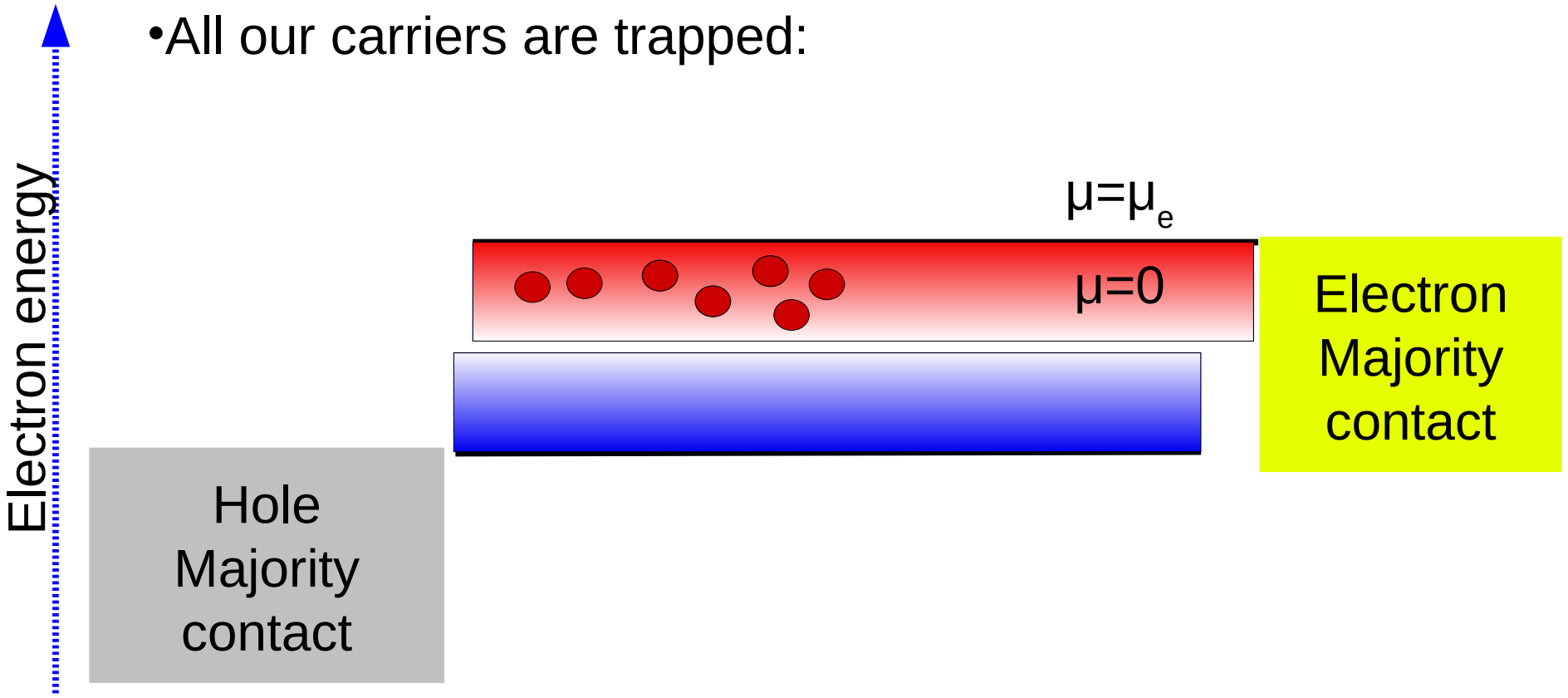
In disordered material it's not constant, imagine the following situation:



- All our carriers have lots of energy and are free:
- What's the mobility? …… μ_e

In disordered material it's not constant, imagine the following situation:

