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Institute of Fundamental Studies (IFS), Kandy

Workshop on

Current Status and Future Trends in Thin Film Solar PV Technology

28-29 June 2012

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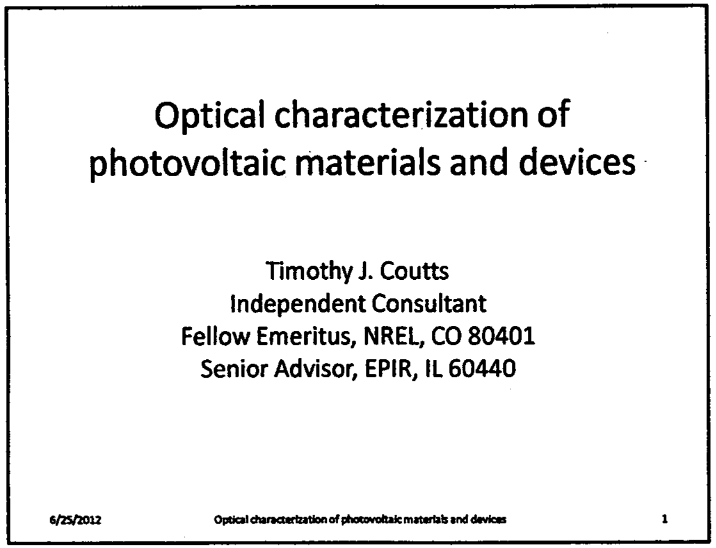
T1-1



Optical characterization of photovoltaic materials and devices

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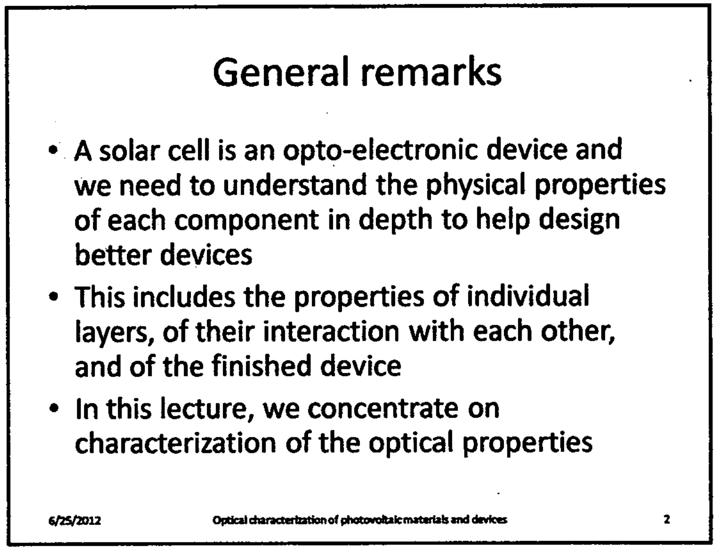
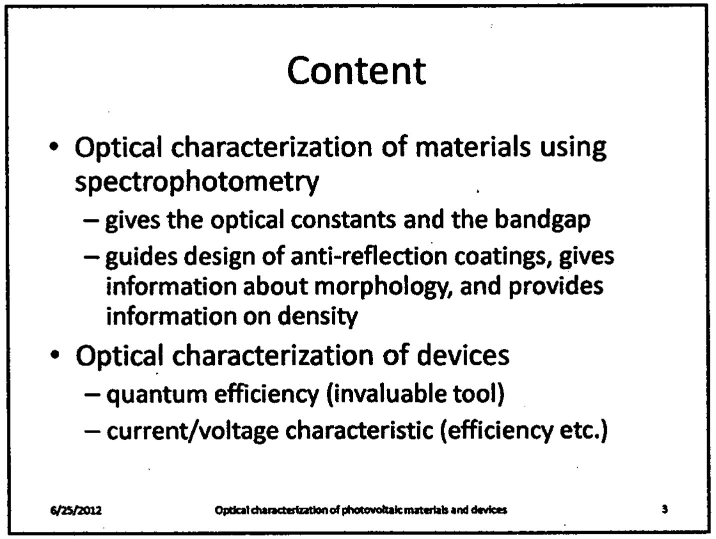


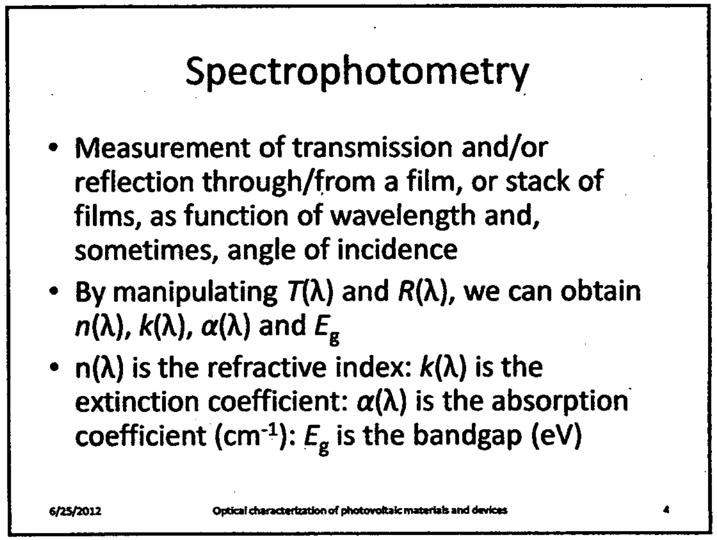
General remarks

- A solar cell is an opto-electronic device and we need to understand the physical properties of each component in depth to help design better devices
- This includes the properties of individual layers, of their interaction with each other, and of the finished device
- In this lecture, we concentrate on characterization of the optical properties



Content

- Optical characterization of materials using spectrophotometry
  - gives the optical constants and the bandgap
  - guides design of anti-reflection coatings, gives information about morphology, and provides information on density
- Optical characterization of devices
  - quantum efficiency (invaluable tool)
  - current/voltage characteristic (efficiency etc.)



Spectrophotometry

- Measurement of transmission and/or reflection through/from a film, or stack of films, as function of wavelength and, sometimes, angle of incidence
- By manipulating $T(\lambda)$ and $R(\lambda)$, we can obtain $n(\lambda)$, $k(\lambda)$, $\alpha(\lambda)$ and E_g
- $n(\lambda)$ is the refractive index: $k(\lambda)$ is the extinction coefficient: $\alpha(\lambda)$ is the absorption coefficient (cm^{-1}): E_g is the bandgap (eV)

T1-2

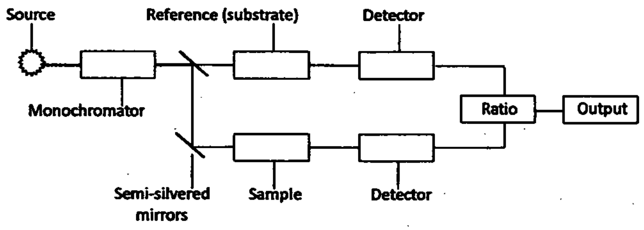
Warnings!

- Need a double-beam spectrophotometer to remove the effect of the substrate(glass)
- Need the film surface to be optically smooth to eliminate diffuse reflection
- Need the film to be free of pores to ensure near-bulk density
- Need the film to be spatially homogeneous
- Can use an integrating sphere spectrophotometer to account for diffuse reflection

Components for double-beam transmission spectrophotometry

- Consists of
  - a source of white light
  - a monochromator
  - holders for test sample and substrate
  - detectors
  - signal processing and output

Schematic of double-beam transmission spectrophotometry



http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/uvvisab3.htm

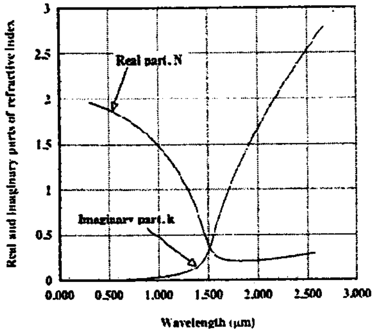
Data processing

- Using tabulated $T(\lambda)$ and $R(\lambda)$, we can obtain the optical constants, $n(\lambda)$ and $k(\lambda)$, provided we know the film thickness
- Commercial software packages available
- From k, we can find the absorption coefficient $\alpha(\lambda)$ from the relationship $\alpha = 4\pi k / \lambda$
- For a direct bandgap semiconductor, we can now obtain the bandgap by making a plot of $(\alpha h\nu)^2$ against $(h\nu)$

T/1-3

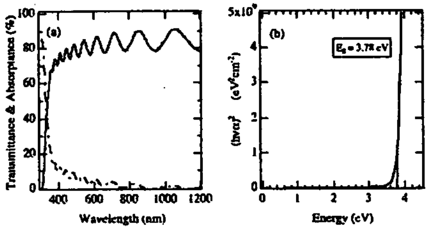
Optical constants of a TCO

- Obtained from *R*/*T* data
- Typical behavior for a TCO with high electron concentration
- TCOs are transparent in the visible but reflective in the infrared
- Typical thickness is about 500 nm
- *n*~2 in the visible



Transmittance output for a typical TCO

- Notice the interference fringes
- Can estimate film thickness from these
- Short wavelength cut-off gives E_g of TCO
- The second figure, shows the bandgap is about 4 eV



Summary

- Relatively simple optical measurements can give useful fundamental information
- Some caution must be exercised in interpretation of the data
- There are many other powerful optical techniques such as ellipsometry, and modulated spectroscopies

Quantum efficiency (i)

- QE defined as the ratio of the number of electron/hole pairs generated per unit time, divided by the photon flux
- It is a function of wavelength
- The light-generated current is given by

$$J_g(\lambda) = eN_0(\lambda)\,QE(\lambda)$$

- This does not necessarily equal the collected current
- $N_0(\lambda)$ is the flux ($cm^{-2}\ s^{-1}$): *e* is the electronic charge (coulombs): and $QE(\lambda)$ is the incremental quantum efficiency

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Quantum efficiency (ii)

- The total light-generated current may be obtained by integrating the incremental current over all wavelengths of the reference spectrum
- Accurate measurement of the QE is central to measuring the current/voltage characteristics and the efficiency

Quantum efficiency (iii)

- Assume a solar cell consists of an n-emitter on a p-base with the space charge (field) region between them
- Long wavelengths are absorbed in the base
- Excess minority electrons generated in the base must diffuse to the space charge to avoid recombination in the quasi-neutral base

Quantum efficiency (iv)

- Short wavelengths are absorbed in the emitter
- Some of the excess excess minority holes (if the emitter is active) recombine at the surface
- Some recombine in the quasi-neutral bulk of the n-emitter
- To be collected, the excess minority holes must diffuse to the space charge

Quantum efficiency (v)

Emitter current

$$J_g(\lambda) = \frac{e\alpha N_0(\lambda)\,L_p^2 \exp(-\alpha(\lambda)d)}{\left(1-\alpha(\lambda)^2 L_p^2\right)}\left(\frac{1}{L_p}-\alpha(\lambda)\right)+\ldots\ldots$$

$$\cdots\frac{e\alpha N_0(\lambda)\,L_n^2}{\left(1-\alpha(\lambda)^2 L_n^2\right)}\left[\frac{1}{L_n}\left(\frac{\left(s\cosh\left(\frac{d}{L_n}\right)+\frac{D_n}{L_n}\sinh\left(\frac{d}{L_n}\right)\right)\exp(-\alpha(\lambda)d)-s-\alpha(\lambda)D_n}{\frac{D_n}{L_n}\cosh\left(\frac{d}{L_n}\right)+s\sinh\left(\frac{d}{L_n}\right)}\right)-\alpha(\lambda)\exp(-\alpha(\lambda)d)\right]$$

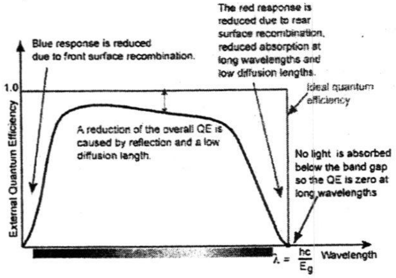
Base current

- This is the equation shown in an earlier lecture and it is equivalent to that shown two slides ago
- It does not include a term for current generated in the space charge region
- In general the variables are functions of temperature and may also be functions of voltage, depending on the nature of the junction

T-7

QE of silicon cells

- For a 2-sided Si solar cell, we can study the effect of the material parameters
- Long diffusion lengths in the base and the emitter ensure large QE
- Increased SRV in emitter reduces blue QE
- Increased SRV in base reduces red QE, for short diffusion lengths
- Much can be learned from the QE!

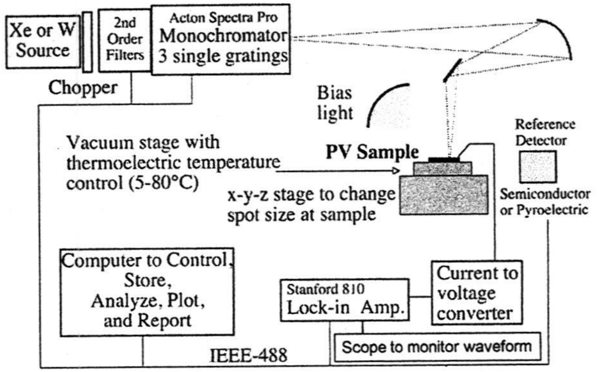


http://pveducation.org/pvcdrom/solar-cell-operation/quantum-efficiency

PV CDROM-Prepared by Christiana Honsberg and Stuart Bowden, formerly of University of Delaware now at Arizona State University

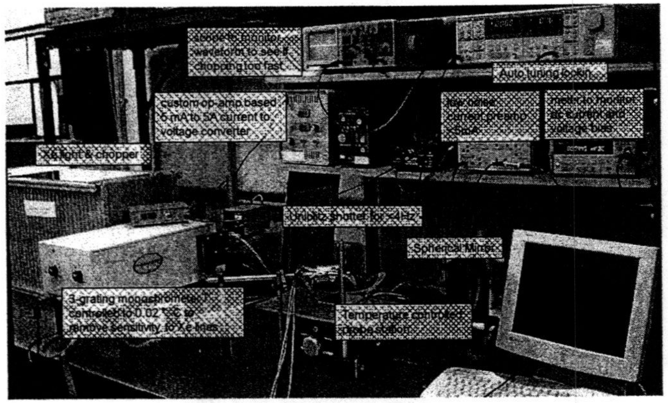
QE measurement

NREL Grating QE system 350 - 2800 nm



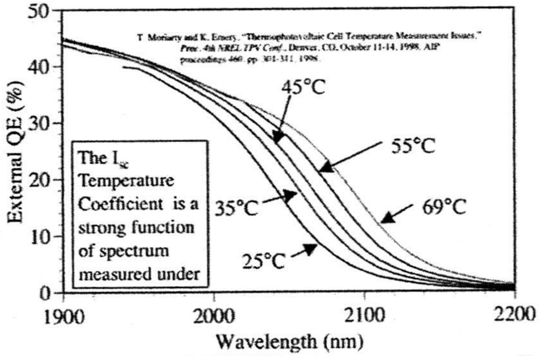
Thanks to Keith Emery of NREL Measurements and Characterization group for this figure.

