Solar Cells: Is Being Thin Better? (It's certainly more fun.)

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The Leading Solar Cell Technologies

- I. Single (and Multi-) Crystal Silicon: 85% of current market
- II. II-VI Based Devices: CdTe
- **III. Chalcopyrite Devices: CIGS**
- **IV. Amorphous Silicon Solar Cells**

≻ Thin Films

Schematic of Atomic Networks

Crystalline Silicon

Polycrystalline CdTe or Cu(InGa)Se₂

Hydrogenated Amorphous Silicon













Growth in Thin Film PV Market Share



Source: IC Insights, June 2009

OUTLINE

Basic Semiconductor Properties

- Defects and Carrier Densities
- Effects of Illumination
- Carrier Transport and Recombination

Basics of Photovoltaic Devices

- Basic Performance Parameters
- Maximum Efficiency of Single Junction Cells

Defects: Carrier Trapping vs. Recombination

Measuring Defect Distributions in Thin Film Cells

- Transient Photocapacitance Spectroscopy
- Measured Defect Distributions vs. Cell Performance



Electronic Structure of Semiconductors

Silicon Band Structure

GaAs Band Structure



Electronic Structure of Semiconductors



From M.L. Cohen and J.R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors*, 2nd ed. (Springer, Berlin, 1988).

Electronic Structure of Semiconductors



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The Density of Electron and Hole Carriers



For intrinsic semiconductors:

$$\mathbf{n} = \mathbf{p} \equiv \mathbf{n}_{\mathrm{i}} \Longrightarrow \qquad E_F = E_F^i = \left(E_C + E_V\right)/2 + \left(k_B T/2\right) \ln\left(N_V/N_C\right)$$

Fermi Level Position in Doped Semiconductors



Fermi Level Position in Doped Semiconductors



Shallow donors added: $n \gg p \Rightarrow n = N_D^+ + p \approx N_D^+$ $n \cong N_C(T) \exp[-(E_C - E_F)/k_B T] = N_D^+$

However, we still have $np = n_i^2 = (N_C N_V) \exp[E_g/(k_B T)]$ (THE LAW OF MASS ACTION: $n + p \leftrightarrow \Box$) January 27, 2010 Oregon State

Fermi Level Position in Doped Semiconductors



Shallow acceptors added: $p >> n \Rightarrow p = N_A^- + n \approx N_A^-$

Again, we have $np = n_i^2 = (N_C N_V) \exp[E_g/(k_B T)]$

Effects of Illumination: Quasi-Fermi Levels

Effects of Illumination: Excess Carriers

In thermal equilibrium $np = n_i^2$. When $np > n_i^2$ we are *not* in thermal equilibrium and we say that we have "excess carriers"

The two most common ways to have excess carriers:

- 1. Carrier injection from a junction
- 2. Addition of carriers by photo-generation

In that case $n_0 \rightarrow n_0 + \Delta n$ and $p_0 \rightarrow p_0 + \Delta p$ with $\Delta n = \Delta p$

The "generation rate" **G** refers to the increase in the density of carriers per unit time (units of $cm^{-3}s^{-1}$)

The inverse process, **R**, the pair-wise annihilation of electrons with holes, is called "recombination" (also has units of $cm^{-3}s^{-1}$)

Note: In thermal equilibrium $G = G_{th}$ and is exactly balanced by R

Defining the Quasi-Fermi Levels

When there are excess carriers, the occupation of levels in the conduction and valence bands is no longer determined by $E_{F_{i}}$

However, if we know *n* and *p* we can always express them in equations similar to those for the carriers in equilibrium:

$$n = N_C(T) \exp\left[-(E_C - E_{Fn})/k_BT\right]$$
$$p = N_V(t) \exp\left[-(E_{Fp} - E_V)/k_BT\right]$$

These equations thus define E_{Fn} and E_{Fp} which are called the "quasi-Fermi levels" for electrons and holes, respectively



Importance of Quasi-Fermi Levels

At first glance it may seem that E_{Fn} and E_{Fp} are just an alternate way to express *n* and *p* and otherwise have no particular utility.