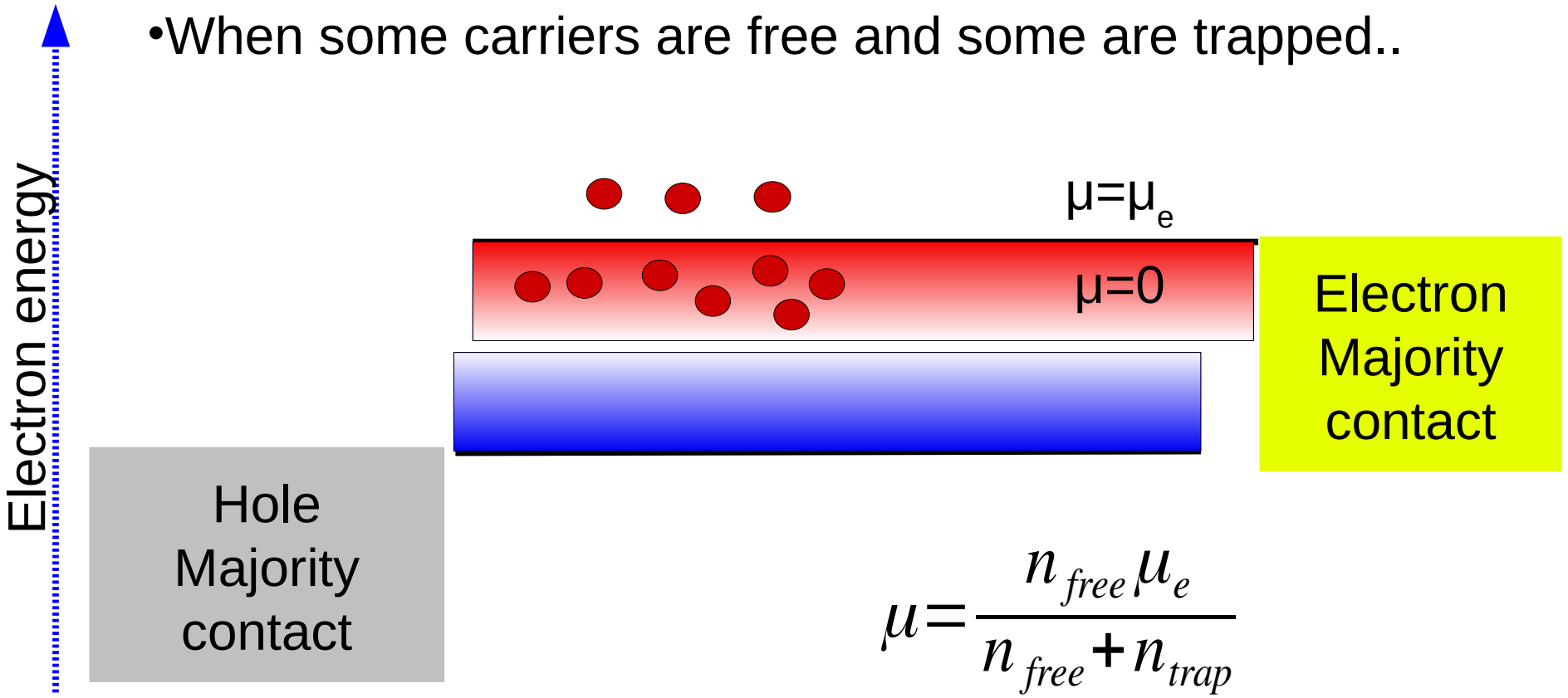
- All our carriers are trapped:



- What's the mobility? ….. 0

In general….

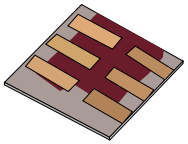
- When some carriers are free and some are trapped..



$$\mu = \frac{n_{free}\mu_e}{n_{free} + n_{trap}}$$

- So if you get n_{trap} wrong you will have the wrong dependence of mobility on voltage, light which will also cause problems for your model..