QE measurement



Thanks to Keith Emery of NREL Measurements and Characterization group for this photograph.

QE *vs.* Temperature

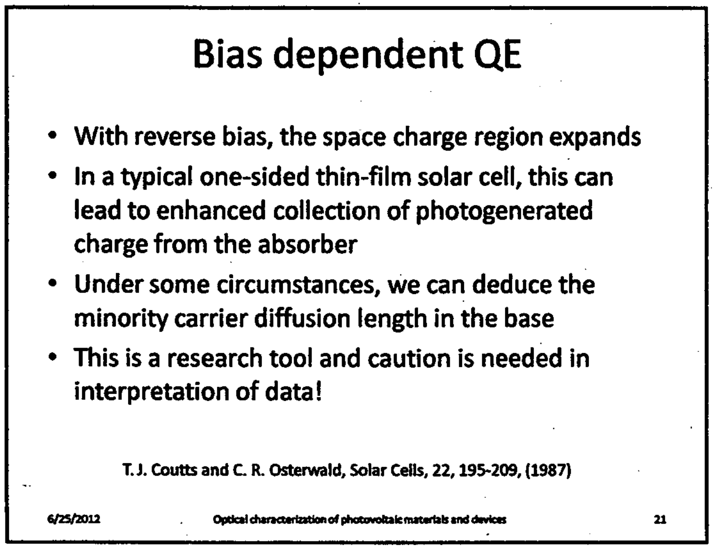


T. Moriarty and K. Emery, "Thermophotovoltaic Cell Temperature Measurement Issues," *Proc. 4th NREL TPV Conf.*, Denver, CO, October 11-14, 1998, AIP proceedings 460, pp. 301-311, 1998.

The I_{sc} Temperature Coefficient is a strong function of spectrum measured under

Thanks to Keith Emery of NREL Measurements and Characterization group for this figure

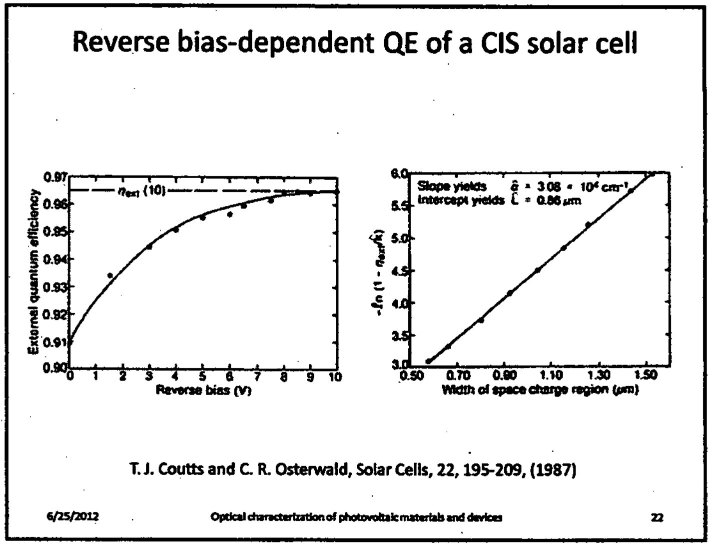
T/-8



Bias dependent QE

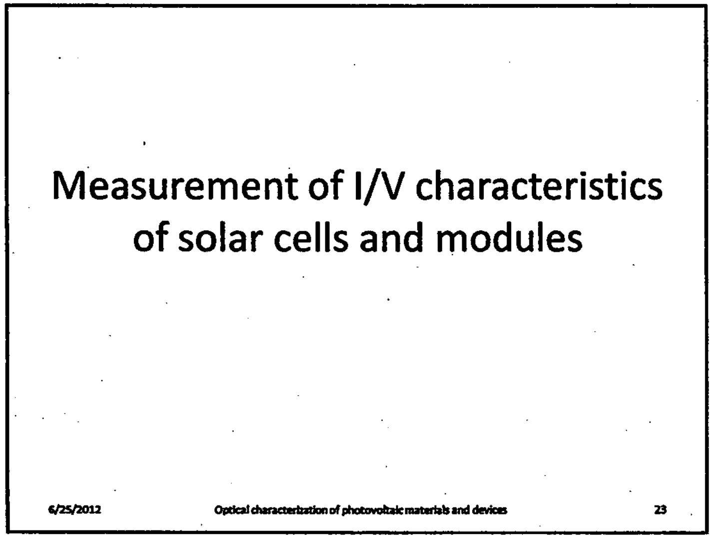
- With reverse bias, the space charge region expands
- In a typical one-sided thin-film solar cell, this can lead to enhanced collection of photogenerated charge from the absorber
- Under some circumstances, we can deduce the minority carrier diffusion length in the base
- This is a research tool and caution is needed in interpretation of data!

T. J. Coutts and C. R. Osterwald, Solar Cells, 22, 195-209, (1987)

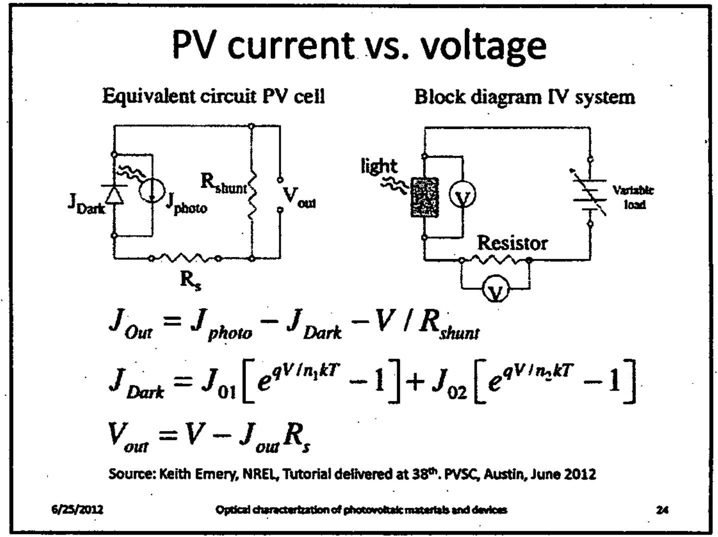


Reverse bias-dependent QE of a CIS solar cell

T. J. Coutts and C. R. Osterwald, Solar Cells, 22, 195-209, (1987)



Measurement of I/V characteristics of solar cells and modules



PV current vs. voltage

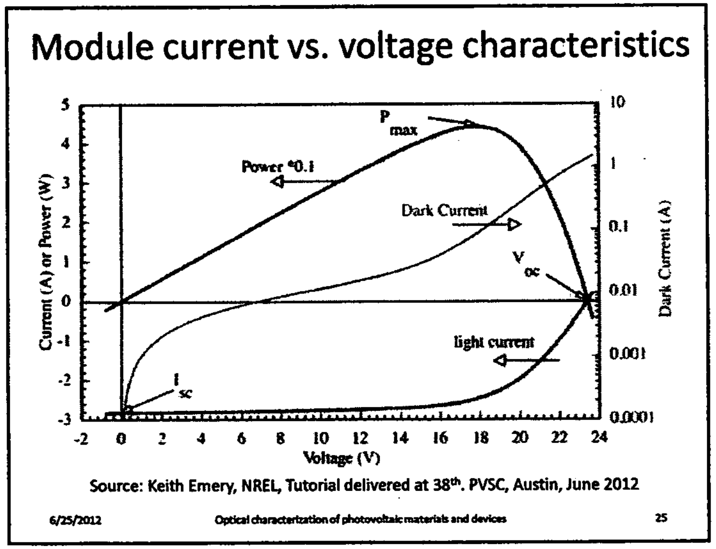
$$J_{Out} = J_{photo} - J_{Dark} - V / R_{shunt}$$

$$J_{Dark} = J_{01}\left[e^{qV/n_1kT} - 1\right] + J_{02}\left[e^{qV/n_2kT} - 1\right]$$

$$V_{out} = V - J_{out}R_s$$

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012

T1-7



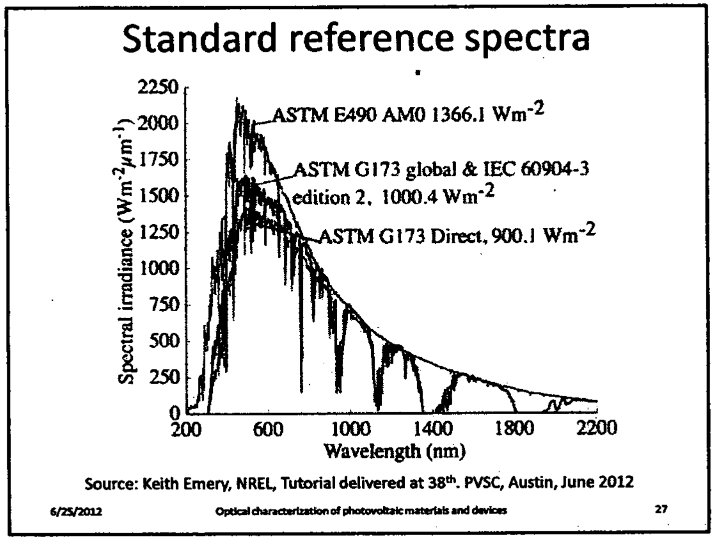
Module current vs. voltage characteristics

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012

Standard reference (test) conditions

- Continuous illumination
- 25° C junction temperature
- 1,000 Watts m^{-2}, total irradiance = 1-sun
- ASTM G173 reference spectrum (direct spectrum used only for concentrators)
- Area definition for efficiency (mesa area minus peripheral bus bars

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012



Standard reference spectra

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012

Theory

$$\text{Efficiency} = \eta = 100\frac{P_{max}}{E_{tot}A}$$

- P_{max} is the maximum power produced when illuminated using standard test spectra
- IEC 60904-3 ed. 2 or ASTM G173 global reference spectrum
- A is the total area of the device including contacts and peripheral bus bars
- E_{tot} is the total irradiance at standard test conditions, 1,000 Watts cm^{-2}
- Need to take into account the difference between the test and reference spectra using the 'spectral mismatch factor'

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012

Features in I/V systems (i)

- Lowest uncertainty-(Calibration lab.). Voltage and current measured to 0.02% accuracy.
- Standards require uncertainty in V_{oc} and I_{sc} of better than 0.02% for an overall accuracy of 0.1%
- For production purposes, the system must be very rapid
- Must be flexible, i.e., accommodate a wide range of currents and voltages
- Lowest possible random error to enable studies of reliability or other changes with time to be made

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012

Features in I/V systems (ii)

- Ability to control bias and light level
- Ability to control sweep rate in both positive and negative directions
- Must be able to save data to a data base rather than to a directory
- Automatic naming of files vs user-selected names
- Ability to examine and modify source code to meet changing needs

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012

Basic definitions

- Cell-the basic PV device that generates electricity when exposed to light
- Reference cell-a solar cell used for irradiance measurement
- Submodule-an array of two or more connected cells intended to demonstrate the materials and interconnect technology
- Module-an environmentally protected device

Source: Keith Emery, NREL, Tutorial delivered at 38th. PVSC, Austin, June 2012

Area definitions

- Cell total area-the entire surface area that is illuminated, including grids and contacts
- Module/submodule aperture area-the total surface area excluding the frame
- Module/submodule total area-the entire projected area of the module including the frame

T2-1

The science and technology of solar cells

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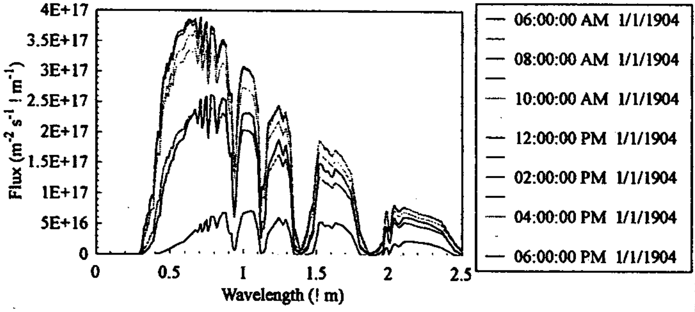
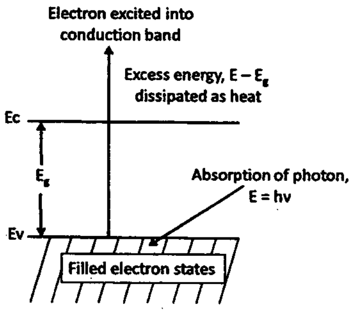
Acknowledgments

Much of the material in this lecture is taken from the University of Delaware Website, http://pvcdrom.pveducation.org/index.html. The information found on this site was prepared by Christiana Honsberg and Stuart Bowden.

Variation of solar flux during the day

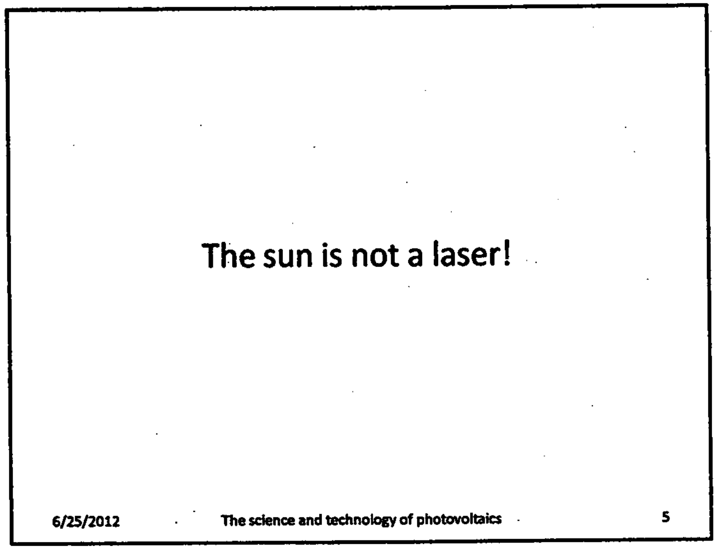


Absorption of light

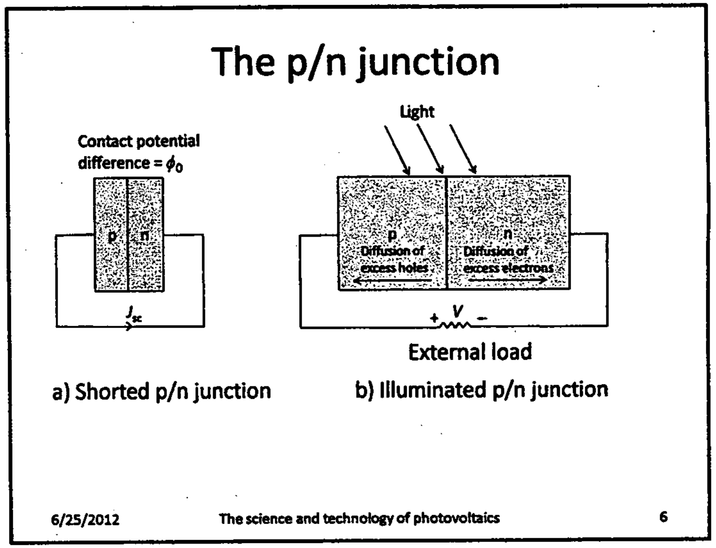


- Absorption of a photon excites an electron to the conduction band
- If the photon energy is greater than the bandgap, the excess energy is dissipated as heat and is wasted
- If the photon energy is less than the bandgap, it is not usefully absorbed
- How can we make better use of the broad-band radiation from the sun?
- Ideally, we need a separate semiconductor to absorb each individual photon
- None of the absorbed energy would then be wasted as heat
- This is the basis of tandem cells!