However, these energies play an important role in solar cell analysis:

I. The electron and hole current densities at each position r can be expressed as:

$$\mathbf{J}_{n}(\mathbf{r}) = -ne\mathbf{v} = n\mu_{n}\nabla_{\mathbf{r}}E_{Fn} \qquad \mathbf{J}_{p}(\mathbf{r}) = +pe\mathbf{v} = p\mu_{p}\nabla_{\mathbf{r}}E_{Fp}$$

II. The quasi-Fermi levels are also often taken as a first order approximation to the "demarcation levels" of the deep defects which determine the role of those defects in recombination.

III. The voltage of a cell under illumination is directly related to these quasi-Fermi levels.

Carrier Transport

- 1. Drift Currents
- 2. Diffusion Currents
- 3. Carrier Mobilities

1. Drift Currents: How Electrons and Holes Respond to an Electric Field

Simple Case: Constant Field & and Carrier densities

In general:

$$\mathbf{J}_{n} = -ne\mathbf{v}_{n} = -ne(\boldsymbol{\mu}_{n}\boldsymbol{\mathcal{E}})$$

"electron mobility" μ_n

In such a case $E_{Fn} \& E_{Fp} \\ ext{are parallel to } E_C \\ ext{and } E_V, \\ respectively. \\ Similarly: \\ \end{tabular}$

 $J_p = pev_p = pe(\mu_p \mathcal{E})$ which defines the "hole mobility" μ_p



2. Diffusion Currents: How Electrons and Holes Move If There is a Density Gradient



Key Parameter for Transport: Carrier Mobility

Total electron current is given by the sum of the drift and diffusion currents: $\mathbf{J}_n = qn\mu_n \mathbf{\mathcal{E}} + qD_n \nabla n(\mathbf{r})$

Similarly, the total hole current is: $\mathbf{J}_p = qp\mu_p \mathbf{\mathcal{E}} - qD_p \nabla p(\mathbf{r})$

Further, the diffusivity *D* can be expressed in terms of the mobility μ by the Einstein relation: $D_{n,p} = (k_B T/q) \mu_{n,p}$

The mobility itself can be expressed as: $\mu_{n,p} = q\tau_{n,p}/m_{n,p}$ that is, it depends on the carrier effective mass and the carrier scattering time, τ .

Carriers scatter due to impurities or other defects, and also due to thermal motion of the lattice (phonons). Usually,

$$\frac{1}{\tau} = \frac{1}{\tau_{impurity}} + \frac{1}{\tau_{thermal}}$$

The Ideal Solar Cell



Ideally, every electron-hole pair generated by an absorbed photon will contribute to current around the circuit under zero load.

 \Rightarrow Current density through the cell, $J_{SC} = q \times (absorbed photon flux)$

Carrier Generation by Light of Different Wavelengths



The Quantum Efficiency (QE) in Ideal Case

Each photon whose energy exceeds the semiconductor bandgap produces an electron-hole pair which gets collected up to some E_{max}



Spectral Response of Carrier Generation



One divides the "Irradience" by the photon energy to obtain the photon flux spectrum

If each photon with an energy above the bandgap produces an electron hole pair we obtain the maximum cell current vs. E_g

Solar spectrum fits a 5960K Planck black body spectrum except for absorption bands



Short Circuit Currents: Ideal Case and Best Realized



The Ideal Solar Cell



What determines the voltage generated across a solar cell under a high impedance load (when little or no current is flowing through the external circuit?)

Fermi Level Position in Thermal Equilibrium



Recall that regardless of position of Fermi level in the gap the **product** of *n* and *p* will be **constant** for a given semiconductor in thermal equilibium at temperature T the "**law of mass action**":

$$n \times p = n_i^2 = N_C N_V exp(-E_g/k_B T)$$

Quasi-Fermi Level Positions under Illumination



Under illumination: $n \times p = n_i^2 exp[(E_{Fn} - E_{Fp})/k_BT] = n_i^2 exp[\Delta \mu/k_BT]$

Electrons reach quasi-equilibrium within their own populations via interactions with phonons fairly quickly ($\tau_{el-ph} \sim picoseconds$).

