

Interface recombination in organic solar cells

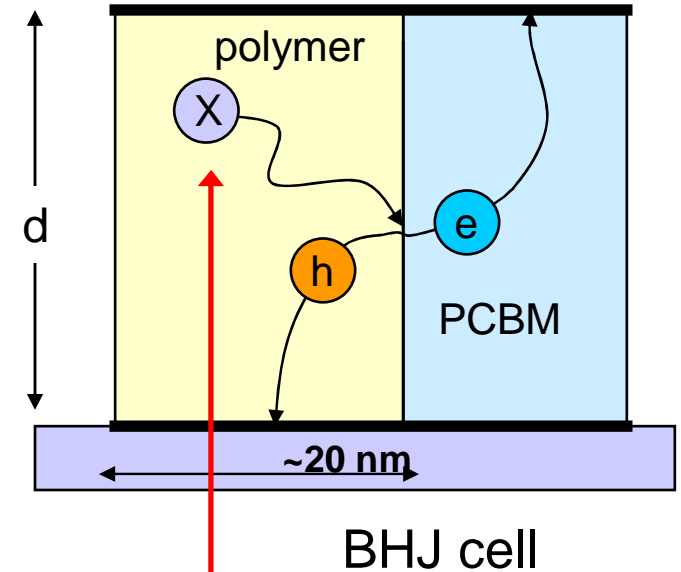
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Acknowledgements

*Alan Heeger and UCSB group, for
PCDTBT:PC70BM solar cells*

Organic solar cell transport

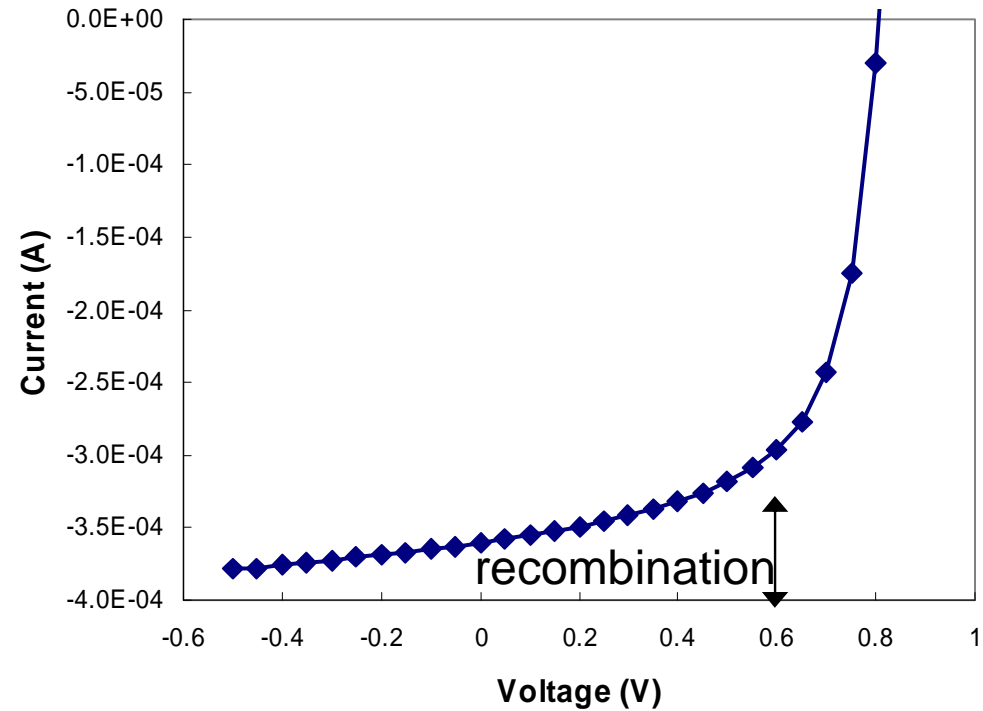
- Exciton migrates to junction in ~ 10 fs
 - Exciton split by band offsets
- Why do the electron and hole separate?
 - Can they overcome the Coulomb force?
- What controls the charge collection?
 - Are there other recombination mechanisms beside the exciton?