T2-2



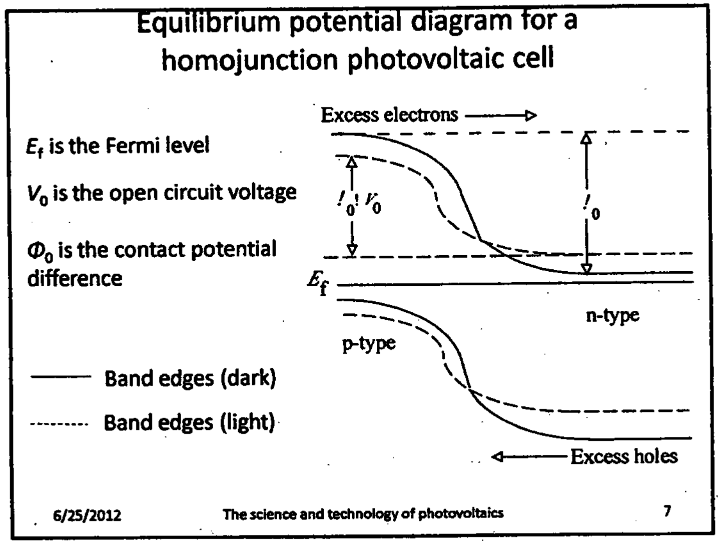
The sun is not a laser!



The p/n junction

a) Shorted p/n junction

b) Illuminated p/n junction



Equilibrium potential diagram for a homojunction photovoltaic cell

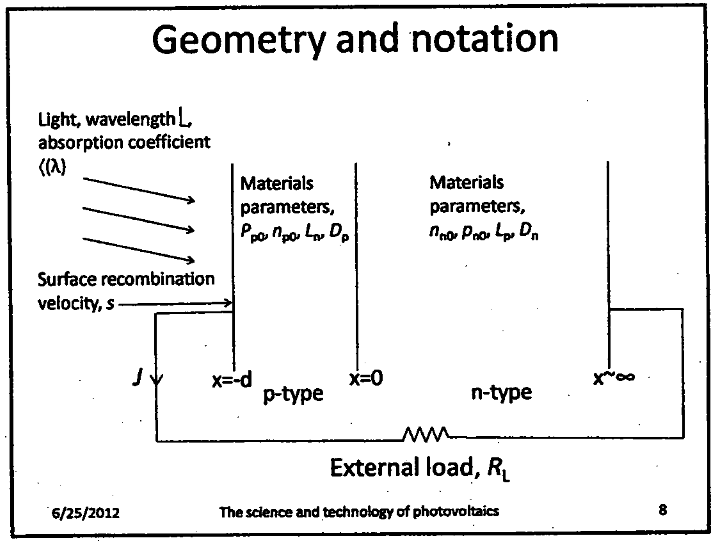
E_f is the Fermi level

V_0 is the open circuit voltage

Φ_0 is the contact potential difference

—— Band edges (dark)

-------- Band edges (light)



Geometry and notation

T2-3

The junction current

After some lengthy algebra, we obtain, an expression for the current as a function of voltage, i.e, the diode equation

$$J = J_0\left[\exp\left(\frac{eV}{kT}\right) - 1\right] - J_g$$

In this expression, we have replaced V_0 by V which includes an applied bias.

$$J_0 = e\left[\frac{D_p p_{n0}}{L_p} + \frac{D_n n_{p0}}{L_n}\left\{\frac{s\cosh\left(\frac{d}{L_n}\right) + \frac{D_n}{L_n}\sinh\left(\frac{d}{L_n}\right)}{\frac{D_n}{L_n}\cosh\left(\frac{d}{L_n}\right) + s\sinh\left(\frac{d}{L_n}\right)}\right\}\right]$$

J_0 is the reverse saturation current density. It is a strong function of E_g through p_{n0} and n_{p0}.

The short-circuit current density

$$J_g = \frac{e\alpha N_0(\lambda)\, L_p^2 \exp(-\alpha d)}{\left(1-\alpha^2 L_p^2\right)}\left(\frac{1}{L_p} - \alpha\right) + \ldots\ldots$$

$$\ldots\frac{e\alpha N_0(\lambda)\, L_n^2}{\left(1-\alpha^2 L_n^2\right)}\left[\frac{1}{L_n}\left(\frac{\left(s\cosh\left(\frac{d}{L_n}\right) + \frac{D_n}{L_n}\sinh\left(\frac{d}{L_n}\right)\right)\exp(-\alpha d) - s - \alpha D_n}{\frac{D_n}{L_n}\cosh\left(\frac{d}{L_n}\right) + s\sinh\left(\frac{d}{L_n}\right)}\right) - \alpha\exp(-\alpha d)\right]$$

The expression for the junction current is over-simplified because:

1. J_g must be integrated over all wavelengths.
2. J_0 is caused by more mechanisms than diffusion alone.
3. The surface recombination condition assumes that there are no fields at the surface.
4. Generation and recombination do not occur exclusively in field-free regions.

The junction current

To take these limitations into account, it is usual to write the current/voltage equation as $J = J_0\left[\exp\left(\frac{eV}{nkT}\right) - 1\right] - J_g$, where

n is the ideality factor. This equation generally represents the characteristics of a solar cell surprisingly well. It is often modified to include parasitic losses called series and shunt resistance. We shall deal with these aspects later.

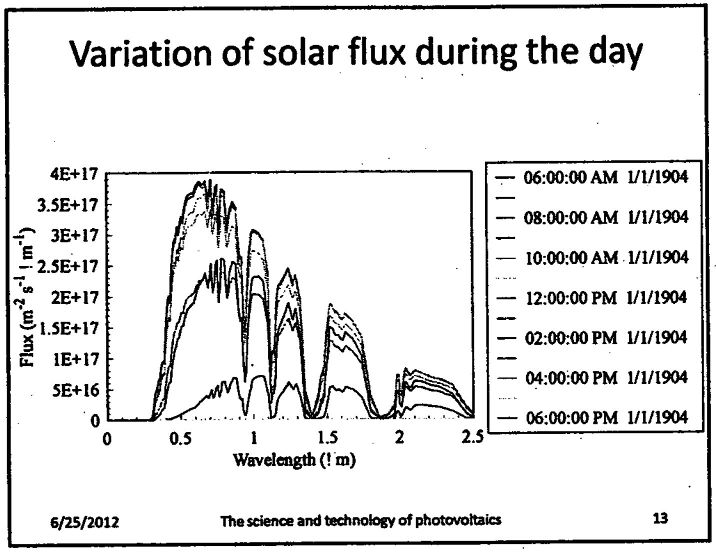
Notice that if $J = 0$, we may solve for the open circuit voltage.

Hence, $V_{oc} = \frac{nkT}{e}\ln\left(\frac{J_{sc}}{J_0}\right)$. Next, we shall examine the J/V characteristics of a solar cell and see how we define the efficiency.

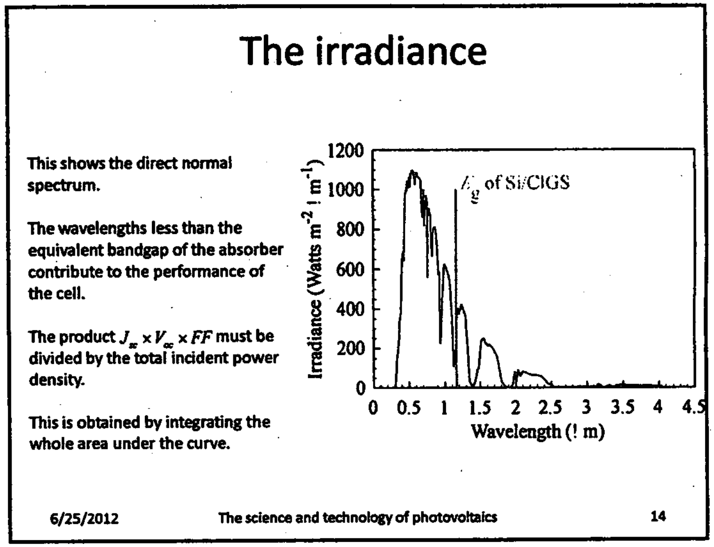
How do we estimate cell performance?

The efficiency is the product of short-circuit current density, J_{sc} the open-circuit voltage, V_{oc}, and the fill-factor, *FF*. We can calculate the maximum value for J_g and there are useful approximations for both J_0 and *FF*. The product must be divided by the total irradiance, which varies during the day. This means that we must measure the performance under standard laboratory conditions.

T2-4



Variation of solar flux during the day



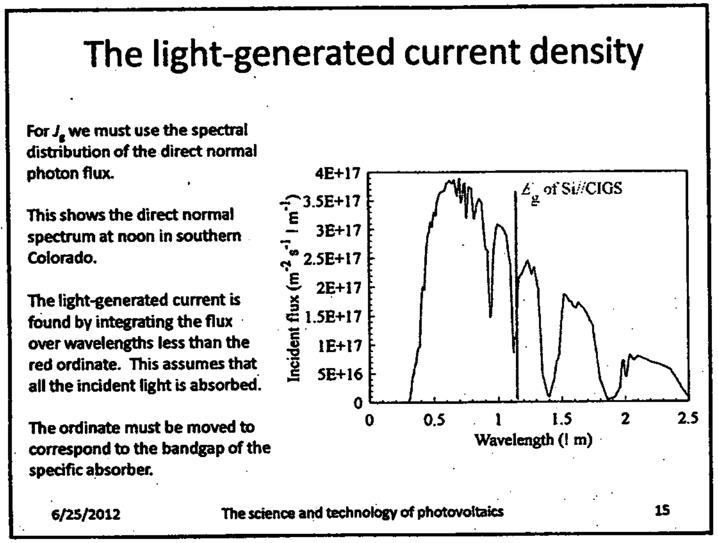
The irradiance

This shows the direct normal spectrum.

The wavelengths less than the equivalent bandgap of the absorber contribute to the performance of the cell.

The product $J_{sc} \times V_{oc} \times FF$ must be divided by the total incident power density.

This is obtained by integrating the whole area under the curve.



The light-generated current density

For J_g we must use the spectral distribution of the direct normal photon flux.

This shows the direct normal spectrum at noon in southern Colorado.

The light-generated current is found by integrating the flux over wavelengths less than the red ordinate. This assumes that all the incident light is absorbed.

The ordinate must be moved to correspond to the bandgap of the specific absorber.

The open-circuit voltage

$$V_{oc} = \frac{nkT}{e}\ln\left(\frac{J_{sc}}{J_0}\right)$$

For a single crystal cell, we can assume that the ideality factor is equal to 1. For a thin-film cell, a value of 1.3-1.5 is more realistic.

For modeling purposes, we assume that the light-generated current and the short-circuit current density (the quantity we measure!) are equal. We shall discuss this in further detail later.

The issue is to determine the reverse saturation current density, J_0.

One approach to this was developed by Nell and Barnett who noted that, for a wide range of single crystal solar cells, J_0 could be expressed by $J_0 = \beta T^3 \exp\left(-E_g/kT\right)$.

The functional form can be understood by referring to the earlier expression for J_0.

This has been repeated for world record thin-film solar cells, which we shall discuss here.

12-2

The J/V characteristics (i)

For a device that is free of parasitic losses, we can see from the J/V equation that the current must be displaced into the fourth quadrant by the light generated current, J_g. Regardless of external load and parasitic losses, the cell always generates J_g. In the absence of series resistance losses, the full light generated current flows through a shorted external load. If series resistance is present in the circuit, then the current delivered is J_{sc} but $J_{sc} < J_g$.

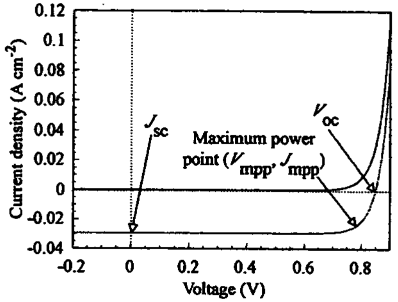
The J/V characteristic depends on the bandgap of the semi-conductor. As E_g increases, J_0 decreases much more than $J_{sc,}$ the result of which is an increase in V_{oc}. The maximum efficiency for the solar spectrum, is a function of bandgap.

The J/V characteristics (ii)

This shows the light and dark *J*/*V* curve for a cell with a bandgap of 1.45 eV.

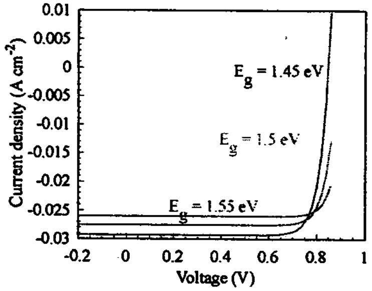
J_{sc}=29.3 mA cm^{-2} (from area under irradiance curve)
V_{oc} = 0.849 V (from the Nell approximation)

There is no power generated at V_{oc} or J_{sc} but there is a point, (V_{mpp}, J_{mpp}), at which maximum power can be delivered.



Current/voltage characteristics vs. bandgap

As the bandgap increases, the open circuit voltage increases and the short circuit current density decreases. Hence, there is a maximum in the efficiency vs. bandgap curve.