Equilibration with the hole population takes much longer because it occurs via recombination events ($\tau_R \sim$ nanoseconds to milliseconds)

Quasi-Fermi Level Positions under Illumination

 $\Delta\mu$ thus represents the difference in chemical potentials between the electron and hole carrier populations

The cell voltage is thus given by $\Delta \mu/q$ under open circuit conditions

The value of $\Delta\mu$ itself will be determined by the balance of carrier generation and carrier recombination in steady-state



Some Types of Recombination Processes



Radiative Recombination: Detailed Balance

Solar Cell in the dark surrounded by ambient at T = 300K

Light absorbed from ambient:

$$\int_{0}^{\infty} \alpha(h\nu) \Phi_{BB}(h\nu, 300K) d\nu$$

$$\approx \int_{E_g}^{\infty} \Phi_{BB}(h\nu, 300K) d\nu$$

By detailed balance this must be exactly balanced by the light emitted from the cell:

$$= \int_{V} \beta_{rad} pn d^{3}r \approx \langle \beta_{rad} \rangle V pn = \langle \beta_{rad} \rangle V n_{i}^{2}$$





where ζ takes into account differences in the optical constants (e.g. reflectivity) between blackbody spectra at 300K and 5960K

Ideal Case Solar Cell (open circuit) Voltage

Photons absorbed with sunlight

Photons absorbed ambient

Radiative Recombination Rate in Sunlight Radiative Recombination Rate in Ambient

$$\Rightarrow 1 + [\text{Geometric Factor}] \times \zeta \frac{\int_{E_g}^{\infty} \Phi_{BB}(hv, 5960K) dv}{\int_{E_g}^{\infty} \Phi_{BB}(hv, 300K) dv}$$

$$=\frac{\langle \beta_{rad} \rangle V pn}{\langle \beta_{rad} \rangle V n_i^2} = \frac{n_i^2 \exp\left[(E_F^n - E_F^p) / k_B T\right]}{n_i^2} = \exp\left(\frac{\Delta \mu}{k_B T}\right)$$

But $\Delta \mu / k_B T = q V_{OC}$. Thus we obtain V_{OC} vs. E_g.

Ideal Case Solar Cell (open circuit) Voltage



Maximum Output Power of Solar Cell

The power delivered to an external load depends on the <u>product</u> of the current and voltage. This is a maximum at (V_m, J_m) or when:



Maximum Possible Efficiency vs. Band Gap

These predicted maximum efficiencies for single junction solar cell devices are often referred to as the "Shockley-Queisser limit".*

Note that the efficiency under concentration exceeds that with 1 sun illumination

WHY?

The current scales with the intensity, but the carrier density (and hence the voltage) goes up too

* W. Shockley and H. Queisser, J. Appl. Phys. **32**, 510-519 (1961).



Ideal solar-cell efficiency at 300K for 1 sun and for a 1000-sun concentration (dashed) January 27, 2010 Oregon State

Summary of Ideal Solar Cell Analysis

- Shockley-Queisser Limit Assumes
- >Only radiative recombination of carriers
- ≻Perfect collection of all electron-hole pairs generated by light
- >All the photons with energies > E_g are absorbed

Loss Processes that remain

- Radiative recombination
- Infrared transparency (low energy photons not absorbed)
- Thermalization (Excess photon energy above gap is lost)
Real Cells: Dominant Recombination Processes



Radiative recombination may only dominate in the purest GaAs based devices Auger and surface recombination dominate in good crystalline silicon devices Defect mediated recombination dominates in a-Si:H, CdTe, and CIGS devices

One Important Length Scale: Diffusion Length

The *diffusion length* indicates how far a carrier (electron or hole) can move from where it was generated before it recombines (in the absence of an electric field).

Mathematically:
$$L_D = \sqrt{D_{n(p)}\tau_{n(p)}}$$
 where $\tau_{n(p)}$ is the recombination
lifetime for electrons (holes)

Approximate minority carrier diffusion lengths:

Crystalline Si	CIGS, CdTe	Amorphous Si
$\tau_n \sim 100 \ \mu s$	$\tau_n \sim 100 ns$	$\tau_{\rm p} \le 1$ ns
$L_D \approx 300 \ \mu m$	$L_{\rm D} \approx 0.3 \ \mu {\rm m}$	$L_{\rm D} < 0.1 \mu{\rm m}$

Some Important Remaining Questions

- 1. How do we construct contacts so that one of them will connect with the hole carrier population only (repelling electrons) and the other will connect with the electron carrier population only (repelling the holes)?
- 2. In the ideal solar cell carrier diffusion will bring the carriers to the contacts before they can recombine. But, when diffusivities are low, carrier collection needs an electric field.