Solar cells from UCSB

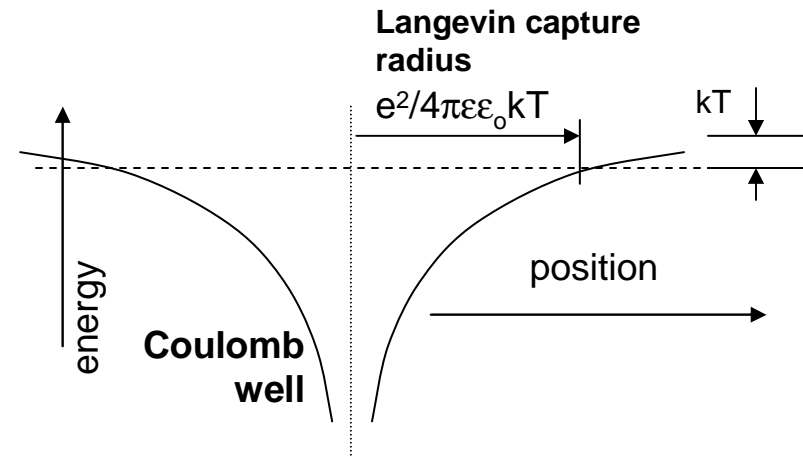
■ PCDTBT:PC₇₀BM

- ~5% efficiency
- V_{OC} ~0.84 eV
- FF ~ 0.6
- I_{SC} ~10 mA/cm²



Langevin / Onsager mechanism

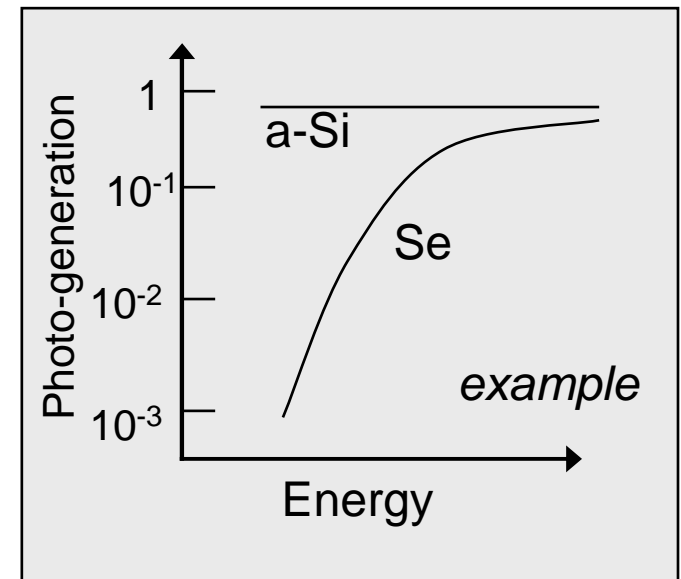
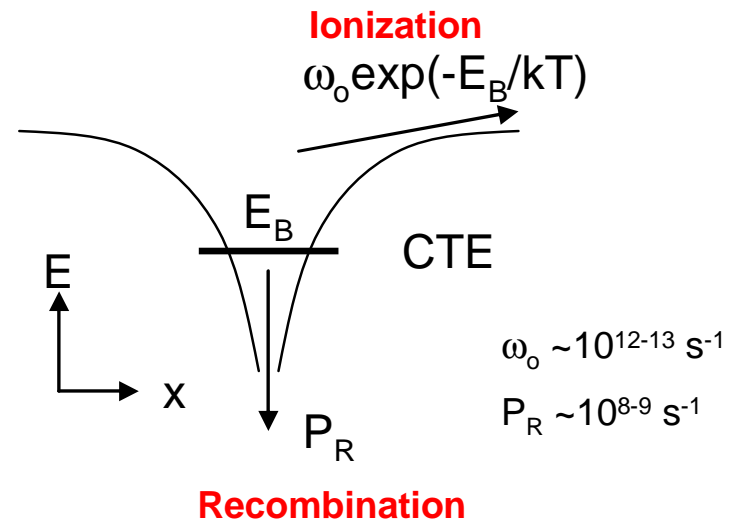
- Applies to low mobility materials
 - diffusion
- Carrier is captured when Coulomb energy $> kT$
 - Capture radius > 10 nm
- Electron and hole start close together and should never escape
- What is wrong?