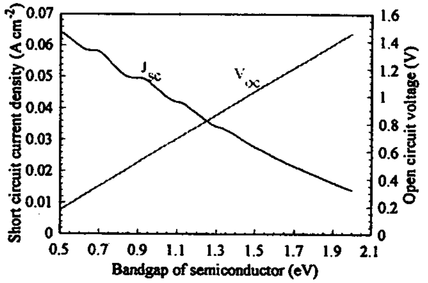
Variation of J_{sc} and V_{oc} with bandgap

J_{sc} decreases with E_g because fewer photons are absorbed.

V_{oc} increases because J_0 decreases.

These calculations use the standard global reference spectrum.

This simulation was done for a single crystal cell.



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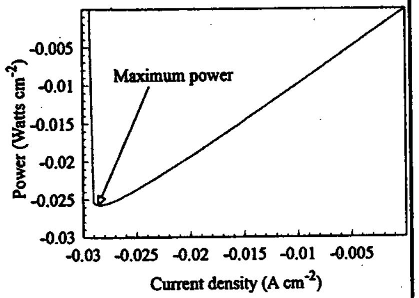
Delivered power

This shows the power delivered to an external load. The bandgap of the semiconductor from which the solar cell is made is 1.45 eV.

The sign is negative because the photocurrent is negative.



Fill-factor (i)

The fill-factor is a common term in photovoltaic technology. It is defined as the ratio of the maximum power divided by the product of V_{oc} and J_{sc}, $FF = {V_{mpp}J_{mpp}}/{V_{oc}J_{sc}}$.

The fill-factor is a measure of the 'squareness' of the *J/V* characteristic. For a good quality, single crystal device, the fill-factor is >80%. For a polycrystalline cell, it is about 75%. The fill-factor increases with the bandgap of the semiconductor and its quality.

Fill-factor (ii)

Fill-factor is usually expressed as a percentage.

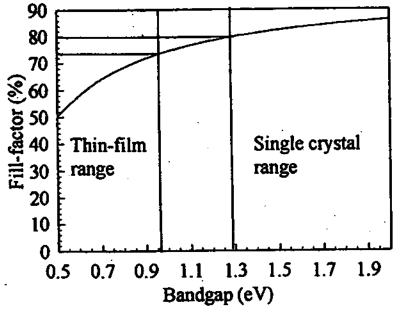
The data shown here were obtained by numerically differentiating the power curve.

Values greater than 80% are typical of high-quality, single crystal materials.

Values less than about 75% are more typical of thin-film materials.

Increasing temperature, reduces the fill-factor.

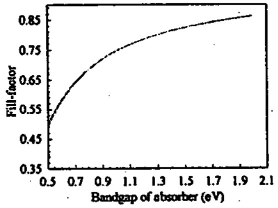
Parasitic losses also reduce the fill-factor.



Fill-factor (iii)

Green also developed a useful approximation to the fill-factor, that may be used over a wide range of energy gaps. This is $FF = \frac{v_{oc} - \ln(v_{oc}+0.72)}{v_{oc}+1}$.

In this expression, $v_{oc} = {eV_{oc}}/{nkT}$. The approximation is better than 3% relative over the range 0.5-2 eV



T-2-7

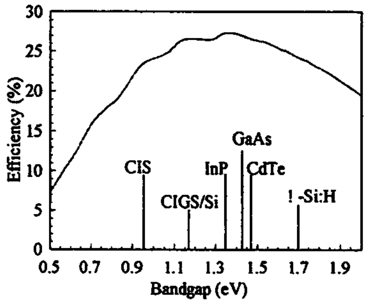
Efficiency

The conversion efficiency is equal to the maximum power divided by the incident optical power. For the standard spectrum used in characterization, the incident power is normalized to 1 k Watt m^{-2}.

For the modeled device shown here, with a bandgap of 1.45 eV, the efficiency is 26.7%, which is much larger than the efficiency of the world record CdTe cell of a comparable bandgap. The reason for the large difference is that the higher result was modeled for a single-crystal device whereas the record was obtained for a polycrystalline cell. The latter has much larger values of J_0 and ideality factor than a single crystal cell. In addition, the modeled device is free of parasitic losses, which we shall discuss next.

Efficiency vs. bandgap

The detail of this curve depends on the reference spectrum. The maximum is broad because of the broad-band nature of the solar spectrum.



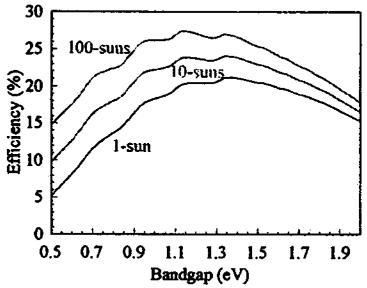
Efficiency vs. concentration ratio

The global reference spectrum, GNREF, was used for this simulation.

A thin-film solar cell was simulated.

The efficiency increases by about 2.5% for each decade increase in concentration ratio.

Notice that the peak shifts to lower bandgaps with increasing concentration ratio.



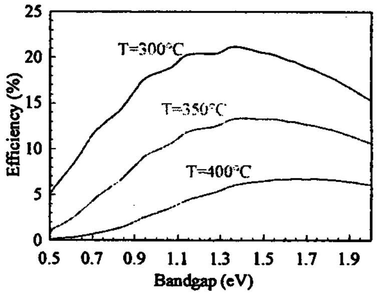
Efficiency vs. temperature

Global reference spectrum.

1-sun irradiance.

Peak efficiency decreases sharply with increasing temperature.

Peak efficiency moves to higher bandgap with increasing temperature.



7-2-8

Quantum efficiency

QE_{ext} is the ratio of collected electron/hole pairs that are collected, divided by the incident photon flux. Both of these quantities are functions of wavelength. The QE_{ext} is usually expressed as a percentage. A high-quality cell will usually have an QE_{ext} equal to 100% over a limited wavelength range. The quantum efficiency characteristic is very useful because it provides guidance about the internal and external loss processes. If we measure the reflectance from a cell then we can obtain the internal QE_{int} from

$QE_{int}(\lambda) = {QE_{ext}(\lambda)}\Big/{(1-R(\lambda))}$. For a homojunction cell, we expect the value of

QE_{int} to follow the expression for J_{g}. Honsberg and Bowden have again provided a useful visualization tool to see the effects of the SRV, the geometrical design and the minority carrier diffusion lengths in the base and the emitter. http://pvcdrom.pveducation.org/index.html Note: this applies for a Si solar cell. The effects are totally different for a thin-film cell.

Examples of QE

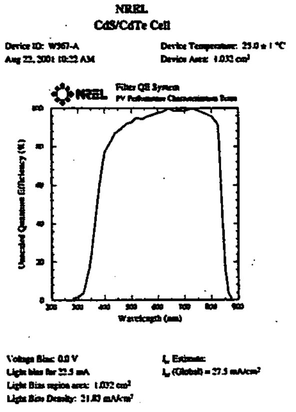
This shows the QE of the former world record CdTe cell. Its efficiency was 16.5%.

The record now is 17.3%

Notice the steep short wavelength cut-off. This is because the thickness of the CdS was very small (~50 nm).

Cell performance decreases for even smaller CdS thicknesses.

The steep long wavelength edge shows that the electron diffusion length in the CdTe was long.

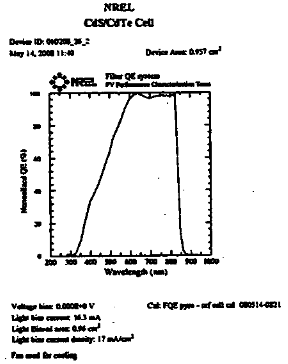


Examples of QE

In this case, the thickness of the n-CdS window layer was much greater and the blue response much poorer.

The minority electron diffusion length in the base is still excellent, based on the sharp turn off at the band-edge of the CdTe.

The efficiency of this device was about 10.6%.



Series resistance

Series resistance, R_s, is due to resistance of the back contact, the grid, and spreading resistance in the emitter. Its main impact is on the fill-factor but it can reduce the short circuit density in extreme cases. The following site provides a useful tool to visualize the impact of R_s. http://pvcdrom.pveducation.org/index.html, prepared by Honsberg and Bowden.

R_s is measured in Ω cm². It is possible to estimate the series resistance from the slope of the J/V characteristic in the region of V_{oc}.

Typical value of series resistance are about 0.5 Ω cm².

L7.1

Shunt resistance

The shunt resistance should be as large as possible. A low value of R_{sh} means that there is an alternative path for the light generated current and a loss of voltage in severe cases. At low light levels, the effect is particularly severe. Again, Honsberg and Bowden have provided a visualization tool.

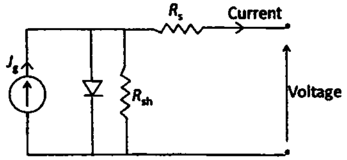
An estimate of the magnitude of the shunt resistance can be found from the slope of the J/V curve in the vicinity of J_{sc}.

The impact of both R_s and R_{sh}

When both series and shunt resistances are present, the current/ voltage equation is given by

$$J = J_0\left[\frac{e(V+JR_s)}{nkT}\right] + \frac{V+JR_s}{R_{sh}} - J_g .$$

This equation can be derived by applying Kirchoff's laws to the equivalent circuit of the solar cell, shown below.



Test the visualization tool to see the combined effects of both series and shunt resistance. http://pvcdrom.pveducation.org/index.html

T3-1

Transparent conducting oxides

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Introduction

- TCOs have RELATIVELY high optical transmittance and RELATIVELY low electrical resistivity
- The production of glass coated with TCOs is growing
- The applications are becoming more demanding and there is a growing need to understand the materials
- To achieve this, the properties of the films must be more thoroughly characterized
- Above all, there is a need to understand the properties of TCOs so that they do not limit device performance
- Also need to deposit films over large areas with uniform properties

Origins of conductivity

- TCOs have wide bandgaps and would not be expected to have significant intrinsic conductivity
- They can be extrinsically doped with cations from one group higher in the periodic table (i.e. Al^{III} in $Zn^{II}O$)
- Intrinsic oxygen vacancies believed to contribute to carrier concentration
- In extrinsically-doped TCOs, not all the impurities are ionized i.e. electrically active
- This often depends on the fabrication conditions

Extrinsic doping

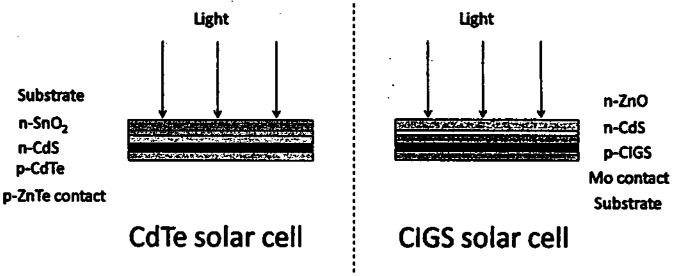
- Doping is always uncertain because the size of the impurities and their chemical activity must be considered
- Ti, for example, should have no effect in SnO_2 because it is from group IV of the periodic table, as is Sn
- However, its chemical affinity for oxygen can cause it to form insulating compounds that cause the resistivity to increase
- Even if impurities are electrically active, they can impair the electron mobility
- If they are ionized there is ionized impurity scattering but, if they remain neutral, there is neutral impurity scattering

T3-2

TCO applications

- Photovoltaics~1 G watt of present-day thin-film cells requires at least 4 sq. miles (~10 km^2)
- American glass companies make > 20 sq. miles of SnO_2-coated glass per year
- Low emissivity coatings in architecture
- ‘Smart’ windows based on electrochromic cells
- Flat-panel displays are an enormous market but thin-film
  PV will become far larger (pressure on glass companies!)

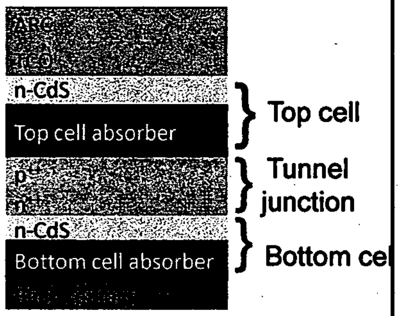
Thin-film solar cells



In both cases, the light passes through the TCO first.

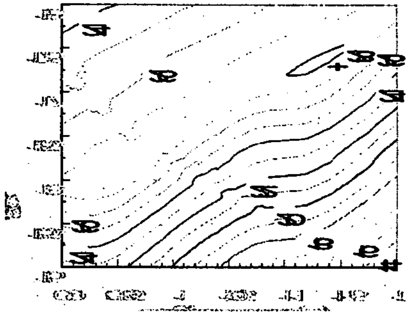
Schematic of modeled thin-film tandem cell

- All interfaces assumed to be specular.
- No interdiffusion.
- Very idealized, parametric modeling.



Modeled tandem efficiency

- Assumes all photons reach the top absorber.
- Absolute maximum is 28.2%.
- Using realistic optical properties of TCO layers, maximum efficiency ~25%, i.e., our goal!



Properties

- TCOs are wide bandgap semiconductors with E_g~3.5 eV
- But they still conduct electricity ()~10^{-4} Ω cm)
- They also transmit much of the solar spectrum (*T*~85%)
- The electrons that conduct electricity also interact with light at longer wavelengths
- How do we improve both) and *T*?

General observations

- TCO properties not improved significantly for many years
- Must find either superior materials (intrinsic) or better ways of making existing materials (extrinsic)
- All TCOs contain cations with filled, active, d-shell electrons
- Emphasis must be on increased carrier mobility
- New approaches needed for low-temperature deposition (process compatibility, plastic substrates etc.)