How can we do this without an external power source?

In both cases the solution is to utilize pn junctions.

The Semiconducting pn Junction

Consider joining together a p-type and an n-type semiconductor



Electrons move from higher E_F to lower E_F material

The resulting current can't last forever!

Ultimately, an electric dipole layer forms whose potential exactly cancels out the difference between the two Fermi energies

The pn Junction

A dipole layer forms as a "depletion region" near pn junction: The potential difference due to this is called the "built-in potential" V_{bi}





Using pn Junctions for Carrier Specific Contacts



Here the majority of the absorber shown contains very little internal electric field.

It thus relies on long diffusion lengths to collect photo-carriers

Structure close to that used for **crystalline Si** solar cells

Other Types of Solar Cell Device Structures





The Schottky device is not favored for photovoltaics due to its lower voltages January 27, 2010 Oregon State

Third Important Length: Absorption Length

Absorption Spectra for Various Semiconductors



The low absorption coefficient for c-Si over the solar spectrum compared to the other (direct gap) semiconductors requires a much thicker active layer in crystalline silicon based PV devices



Jianhua Zhao, Aihua Wang, and Martin A. Green, Prog. Photovoltaics **7**, 471 (2000),

Ingrid Repins, Miguel A. Contreras, et al, Prog. Photovoltaics: Res. Appl. **16**, 235 (2008).



Hydrogenated Amorphous Silicon Cells (a-Si:H)



- Intrinsic absorber
- Highest Efficiency ~10% for the structure shown
- Manufactured into tandem or triple junction structures to improve efficiencies
- Thin: Even the triple cell is only roughly ~0.7 µm in total thickness

Current Best a-Si:H Cells Use Triple Junctions



Such a "monolithic" stack must be designed so that the current matches in each cell.

The voltages add in series.

The highest stabilized efficiency to date is 13.0%

Modules with this structure are now being produced and sold by United Solar.



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Quantum Efficiency of a Triple Junction Cell

Analysis of the performance of a a-Si:H/a-SiGe:H/a-SiGe:H triple junction device showing the contribution of the component cells



Short-circuit current Ja	SC
[mA/cm ²]	50

	AM1.5	Xenon
Тор	6.87	7.19
Middle	7.84	7.98
Bottom	8.62	7.34
Total	23.33	22.51

W. Wang, H. Povolny, W. Du, X. Liao, and X. Deng, 29th IEEE PVSC (2002)

Leading Solar Module Technologies

Absorber Material	Best Cell Efficiency	Module Typical	Cost (Market Share)
Crystal Si	24.7%	14-15%	\$3/W _p (85%)
Cu(InGa)Se ₂	20.0%	11-12%	? (<2%)
CdTe	16.5%	11-13%	\$0.8/W _p (8%)
a-Si:H Triple	13%	8-9%	\$1.70/W _p (5%)

Physics of Impurity Mediated Recombination: Carrier Recombination vs. Carrier "Trapping"







Important Distinction between Trapping and Recombination

Carriers in trapped in shallow defects are likely to be thermally reemitted and ultimately be collected. These affect carrier mobilities, but do not greatly impact device performance.





Carriers caught by deep states remain there long enough that recombination is much more likely to be their ultimate fate.

However, this distinction between "shallower trapping" states and "deeper recombination" centers depends on the light intensity.

Distinguishing Traps from Recombination Centers

Occupancy dominated by electron emission so that states are mostly empty Carrier capture and optical transitions dominate: leads to a *partial occupation* Occupancy dominated by hole emission so that states are mostly full



An electron lying in a state right at D_n is equally likely to be thermally excited into the conduction band and to capture a free hole. Thus it will have an equal role as a trap vs. a recombination center.