When Langevin / Onsager does not apply

- The electron and hole form a bound state – the charge transfer exciton (CTE)
 - Ionization or recombination depends on exciton energy
- Recombination competes with ionization
 - Ionization dominates when

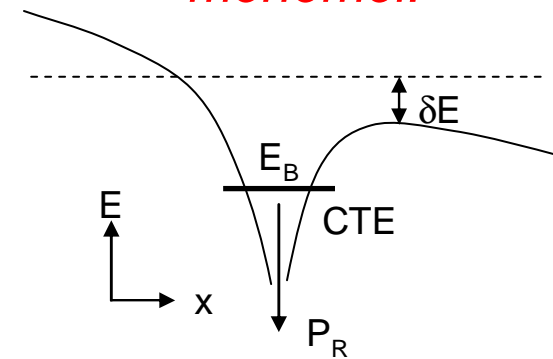
$$E_B < kT \ln(\omega_o/P_R) \sim 0.25 \text{ eV}$$
- E_B is reduced by
 - Separation of electron and hole
 - Much smaller polaron effect
 - Larger radius electron and hole states
- E_B can easily be $< 0.25 \text{ eV}$
 - Ionization dominates; problem solved!



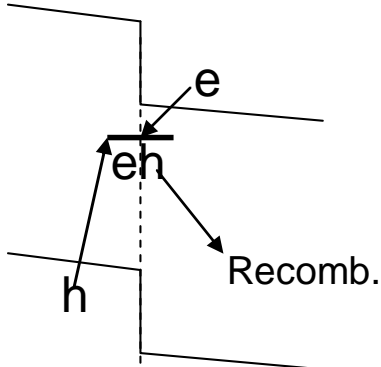
Possible recombination mechanisms

- Field ionization of geminate CTE
- Non-geminate CTE
- Auger recombination
 - Hole recombines with photo-excited exciton
 - Exciton lifetime is too small
- Interface defects
 - electron and hole trap at interface defect states.

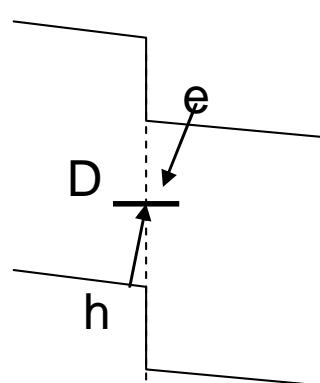
Geminate CTE
monomol.