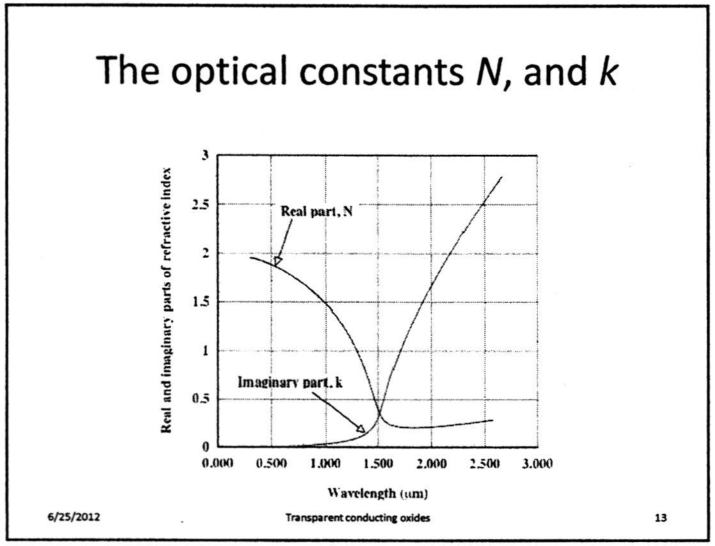
Long-term goals

- Resistivity of less than 10^{-4} Ω cm (< 2 Ω/∂ for 0.5 µm film thick)
- Transmittance > 85% at visible wavelengths
- Minimal free-carrier absorbance in the visible
- Mobility > 100 $cm^2 V^{-1} s^{-1}$ required
- Deposition and post-deposition temperatures compatible with device interfaces and materials

Optical properties of TCOs

- For most applications, the most important properties of TCOs are their optical transmittance in the visible
- For some applications, the infrared reflectance and the transmittance in the near-ultra-violet are also important
- The approach to gaining knowledge about the optical properties is to use Maxwell's equations, first derived in the late nineteenth century
- This shows that the electrical and optical properties are closely linked

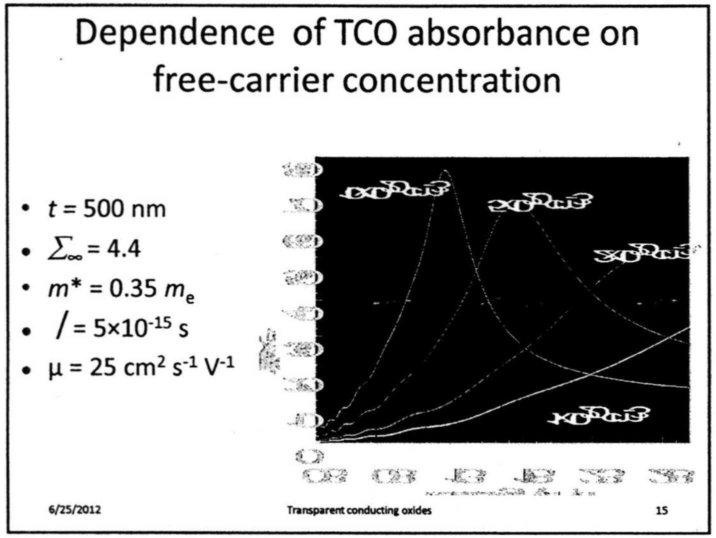
T3-4



The optical constants *N*, and *k*

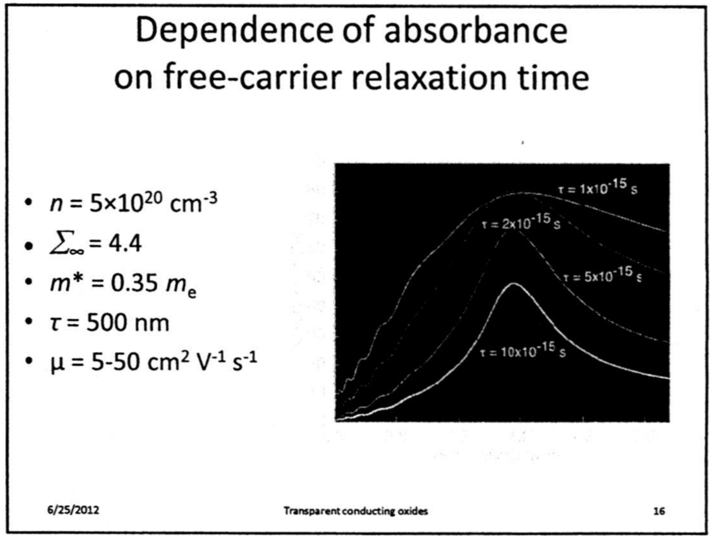
The conductivity

- The d.c. conductivity is given by $\sigma = ne\mu$
- μ is the mobility (cm^2 V^{-1} s^{-1}), *n* is the concentration of free carriers (cm^{-3}), and *e* is the electronic charge (~1.6x10^{-19} coulombs)
- In turn $\mu = ne\tau / m^*$
- If we wish to change (increase) the mobility of a TCO, we can only do by changing the scattering time of the free-carriers (extrinsic) or the effective mass (intrinsic)
- Next, we shall show the influence of changing the parameters on the optical properties.



Dependence of TCO absorbance on free-carrier concentration

- $t = 500$ nm
- $\Sigma_\infty = 4.4$
- $m^* = 0.35\ m_e$
- / = 5×10^{-15} s
- μ = 25 cm^2 s^{-1} V^{-1}



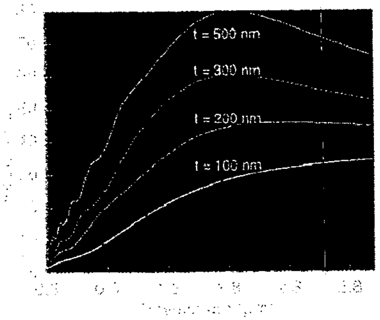
Dependence of absorbance on free-carrier relaxation time

- $n = 5\times10^{20}$ cm^{-3}
- $\Sigma_\infty = 4.4$
- $m^* = 0.35\ m_e$
- τ = 500 nm
- μ = 5-50 cm^2 V^{-1} s^{-1}

13-9

Dependence of absorbance on film-thickness

- $n = 5\times10^{20}$ cm^{-3}
- $\Sigma_\infty = 4.4$
- $/ = 5\times10^{-15}$ s
- $m^* = 0.35\ m_e$
- $\mu = 25$ cm^2 V^{-1} s^{-1}



Summary of optical properties modeling

- Must minimize the carrier concentration to reduce the free-carrier absorbance
- Also need as high a mobility as possible
- Long relaxation time is more beneficial than low effective mass
- Reduced film thickness also helps but may compromise the sheet resistance

The Burstein-Moss effect (i)

- This always occurs for high carrier concentrations and it manifests itself as a shift to higher energy of the bandgap
- It happens because the states at the bottom of the conduction band are filled and more energy is needed to excite charge from the valence band
- The magnitude of the shift is given by

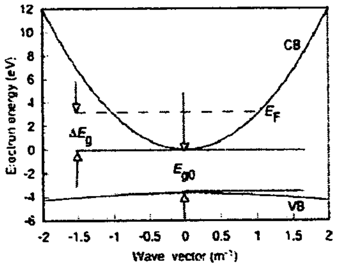
$$\Delta E_{opt} = \left(\frac{3}{\pi}\right)^{2/3}\left(\frac{h^2}{8m_{cv}^*}\right)n^{2/3}.$$

- In this equation m_{cv}^* is the 'reduced effective mass' which is given by

$$\frac{1}{m_{cv}^*} = \frac{1}{m_c^*} + \frac{1}{m_v^*}.$$

The Burstein-Moss effect (ii)

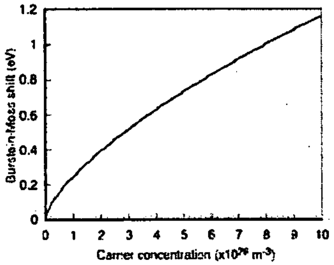
- In this figure, I took the fundamental band-gap as 3.7 eV
- m_c^* was taken as 0.33 m_e
- m_v^* was taken as 6 m_e
- These are reasonable guesses



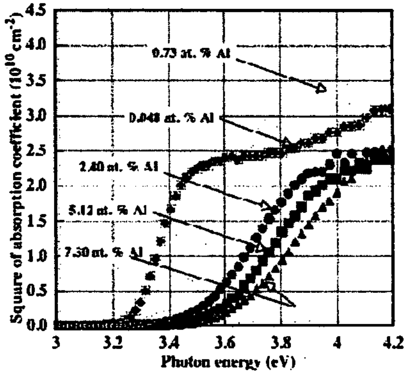
T3-6

The Burstein-Moss effect (iii)

- This is the magnitude of the effect
- Calculated using the same values as last slide
- The shifts shown here are typical of measured values
- Only applies for parabolic bands



The Burstein-Moss effect (iv)



Summary

- We have concentrated on optical properties but electrical properties are also important
- In thin-film solar cells, TCOs are critical elements, both optically and electrically
- The electronic band structure is also important
- Must focus on developing materials with high mobilities and 'reasonable' electron concentrations

T4-1

Multijunction solar cells

Novel solar cells

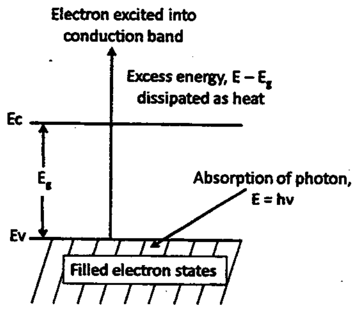
- Thermophotovoltaic cells
- Organic PV
- Graetzel cell
- Intermediate bandgap solar cells
- Nanoparticle solar cells
- Quantum well cells
- Up/down converters

With the possible exception of the first three devices, in my view, it will be many years before high efficiencies are achieved for any of these devices

The PV challenge

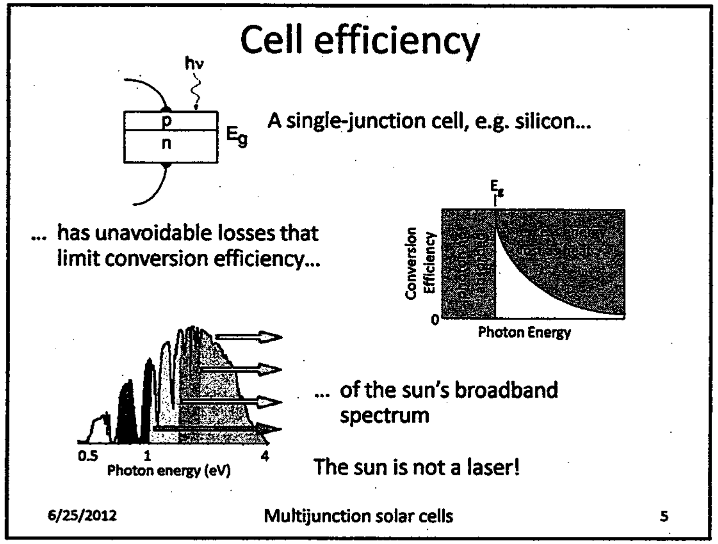
- Energy density of sunlight is only ~1 kW m^{-2}
- Can only convert a fraction of this
- 20% system efficiency is excellent
- 1 GW of electricity needs ~5 km^2 of PV!
- How can this be achieved cost-effectively?
- Either use low cost, moderate efficiency devices, or
- High efficiency concentrator devices
- In this lecture, we shall study both of these options

Absorption of light



- Absorption of a photon excites an electron to the conduction band
- If the photon energy is greater than the bandgap, the excess energy is dissipated as heat and is wasted
- If the photon energy is less than the bandgap, it is not usefully absorbed
- How can we make better use of the broad-band radiation from the sun?
- We need a different semiconductor to absorb each wavelength band of photons
- None of the absorbed energy would then be wasted as heat
- This is the basis of tandem cells!

T4-2



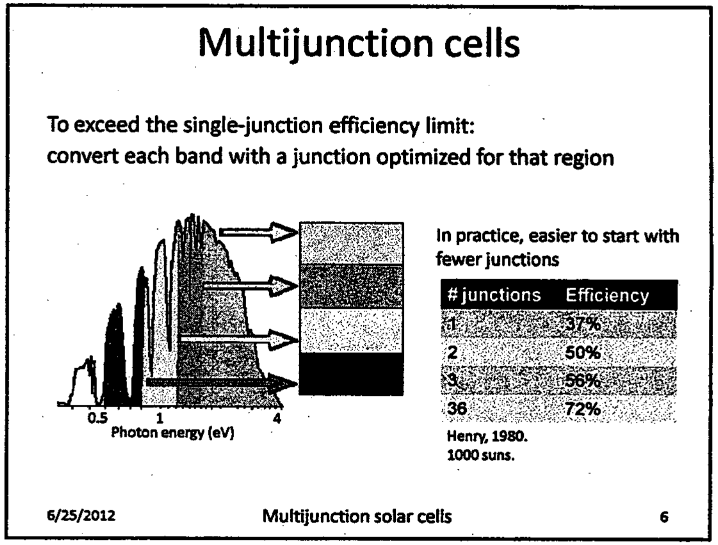
Cell efficiency

A single-junction cell, e.g. silicon…

… has unavoidable losses that limit conversion efficiency…

… of the sun's broadband spectrum

The sun is not a laser!



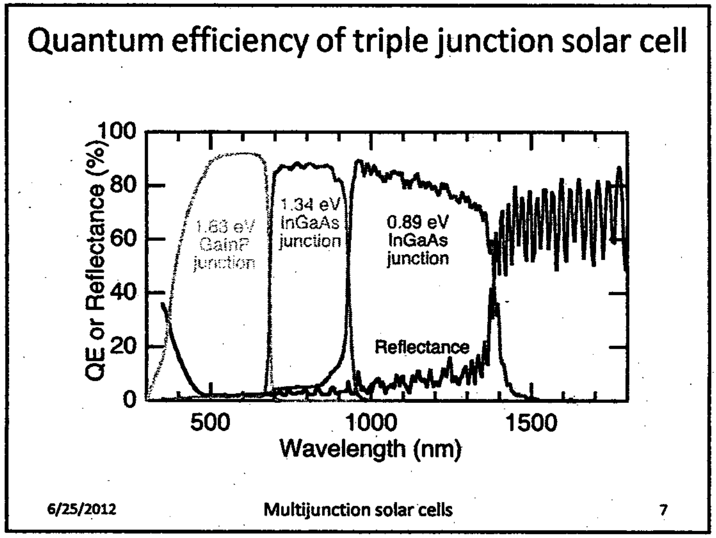
Multijunction cells

To exceed the single-junction efficiency limit:
convert each band with a junction optimized for that region

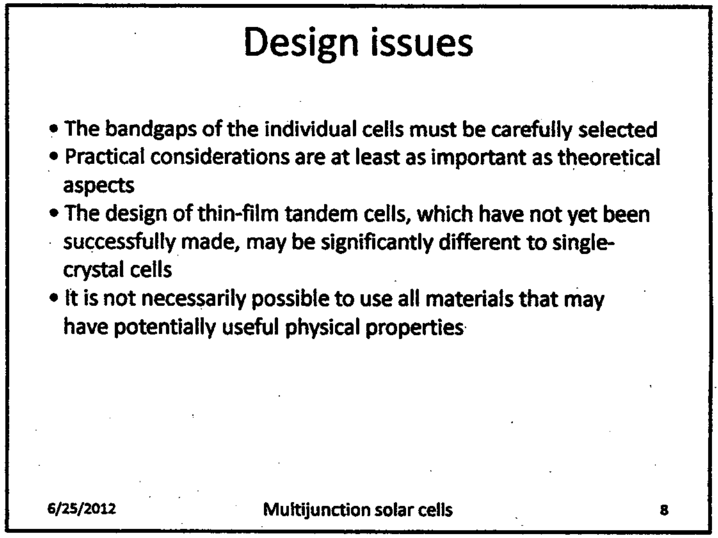
In practice, easier to start with fewer junctions

# junctions	Efficiency
1	37%
2	50%
3	56%
36	72%

Henry, 1980.
1000 suns.