Overview



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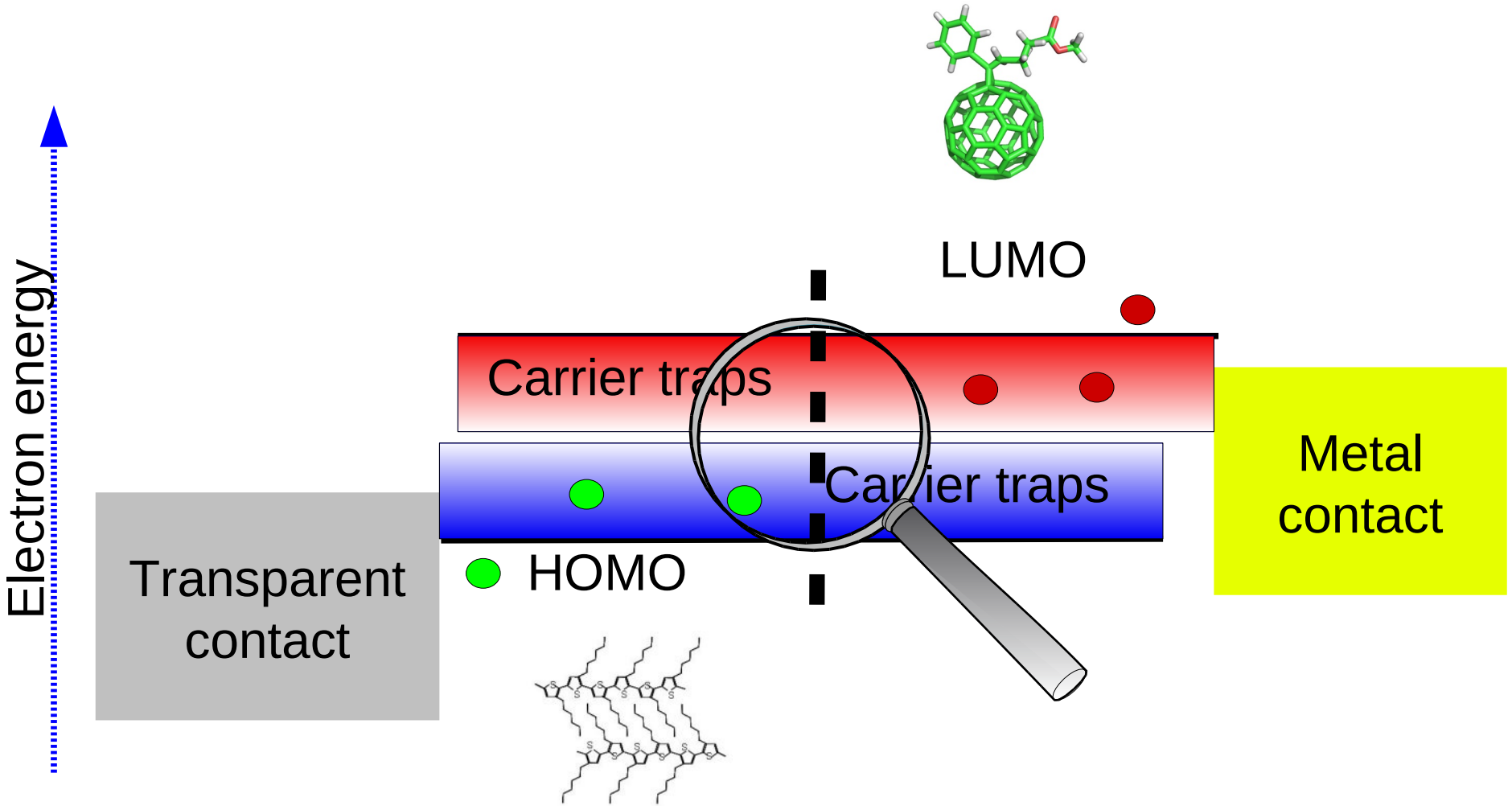
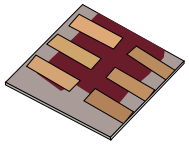
Let’s slice through the device in energy space



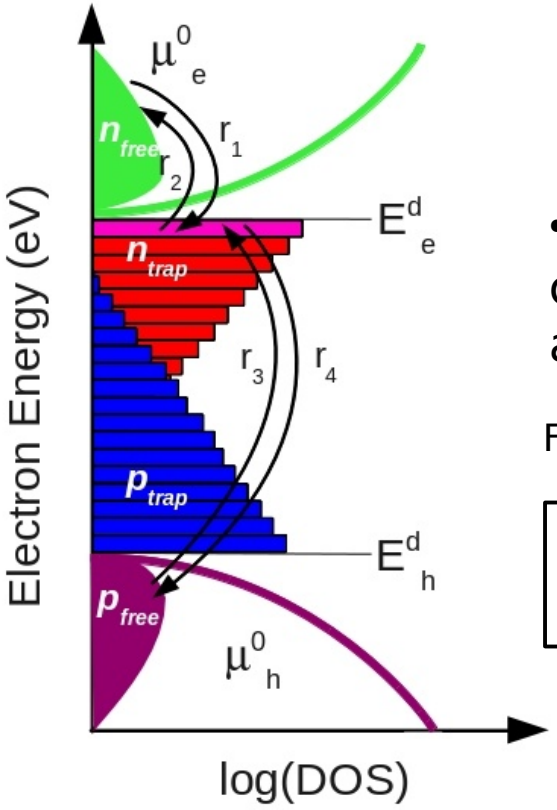
We therefore need to solve for the charge density of each trap state explicitly.