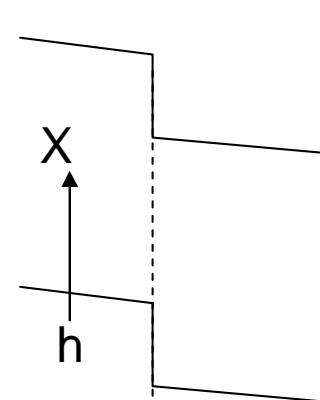
n.g. CTE
bimolecular



Interface defects
monomolecular

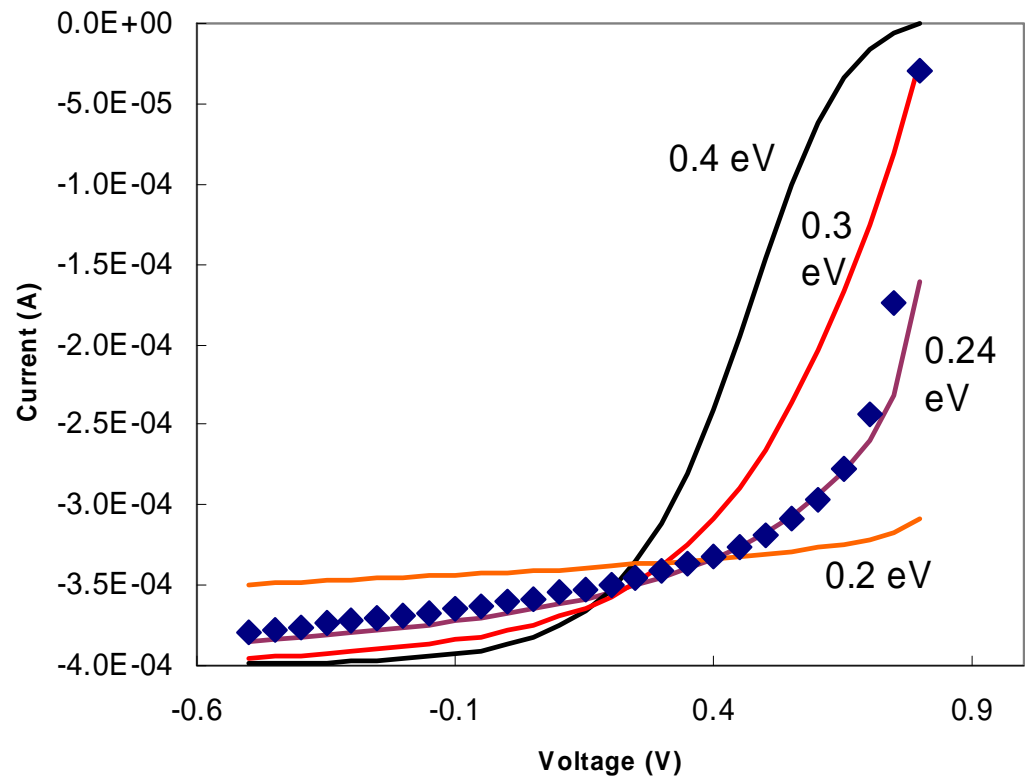
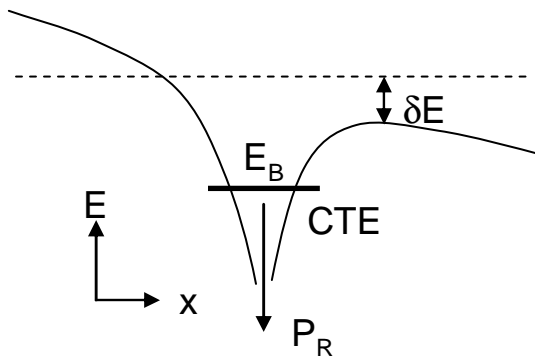


Auger
bimol.



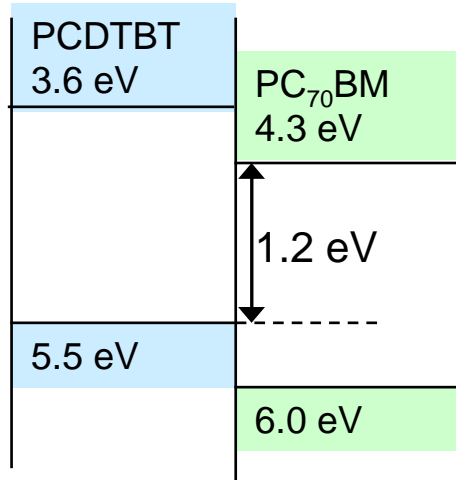
Field ionization of geminate CTE

- Only works if the binding energy is just right and the field is high
 - Seems an unlikely coincidence