Quantum efficiency of triple junction solar cell



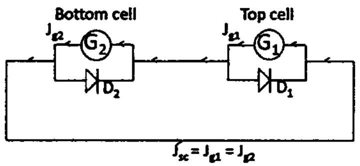
Design issues

- The bandgaps of the individual cells must be carefully selected
- Practical considerations are at least as important as theoretical aspects
- The design of thin-film tandem cells, which have not yet been successfully made, may be significantly different to single-crystal cells
- It is not necessarily possible to use all materials that may have potentially useful physical properties

T 4-3

Equivalent circuit of tandem cell (i)

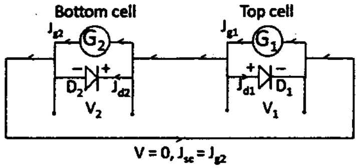
The short circuit condition: $J_{g1} = J_{g2}$, i.e. current matched



- When the two light-generated currents are equal, no current flows through the parallel diodes

Equivalent circuit of tandem cell (ii)

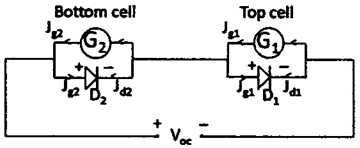
The short circuit condition: $J_{g1} \neq J_{g2}$, i.e. current mismatched. Assume $J_{g1} > J_{g2}$



- If J_{g1} is greater than J_{g2}, we have a more interesting problem
- The difference, J_{g1}-J_{g2} can not flow through G_2
- Part of it must flow through D_1 and part through D_2
- D_1 is forward biased and D_2 is reverse biased
- The sum of these two biases must equal zero
- Hence, a tandem cell will only pass the smaller of the two light-generated currents

Equivalent circuit of tandem cell (iii)

The open circuit condition: $J_{g1} \neq J_{g2}$, i.e. current mismatched. Assume $J_{g1} > J_{g2}$

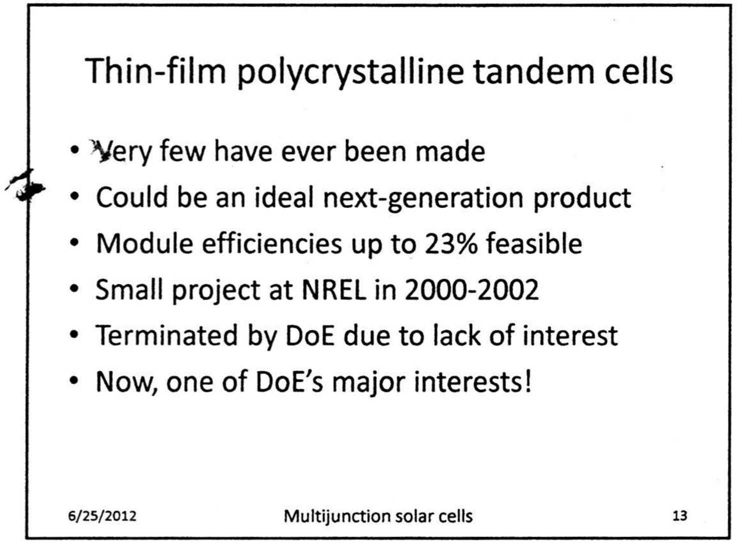


- When the tandem cell is open circuited, The voltage appearing across the terminals equals the sum of the individual V_{oc}s, i.e, $V_{oc} = V_{oc1} + V_{oc2}$
- In this case, the two subcells do not interact and the mismatched currents are not relevant
- $J_{g1} = J_{d1}$ and $J_{g2} = J_{d2}$ and no excess current flows through either diode

Design considerations

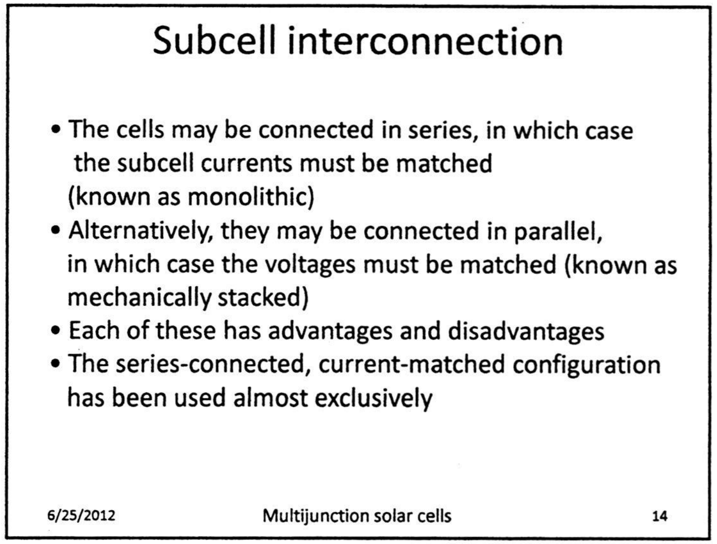
- A tandem cell can only pass the smaller(est) short circuit current density generated by either (any) of the subcells
- The choice of the bandgaps of the subcells is governed by the particular spectrum, and practical considerations
- The currents will become mismatched during the day as the sun moves through the sky and the spectral content changes
- Ideally, we need to match the currents at the maximum power point but usually based on the *Jsc*'s
- Should model by maximizing the diurnal energy generated

T4-4



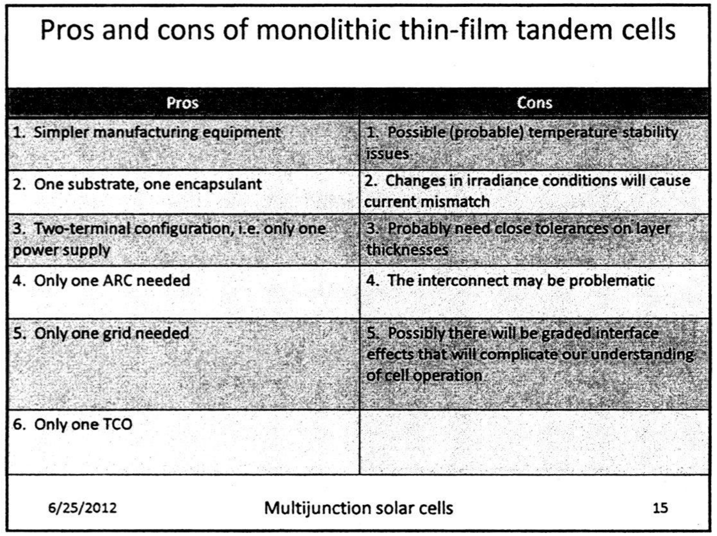
Thin-film polycrystalline tandem cells

- Very few have ever been made
- Could be an ideal next-generation product
- Module efficiencies up to 23% feasible
- Small project at NREL in 2000-2002
- Terminated by DoE due to lack of interest
- Now, one of DoE's major interests!



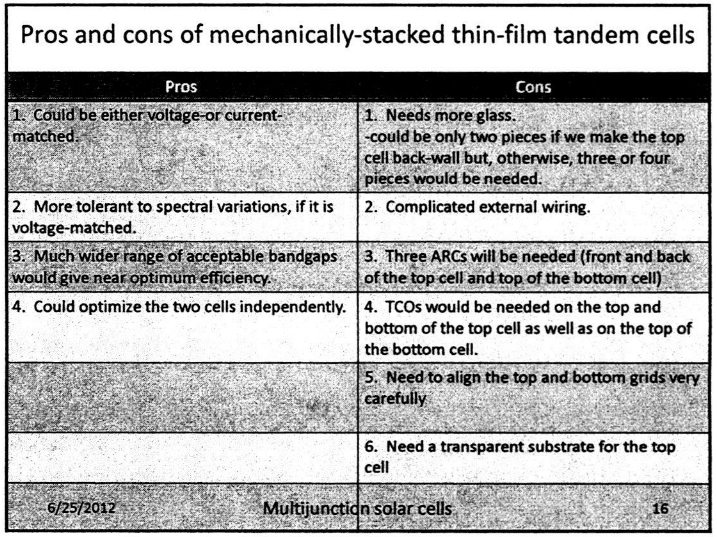
Subcell interconnection

- The cells may be connected in series, in which case the subcell currents must be matched (known as monolithic)
- Alternatively, they may be connected in parallel, in which case the voltages must be matched (known as mechanically stacked)
- Each of these has advantages and disadvantages
- The series-connected, current-matched configuration has been used almost exclusively



Pros and cons of monolithic thin-film tandem cells

Pros	Cons
1. Simpler manufacturing equipment	1. Possible (probable) temperature stability issues
2. One substrate, one encapsulant	2. Changes in irradiance conditions will cause current mismatch
3. Two-terminal configuration, i.e. only one power supply	3. Probably need close tolerances on layer thicknesses
4. Only one ARC needed	4. The interconnect may be problematic
5. Only one grid needed	5. Possibly there will be graded interface effects that will complicate our understanding of cell operation
6. Only one TCO	



Pros and cons of mechanically-stacked thin-film tandem cells

Pros	Cons
1. Could be either voltage-or current-matched.	1. Needs more glass. -could be only two pieces if we make the top cell back-wall but, otherwise, three or four pieces would be needed.
2. More tolerant to spectral variations, if it is voltage-matched.	2. Complicated external wiring.
3. Much wider range of acceptable bandgaps would give near optimum efficiency.	3. Three ARCs will be needed (front and back of the top cell and top of the bottom cell)
4. Could optimize the two cells independently.	4. TCOs would be needed on the top and bottom of the top cell as well as on the top of the bottom cell.
	5. Need to align the top and bottom grids very carefully
	6. Need a transparent substrate for the top cell

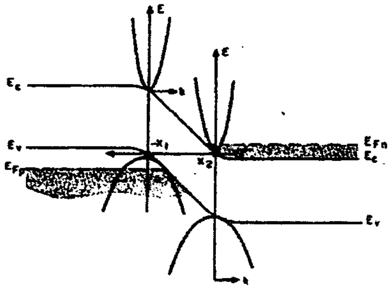
Tunnel junctions for monolithic tandem cells

- A tunnel junction has mainly been used to connect the subcells
- A tunnel junction is simply a p/n diode with both sides very heavily doped so that they are 'degenerate'
- On the p-type side of the junction, the Fermi level moves into the valence band
- On the n-type side of the junction, the Fermi level moves into the conduction band
- We indicate very heavy doping by using a plus (or double plus sign as a superscript, i.e., p^+/n^+ or p^{++}/n^{++}
- Doping levels greater than 10^{18} cm^{-3} are typically required
- The width of the space charge is very small and charge can tunnel relatively unimpeded from the conduction band of one side to the valence band of the other side

Comments on tunnel junction interconnects

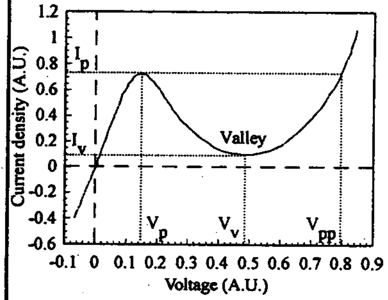
- Tunnel junctions for tandem solar cells have only been made in III-V materials
- Polycrystalline thin-film tandem cells have not yet been made but remain an exciting potential means of increasing the efficiency of thin-film modules
- It is not clear that sufficiently high quality thin-film semiconductors can be made for true tunnel junctions
- However, interconnecting layers are routinely made for multijunction cells based on amorphous and microcrystalline Si, so there is no fundamental limitation

Band diagram of tunnel junction



- For Si, each side of the junction must be doped to about 10^{20} cm^{-3}
- For III-V materials, they must be doped to about $5x10^{18}$ cm^{-3}
- The points x_1 and x_2 are the edges of the space charge region and x_2-x_1 is approximately equal to the tunneling barrier

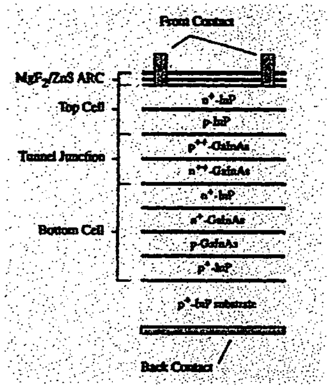
J/V characteristic of a tunnel junction



- This is typical of the J/V characteristic for a TJ
- The steep region near the origin shows low resistance
- This is the region of relevance to a tandem cell
- The negative slope region is the signature of a TJ
- We need I_p/I_v to be as large as possible

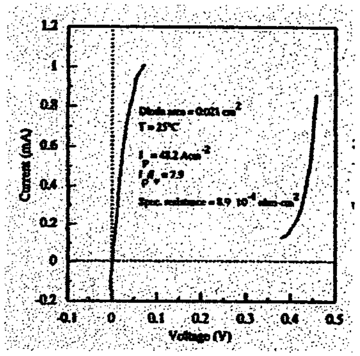
T4-6

Schematic of tandem cell



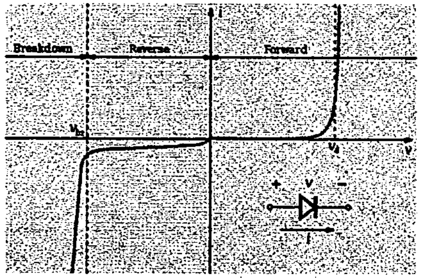
- This is a device we developed at NREL 17 years ago
- InP has a bandgap of about 1.35 eV
- The alloy $Ga_{0.47}In_{0.53}As$ has a bandgap of 0.73 eV, and it is lattice-matched to InP
- The tunnel junction was made from heavily doped GaInAs
- The layer of n$^+$-InP passivates the surface of the GaInAs bottom cell
- The p$^+$-InP performs the same function on the back of the bottom cell

Tunnel junction characteristic



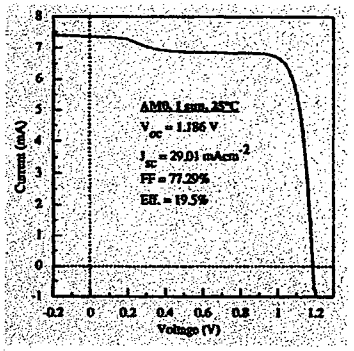
- This is a tunnel junction made using the alloy $In_{0.53}Ga_{0.47}As$
- The specific resistance is too high for very high concentration ratios
- The negative slope region doesn't show up because of limitations in the oscilloscope used
- It is due to the filled states in the CB crossing and then uncrossing empty states in the VB