Electrons lying in states above D_n are exponentially more likely to be thermally re-emitted (by 100X for $D_n + 0.1eV$ at 300K) \Rightarrow *trap*

For electrons lying in states below D_n the kinetic process of capturing a free hole is much more likely \Rightarrow *recombination*

Similarly for holes lying in states below and above D_{January 27,2010} Oregon State

Electron Density of States: Role of Defects

Perfect Crystal: No States in Band Gap



Defects in Crystalline Silicon



Crystalline Silicon Native Defects in c-Si:

Vacancy V_{Si} and Self Interstitial Si_i

Both of these produce a host of defect levels in the gap; however, neither is present at very high concentrations at room T unless they are complexed with an impurity.

Therefore, the relevant defects that can degrade cell performance are due to impurities in the silicon lattice

Impact of Impurities on c-Si Cell Performance

Transition metal impurities at levels of ppb can have an enormous negative impact on silicon cell performance



J. Davis Jr., *et al.* IEEE Trans. Electron. Devices **Ed-27**, 677-687 (1980)

Crystal Structure and Native Defects



Types of Native Defects: Antisites: Cd_{Te} (Te_{Cd}) Vacancies: V_{Te}, V_{Cd} Interstitials: Cd_i (Te_i)



Calculated, from Wei and Zhang, Phys.Rev.B **66**,155211 (2002)

Crystal Structure and Native Defects



E_c

Ε.,



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 $V_{Cu}(-/0)$

Possible Distribution of Energy Levels in a Disordered Semiconductor



Possible Distribution of Energy Levels in a Disordered Semiconductor

(eV)

ENERGY

Deviation from pure periodic symmetry leads to band-tailing

Bandtailing affects carrier mobilities and doping efficiencies

Point defect gap states are broadened into gaussian defect bands

These usually dominate carrier recombination and affect bandbending near junctions

Concept of "band gap" replaced by "mobility gap" and/or "optical gap"



<u>All of these</u> are important for understanding electronic properties for device applications <u>as well as</u> carrier densities, their mobilities, defect capture cross sections, etc.

More Complete Set of Equations for Device Analysis

We previously discussed the transport equations:

$$\mathbf{J}_n = qn\mu_n \mathbf{\mathcal{E}} + qD_n \nabla n(\mathbf{r}) \qquad \qquad \mathbf{J}_p = qp\mu_p \mathbf{\mathcal{E}} - qD_p \nabla p(\mathbf{r})$$

We also discussed carrier generation and recombination:

$$\frac{\partial n(\mathbf{r},t)}{\partial t} = G_n - R_n \quad (*) \qquad \qquad \frac{\partial p(\mathbf{r},t)}{\partial t} = G_p - R_p \quad (**)$$

However, a second way carriers can increase in a particular region is if they flow into it from surrounding regions. This is governed by the "**continuity equations**": $\partial n/\partial t = \nabla \cdot J_n$ and $\partial p/\partial t = -\nabla \cdot J_p$

Adding these terms to the right hand sides of (*) and (**), and then using the expressions for J_n and J_p above we obtain for the "1D" case:

$$\frac{\partial n}{\partial t} = n \mu_n \frac{\partial \mathcal{E}}{\partial x} + \mu_n \mathcal{E} \frac{\partial n}{\partial x} + D_n \frac{\partial^2 n}{\partial x^2} + G_n - \mathcal{R}_n = 0 \quad \text{in steady-state, and} \\ \frac{\partial p}{\partial t} = -p \mu_p \frac{\partial \mathcal{E}}{\partial x} - \mu_p \mathcal{E} \frac{\partial p}{\partial x} + D_p \frac{\partial^2 p}{\partial x^2} + G_p - \mathcal{R}_p = 0 \quad \text{in steady-state, and} \\ \text{Key Quantities} \quad \text{in steady-state.} \end{cases}$$

Physical Parameters Needed for Cell Modeling

Example from SCAPS modeling program: see M. Burgelman, et al., Thin Solid Films 361, pp. 527-532 (2000)