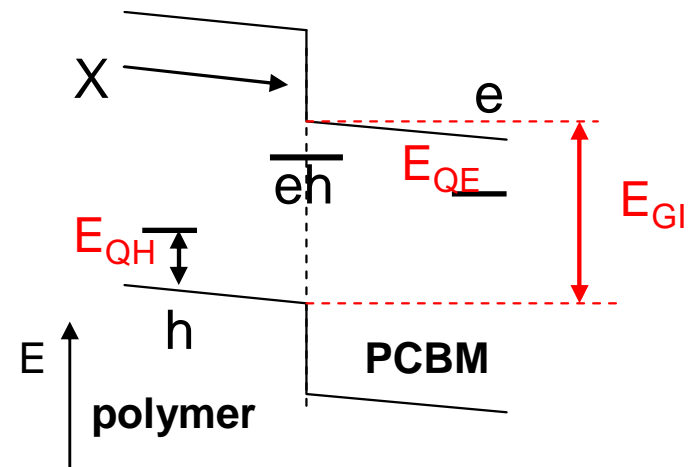
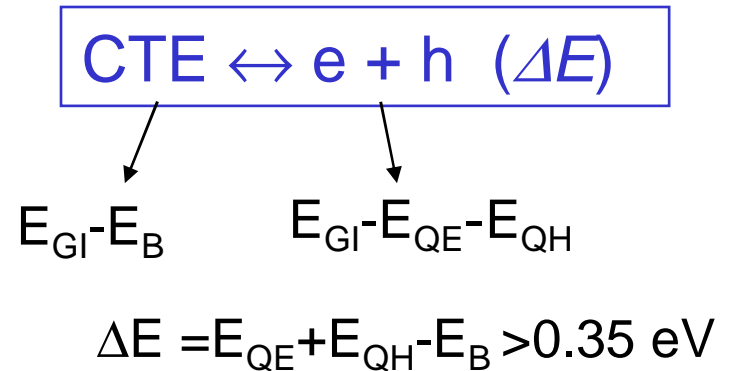


Non-geminate CTE

- CTE interchanges with electron and hole
 - Dominant state depends on energies
- Electron and hole quasi-Fermi energy, $E_{QE,H}$
 - $E_{QH} = kT \ln [N_V kT / N_G] \sim 12 kT = 0.3 \text{ eV}$
- **Non-geminate CTE recombination is suppressed by $\exp[-\Delta E/kT] \sim 10^{-6}$**