Current/voltage characteristics of a diode



- In forward bias, the current increases exponentially with bias
- In reverse bias, the current remains very small until the breakdown voltage is reached (the pink region)
- We must keep this characteristic in mind when examining tandem solar cells

Current/voltage characteristic of series-connected tandem cell



- Notice the kink in the characteristic
- This is due to the currents being mismatched
- The bottom cell is in reverse bias and is too heavily doped
- Hence, it breaks down
- The individual J_{sc} values can be read from the figure
- Voltage addition is evident
- An efficiency of 31.8% was later obtained for a conc. ratio of about 200X

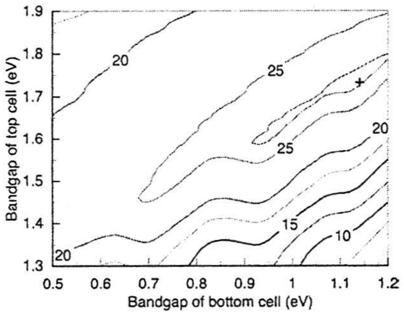
T4-7

Summary of tunnel junction needs

- Need N_D and N_A to be as large as possible
- Low effective masses help successful tunnel diodes
- The n^+ and p^+ layers need to be as thin as possible (~10-20 nm)
- Dopants should be stable up to at least the temperature used to make the second cell
- The specific resistance of the tunnel junction should be ~$10^{-1}\ \Omega\ cm^2$, for non-concentrator cells
- For higher optical concentrations, smaller values are required

Thin-film tandem cell efficiency

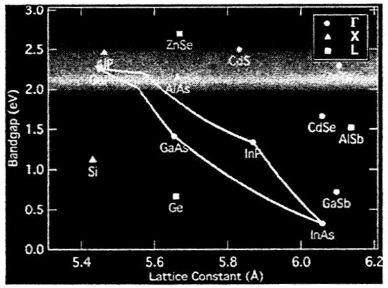
- The global spectrum was used for this modeling
- The optimum bandgap pair is 1.74 and 1.14 eV
- The lossless efficiency is 28.2%
- Assumes the QE of both subcells was unity
- The efficiencies are not a fundamental limit!
- An efficiency of 32.1% seems feasible with reductions in J_0



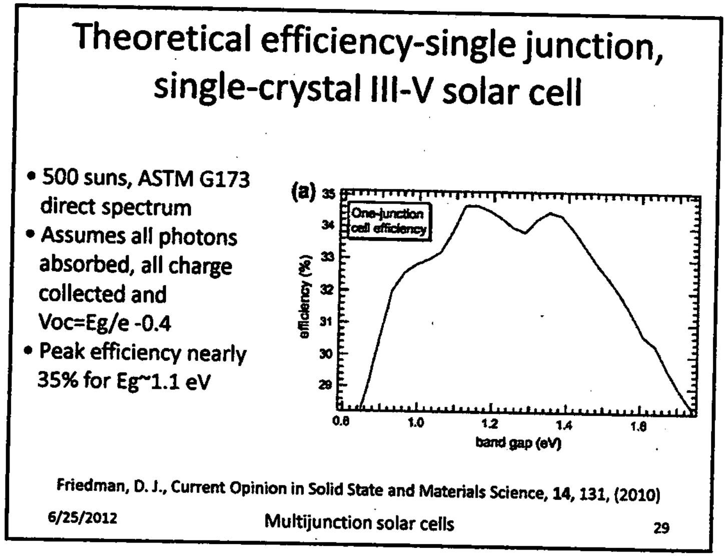
Potentially relevant semiconductors for thin-film tandem solar cells

Top cell	Bottom cell
CIGS	CIGS
$Cd_x(Zn,Mn,Mg)_{1-x}Te$	Si
CdTe	$Cd_xHg_{1-x}Te$
CdSe	$CuIn(Sn,Ge)Se_2$
	Ge
	$Ga_xIn_{1-x}As$

Energy gap vs. lattice constant for single-crystal III-V compounds and alloys



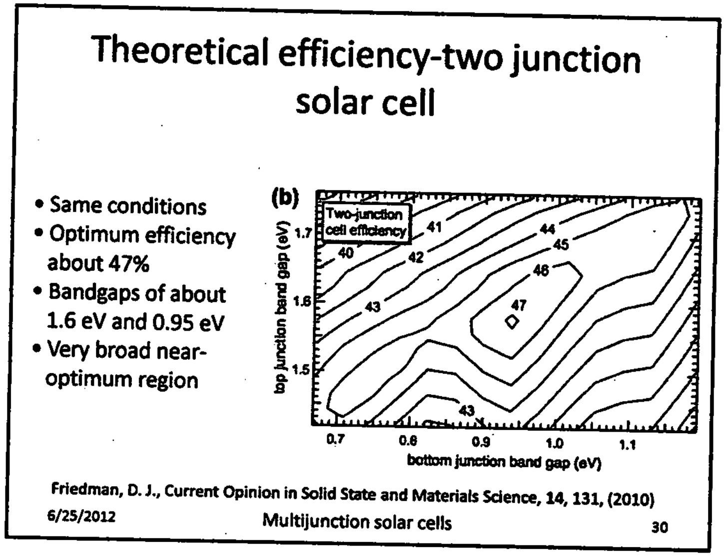
- This helps us select pairs of materials that are lattice matched
- This is necessary for very high efficiency cells to ensure high quality interfaces
- It does not ensure current-matching
- This must be done by modeling



Theoretical efficiency-single junction, single-crystal III-V solar cell

- 500 suns, ASTM G173 direct spectrum
- Assumes all photons absorbed, all charge collected and Voc=Eg/e -0.4
- Peak efficiency nearly 35% for Eg~1.1 eV

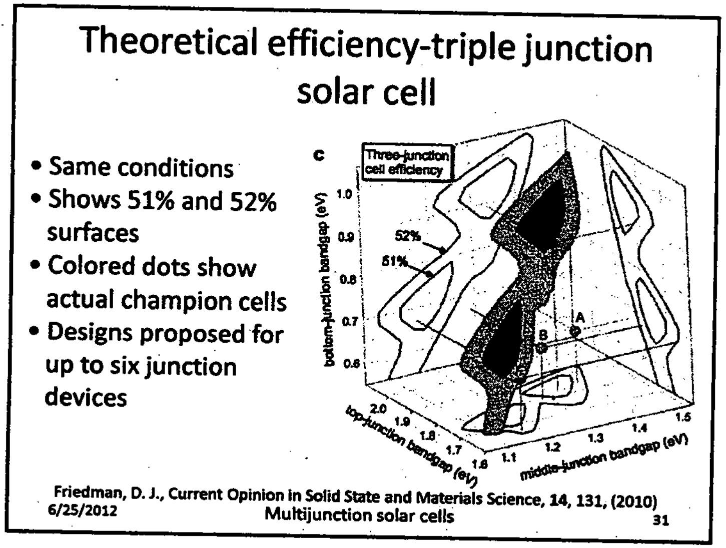
Friedman, D. J., Current Opinion in Solid State and Materials Science, 14, 131, (2010)



Theoretical efficiency-two junction solar cell

- Same conditions
- Optimum efficiency about 47%
- Bandgaps of about 1.6 eV and 0.95 eV
- Very broad near-optimum region

Friedman, D. J., Current Opinion in Solid State and Materials Science, 14, 131, (2010)



Theoretical efficiency-triple junction solar cell

- Same conditions
- Shows 51% and 52% surfaces
- Colored dots show actual champion cells
- Designs proposed for up to six junction devices

Friedman, D. J., Current Opinion in Solid State and Materials Science, 14, 131, (2010)

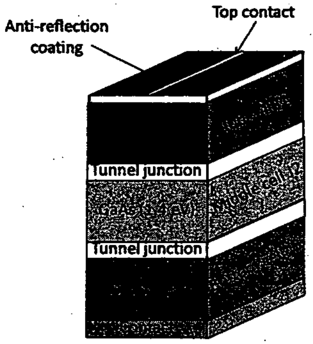
Possible means of increasing Jsc

- Improve current matching to direct spectrum-adjust bandgaps of sub-cells but maintain high quality materials
- Decrease minority carrier recombination at back contact
- Improve top cell emitter transmittance
- Improve broad band anti-reflection coating

T4-9

Conventional triple-junction cell

- The substrate and bottom junction are Ge
- Too low a bandgap, so current is wasted
- Several groups have achieved η > 40%
- Need a 1 eV bottom cell for ideal triple junction tandem



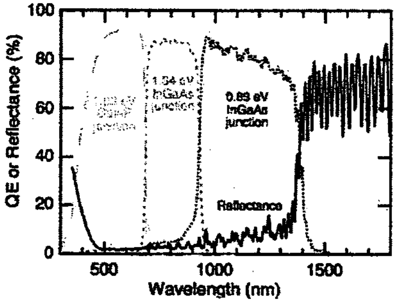
Inverted metamorphic module

- Grow an inverted structure of $Ga_{0.37}In_{0.63}As/Ga_{0.96}In_{0.04}As/Ga_{0.5}In_{0.5}P/GaAs$ with bandgaps of 0.9 eV, 1.34 eV, and 1.83 eV
- Substrate removed, structure inverted and mounted on a suitable handle
- Efficiency of 40.8% at 326 suns (direct spectrum)

Geisz, J. F. et al., J. Appl. Phys., 93, 123505, (2008)

QE of inverted IMM triple junction cell

- Efficiency of best cell was 40.8% at 326 suns
- Fill-factor was 88.4% and Voc = 3.28 V
- Efficiency was 39.2% at C = 841 suns
- Currents of all three cells were matched
- Area = 0.1 cm²



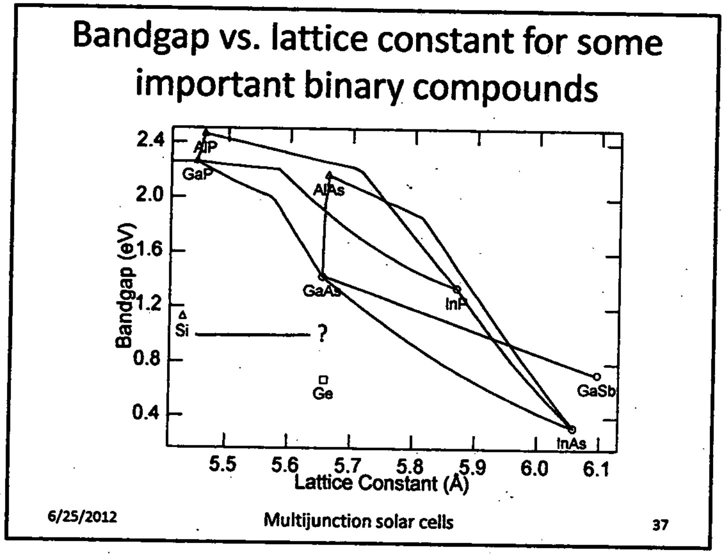
Geisz, J. F. et al., J. Appl. Phys., 93, 123505, (2008)

Broad-band anti-reflection coating

- Large increase in reflectance at long-and short-wavelength ends of spectral response
- Not possible to eliminate this with single, double or even triple layer ARC
- The loss amounts to about 2% absolute in efficiency
- Possibly use graded index coatings or graded porosity

Friedman, D. J., Current Opinion in Solid State and Materials Science, 14, 131, (2010)

T4-70



Bandgap vs. lattice constant for some important binary compounds

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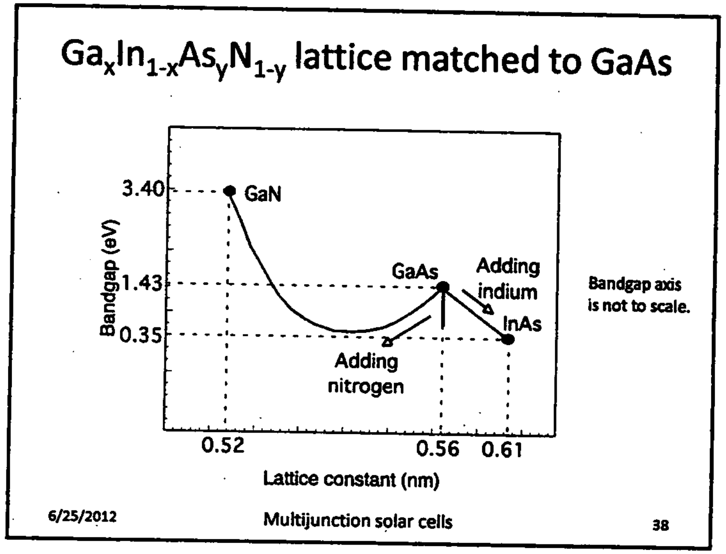

$Ga_xIn_{1-x}As_yN_{1-y}$ lattice matched to GaAs

Bandgap axis is not to scale.