- We split energy space up into energy slices.
- And use the SRH equations but don't assume steady state, so solve the SRH equations explicitly in time domain.
- Each trap state gets its own rate equation:

$$\frac{\partial n}{\partial t} = r_1 - r_2 - r_3 + r_4$$

Process	
electron capture	r_1
electron emission	r_2
hole capture	r_3
hole emission	r_4



- Recombination can be calculated as:

Free carrier recombination

$$R_n = \sum_{0}^{n_{band}} \left(r_1^e - r_2^e \right)$$

Detailed balance is maintained.

SRH recombination and trapping model.

PHYSICAL REVIEW VOLUME 87, NUMBER 5 SEPTEMBER 1, 1952

Statistics of the Recombinations of Holes and Electrons

W. SHOCKLEY AND W. T. READ, JR.
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received April 29, 1952)

The statistics of the recombination of holes and electrons in semiconductors is analyzed on the basis of a model in which the recombination occurs through the mechanism of trapping. A trap is assumed to have an energy level in the energy gap so that its charge may have either of two values differing by one electronic charge. The dependence of lifetime of injected carriers upon initial conductivity and upon injected carrier density is discussed.

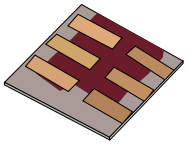
SECTION 1. INTRODUCTION

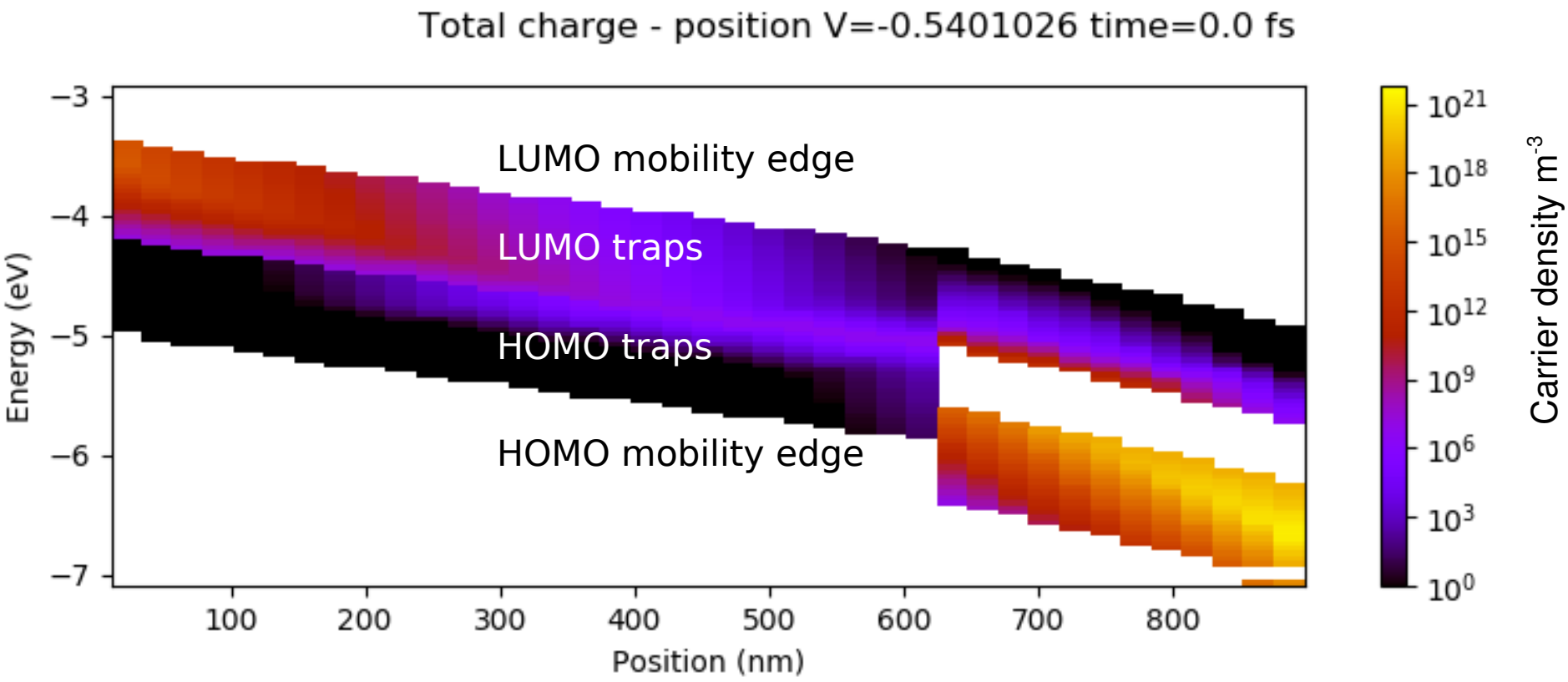
IN connection with studies of transistor physics, the recombination of holes and electrons plays an important role. The lifetime of injected carriers in germanium has been found to be a structure sensitive property of the material. This suggests that the recombination process takes place through the medium of imperfections of some sort in the germanium crystal.[1] It is the purpose of this paper to investigate the mathe-