$$V_{OC} + E_{QE} + E_{QH} \sim 1.4 \text{ eV}$$

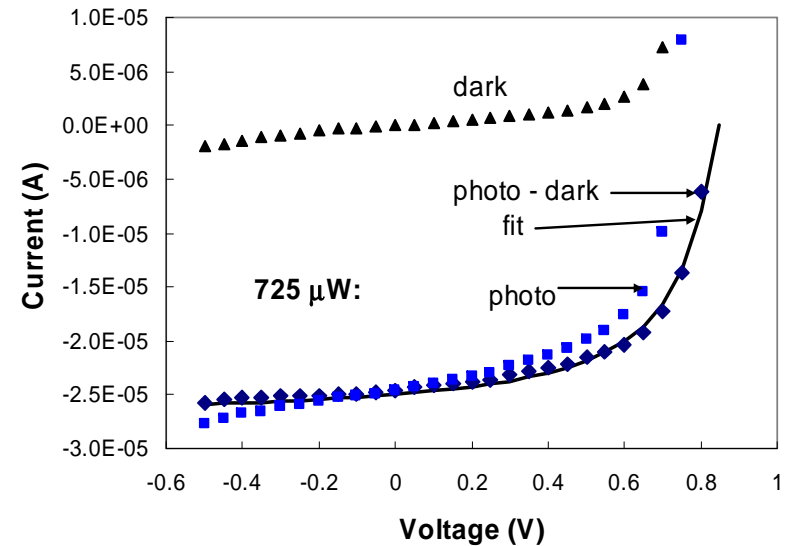
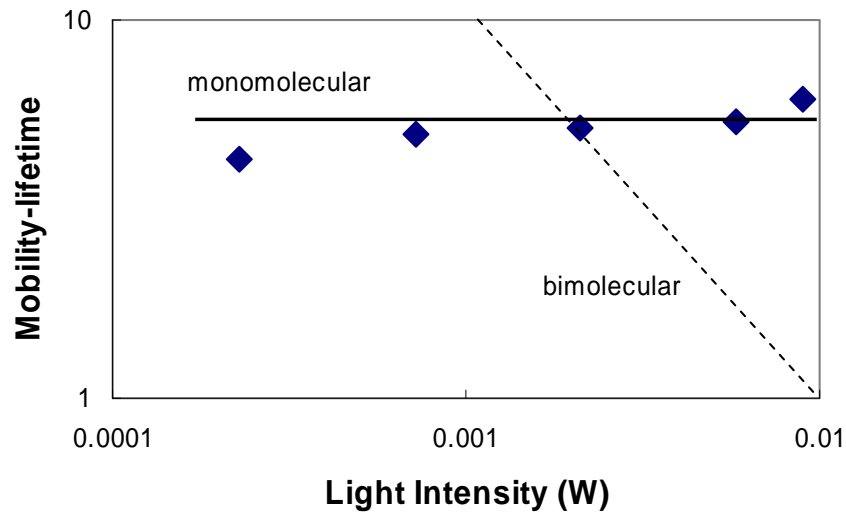
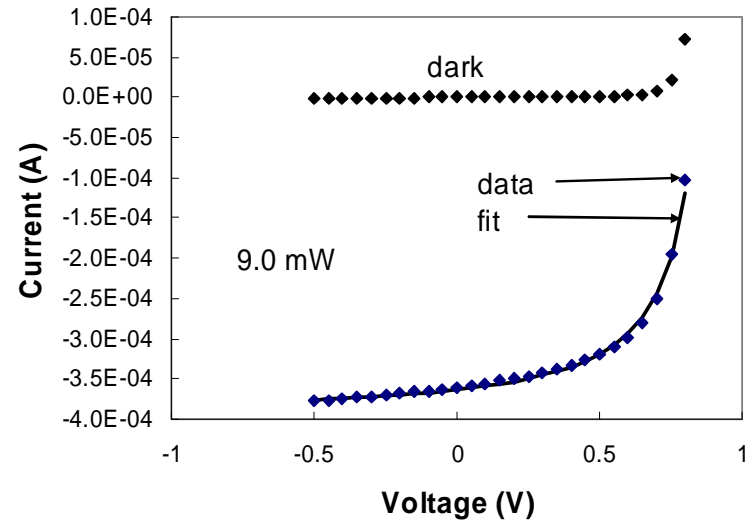


Interface states - charge collection

- Good fit to charge collection model

$$\frac{Q}{Q_0} = \frac{\mu\tau(V + V_S)}{d^2} \left[1 - \exp\left(-\frac{d^2}{\mu\tau(V + V_S)}\right) \right]$$

- Recombination almost independent of light intensity – monomolecular
- $\mu\tau/d^2 \sim 5$; $\mu\tau \sim 3 \cdot 10^{-10} \text{ cm}^2/\text{V}$