Cell Parameters Defect parameters CIGS Name of layer : LAYER 1 Defect 1 of CIGS donor 1,000 thickness (µm) defect type 1,200 bandgap (eV) capture cross section electrons (cm²) 1.00E-13 electron affinity (eV) 4.500 capture cross section holes (cm²) 1.00E-13 10,000 dielectric permittivity (relative) 🛢 gauß energetic distribution CB effective density of states (1/cm^3) 2.000E+18 2 000E+18 VB effective density of states (1/cm^3) energy level (from top of VB) (eV) 0.95 electron thermal velocity (cm/s) 1.000E+7 characteristic energy (eV) 0.10 1.000E+7 hole thermal velocity (cm/s) Constant spatial distribution electron mobility (cm²/Vs) 5.000E+1 characteristic length (µm) 0.10 hole mobility (cm²/Vs) 2.000E+1 shallow donor density (1/cm^3) 0 000E+0 concentration left (1/ cm^3 eV) 1.00E+15 shallow acceptor density (1/cm^3) 5.500E+15 1.00E+14 concentration right (1/ cm⁴3 eV)

Many of these quantities are poorly known and they vary in importance.

On the left, knowing the carrier mobilities is very important, and knowing almost all of the defect band parameters are important.

Characterization Methods

	Experimental Method	Quantities Deduced
•	Capacitance Voltage (C-V)	Carrier densities, profiles
•	Admittance Spectroscopy (AS)	Deep defect energies
•	Drive-level capacitance profiling (DLCP)	Carrier and defect profiles
•	Modulated photocurrent method (MPC)	Majority carrier traps
•	Electron Spin Resonance (ESR)	Deep defect densities, local environment
	Photo- and/or Electroluminescence (PL,EL)	Defect transition energies
•	Constant Photocurrent method (CPM) *	Sub-band-gap spectra: Bandtailing, defect bands
	Photo-thermal deflection spectroscopy (PDS) *	Same as above
	Transient photocurrent or time-of-flight TOF)	Carrier mobilities
	Time Resolved Photoluminescence (TRPL)	Defect levels, carrier lifetimes
•	Deep-level transient spectroscopy (DLTS)	Defect densities, thermal excitation energies, capture cross sections for carriers
•	Transient Photocapacitance spectroscopy (TPC)	Sub-band-gap spectra, Bandtailing, defect bands
	Photo-emission Methods (XPS, UPS) *	Band offsets at heterojunctions

• Methods Employed in Cohen lab

* Methods that <u>cannot</u> be applied directly to working devices January 27, 2010 Oregon State

Three Generations of Photovoltaic Technology

- 1. Single or multicrystal silicon or other semiconductor in a single junction device (typically a pn junction).
- 2. Thin semiconducting film on inexpensive substrates such as glass, metal foil, or plastic. Most successful materials include amorphous Si, CdTe, and the alloys of CuInSe₂
- 3. Advanced materials designs, such as nanostructured semiconducting materials, organics, etc. Such approaches still require significant basic research.

United Solar Roll-to-Roll a-Si:H Process



United Solar's 180MW/yr capacity accounted for ~ 1/3 of total a-Si:H based PV in 2008

Cost is now below \$2/W_p

Only 5% of the weight of modules deposited on glass



Nanosolar's Nanoparticle Ink Technology



Nanosolar combines a host of innovations to deliver a distinct overall cost reduction.

Nanosolar's New Berlin Factory



Completion and Inauguration September 2009

Designed to produce 640MW/yr !


First Solar CdTe Modules



1.2 GW Production capacity

Grid parity recently achieved: $(<\$1/W_p)$



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Some Acknowledgements

Research Area	Students Involved
Fundamental Properties	Jerry Gelatos (Applied Materials), Carol Michelson,
of a-Si:H	Tom Leen (HP), Fan Zhong, Daewon Kwon
a-Si:H/c-Si Interfaces	John Essick (Reed College)
a-Si,Ge:H Alloys	Thomas Unold (Helmholtz Institute Berlin),
	Arthur Chen, Kimon Palinginis
Cu(InGa)Se ₂ Materials	Jennifer Heath (Linfield College), JinWoo Lee (LG)
CIGS Alloys with Sulfur	Adam Halverson (NREL)
CIGS Alloys with Silver	Pete Erslev
Nanocrystalline Silicon	Peter Hugger
(Funding from NSF & DOE)	



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Thank You !