an electron from the conduction band. The energy loss of the electron is then converted into heat or light or both depending upon the nature of the trapping process. It may also capture an electron from the valence band represented by part (d) of the figure, in which case it acquires a negative charge and leaves a hole in the valence band. Parts (b) and (c) represent the emission of an electron and the capture of a hole.

The effects which we shall consider in this study

This enables us to know where the charge carriers are in position/energy space.





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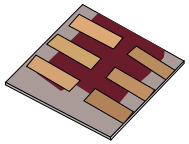

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Steady state SRH v.s. fully time/spatially resolved SRH.

Mechanism	Symbol	Description
Electron capture rate	r_{ec}	$nv_{th}\sigma_n N_t(1-f)$
Electron escape rate	r_{ee}	$e_n N_t f$
Hole capture rate	r_{hc}	$pv_{th}\sigma_p N_t f$
Hole escape rate	r_{he}	$e_p N_t(1-f)$

Table 1: Shockley-Read-Hall trap capture and emission rates, where f is the fermi-Dirac occupation function and N_t is the trap density of a single carrier trap.

For each trap level the carrier balance [12] is solved, giving each trap level an independent quasi-Fermi level. Each point in position space can be allocated between 10 and 160 independent trap states. The rates of each process r_{ec}, r_{ee}, r_{hc}, and r_{he} are give in table [1].

$$\frac{\delta n_t}{\partial t} = r_{ec} - r_{ee} - r_{hc} + r_{he} \tag{12}$$

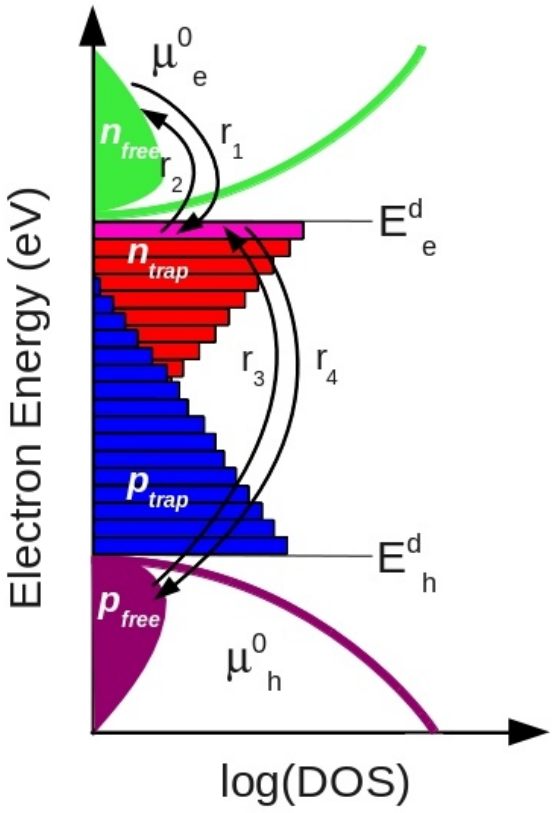
The escape probabilities are given by:

$$e_n = v_{th}\sigma_n N_c exp\left(\frac{E_t - E_c}{kT}\right) \tag{13}$$

and

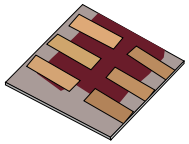
$$e_p = v_{th}\sigma_p N_v exp\left(\frac{E_v - E_t}{kT}\right) \tag{14}$$

where $\sigma_{n,p}$ are the trap cross sections, v_{th} is the thermal emission velocity of the carriers, and $N_{c,v}$ are the effective density of states for free electrons or holes. The distribution of trapped states (DoS) is defined between the mobility edges as



$$R^{SRH} = \frac{np - n_0 * p_0}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

Steady state SRH v.s. fully time/spatially resolved SRH.



- Using the steady state SRH approach acknowledges that carrier traps are important in recombination.

- You won't get the correct carrier density voltage dependence in the device.

- And the charge in the trap states is not linked back to the electrostatic potential.

- But it assumes the distribution of trap states has reached equilibrium. This is OK for steady state but not for time domain.

- It also fails to take into account the distribution of trap states.