More evidence for interface traps

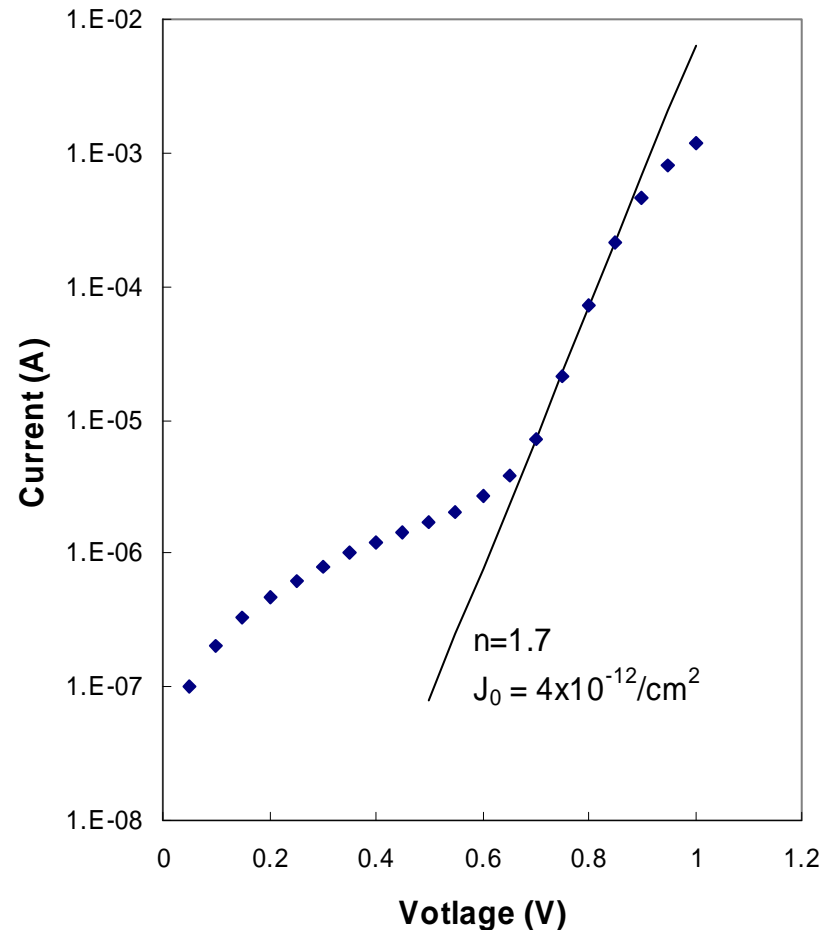
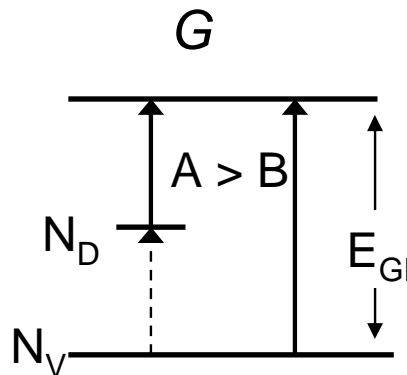
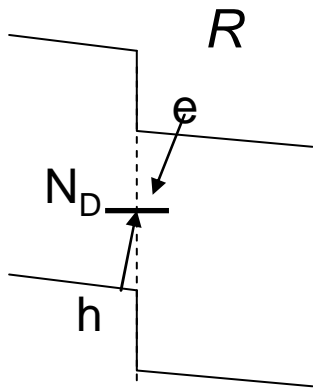
- Dark forward bias

$$J = J_0 [\exp(eV/nkT) - 1]; n \sim 1.7$$

- Ideality factor suggests generation-recombination (GR) mechanism

- GR should dominate when

- $N_D \exp(-E_{GI}/2kT) > N_V \exp(-E_{GI}/kT)$
- $N_D > 10^6 \text{ cm}^{-2} \text{ eV}^{-1}$
- Only very good interfaces have fewer states.



Trap density

- From charge collection
 - $\mu\tau \sim 10^{-10} - 10^{-9} \text{ cm}^2/\text{V}$
 - For a typical trap; $\mu\tau N_D \sim 10^{7-8}$
 - N_D (bulk) $\sim 10^{16-18} \text{ cm}^{-3}$
 - N_D (surface) $\sim 10^{10-12} \text{ cm}^{-2}$
- From forward bias
 - $J_0 = A e N_D kT \omega_0 \exp(-E_{GI}/1.7kT)$
 - N_D (surface) $\sim 10^{8-10} \text{ cm}^{-2}$
- Reasonably consistent estimates
(but very approximate)

$$\mu\tau N_D = c/\sigma$$

σ ; capture cross section

Summary

Recombination at interface traps may be the dominant mechanism

- Interface defects are expected, particularly in a disordered material
- Good fit to the charge collection model
 - Reasonable defect density
- Consistent with forward diode characteristics
- Field ionization of CTE has problems