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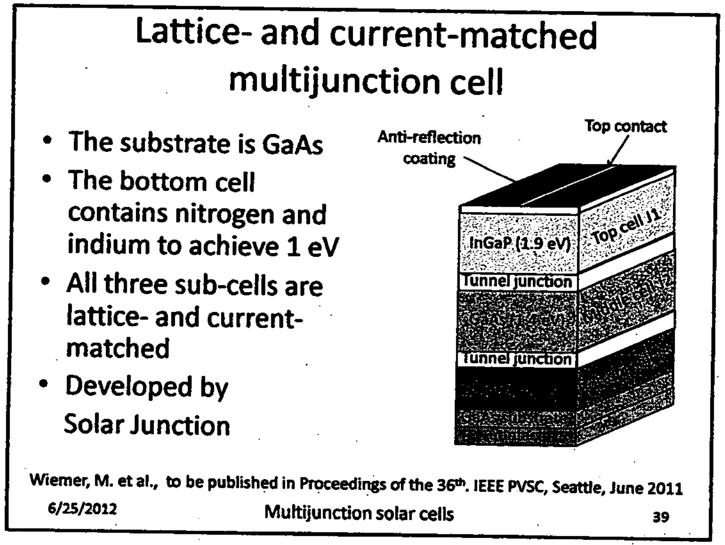

Lattice- and current-matched multijunction cell

- The substrate is GaAs
- The bottom cell contains nitrogen and indium to achieve 1 eV
- All three sub-cells are lattice- and current-matched
- Developed by Solar Junction

Wiemer, M. et al., to be published in Proceedings of the 36th. IEEE PVSC, Seattle, June 2011

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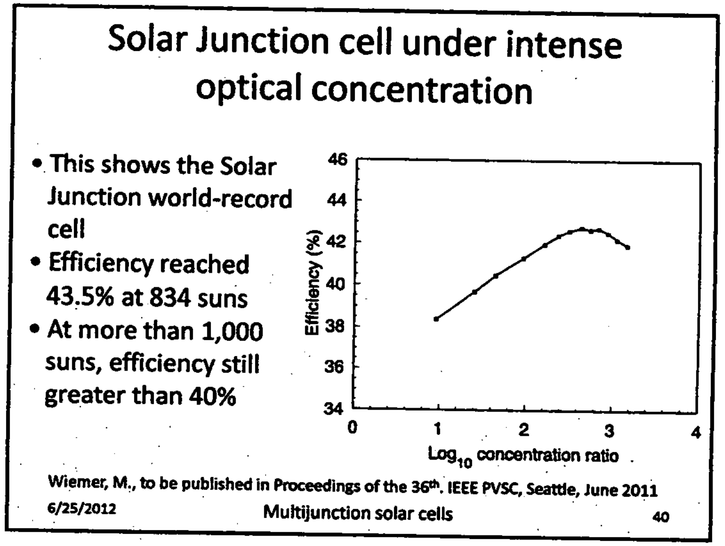

Solar Junction cell under intense optical concentration

- This shows the Solar Junction world-record cell
- Efficiency reached 43.5% at 834 suns
- At more than 1,000 suns, efficiency still greater than 40%

Wiemer, M., to be published in Proceedings of the 36th. IEEE PVSC, Seattle, June 2011

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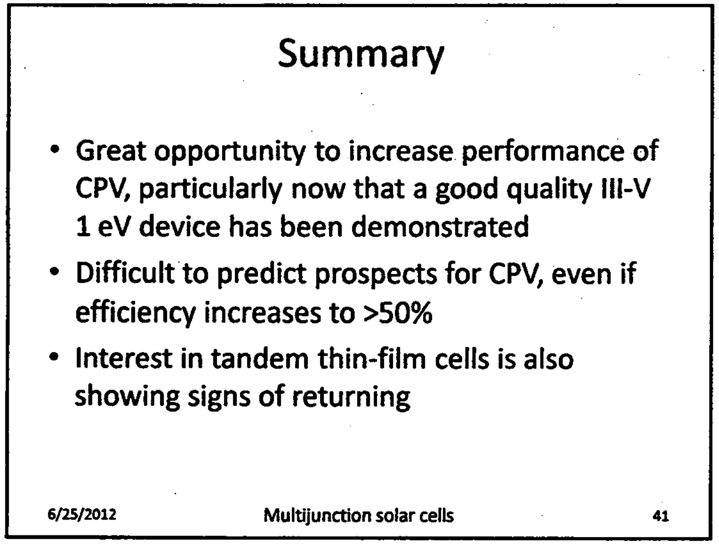
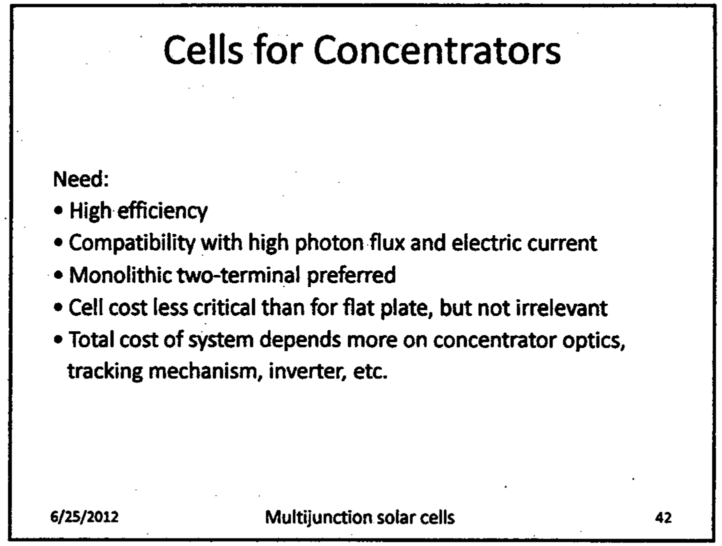
T4-11



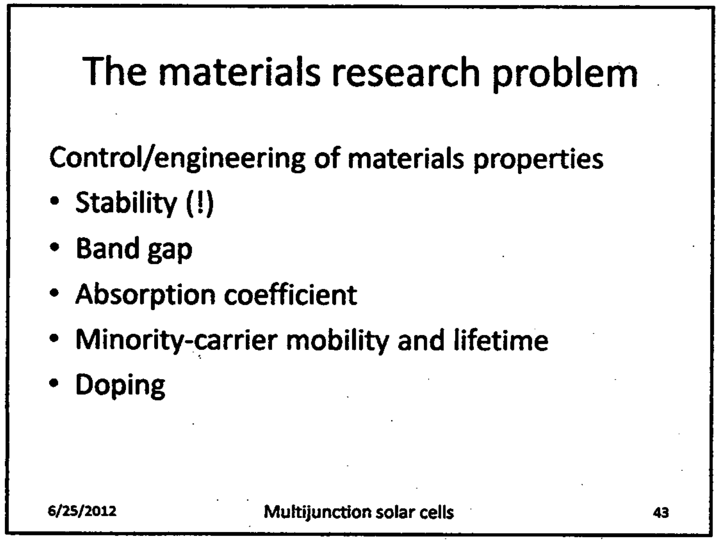
Summary

- Great opportunity to increase performance of CPV, particularly now that a good quality III-V 1 eV device has been demonstrated
- Difficult to predict prospects for CPV, even if efficiency increases to >50%
- Interest in tandem thin-film cells is also showing signs of returning



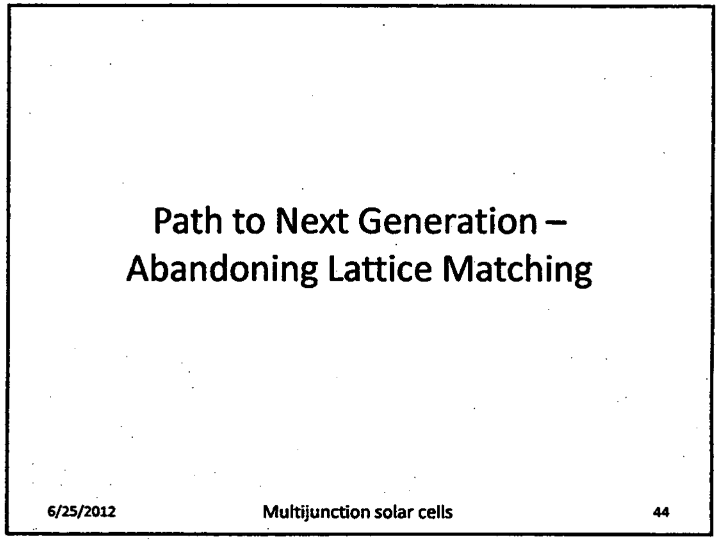
Cells for Concentrators

Need:
- High efficiency
- Compatibility with high photon flux and electric current
- Monolithic two-terminal preferred
- Cell cost less critical than for flat plate, but not irrelevant
- Total cost of system depends more on concentrator optics, tracking mechanism, inverter, etc.



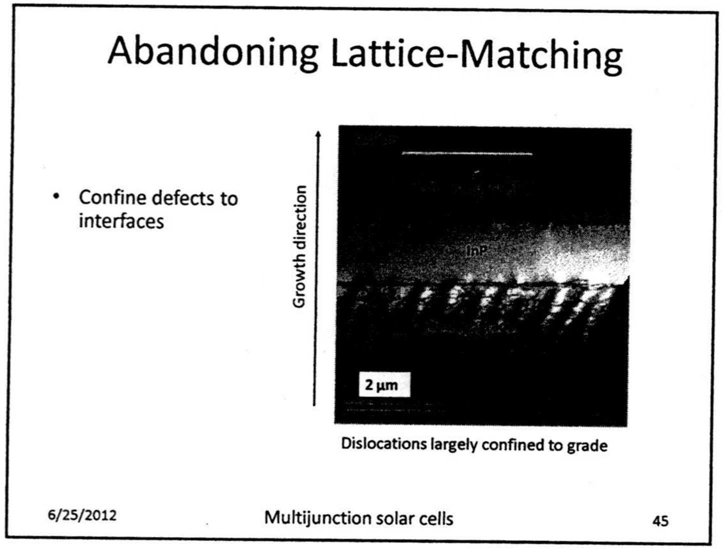
The materials research problem

Control/engineering of materials properties
- Stability (!)
- Band gap
- Absorption coefficient
- Minority-carrier mobility and lifetime
- Doping



Path to Next Generation – Abandoning Lattice Matching

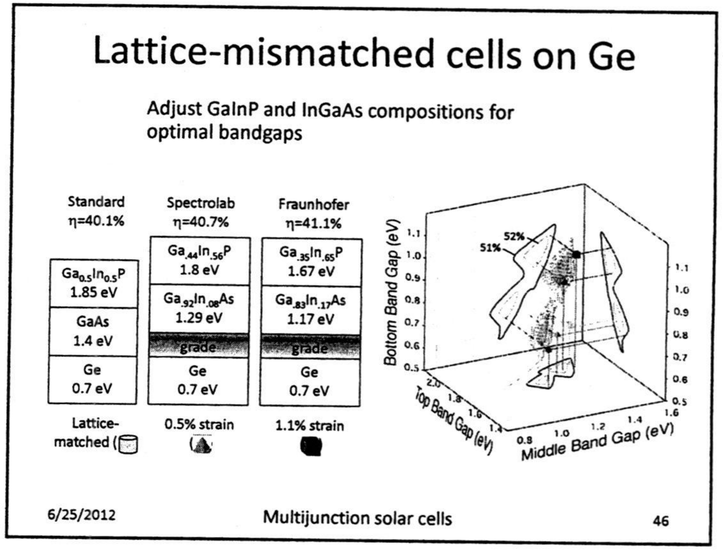
7-4-12



Abandoning Lattice-Matching

- Confine defects to interfaces

Dislocations largely confined to grade



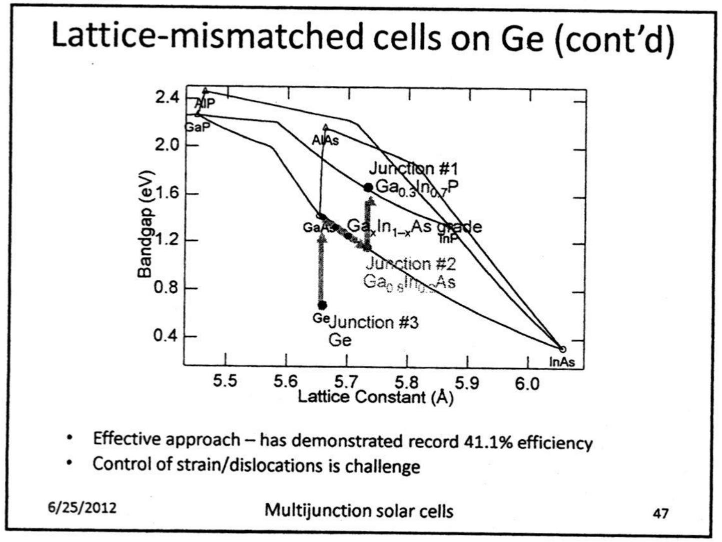
Lattice-mismatched cells on Ge

Adjust GaInP and InGaAs compositions for optimal bandgaps

Standard
η=40.1%
$Ga_{0.5}In_{0.5}P$ 1.85 eV
GaAs 1.4 eV
Ge 0.7 eV
Lattice-matched (

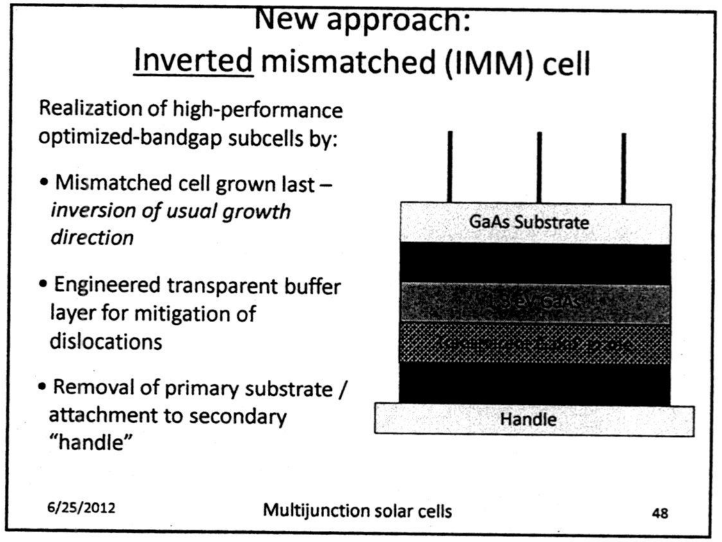
Spectrolab
η=40.7%
$Ga_{.44}In_{.56}P$ 1.8 eV
$Ga_{.92}In_{.08}As$ 1.29 eV
grade
Ge 0.7 eV
0.5% strain

Fraunhofer
η=41.1%
$Ga_{.35}In_{.65}P$ 1.67 eV
$Ga_{.83}In_{.17}As$ 1.17 eV
grade
Ge 0.7 eV
1.1% strain



Lattice-mismatched cells on Ge (cont'd)

- Effective approach – has demonstrated record 41.1% efficiency
- Control of strain/dislocations is challenge

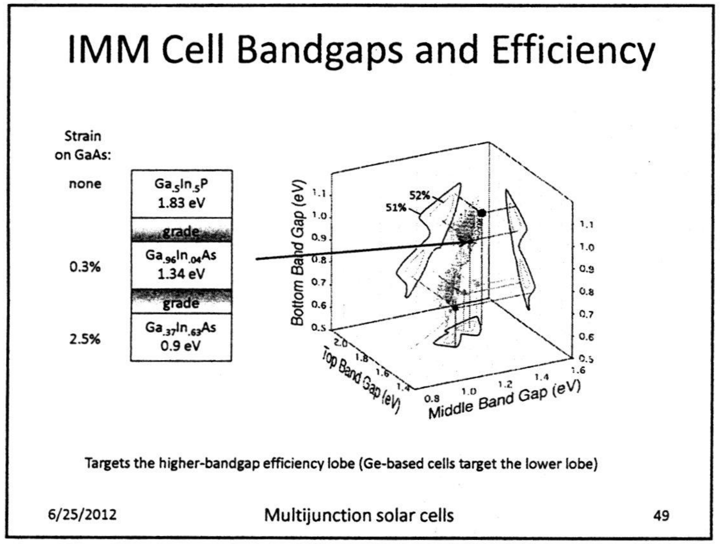


New approach: Inverted mismatched (IMM) cell

Realization of high-performance optimized-bandgap subcells by:

- Mismatched cell grown last – *inversion of usual growth direction*
- Engineered transparent buffer layer for mitigation of dislocations
- Removal of primary substrate / attachment to secondary "handle"

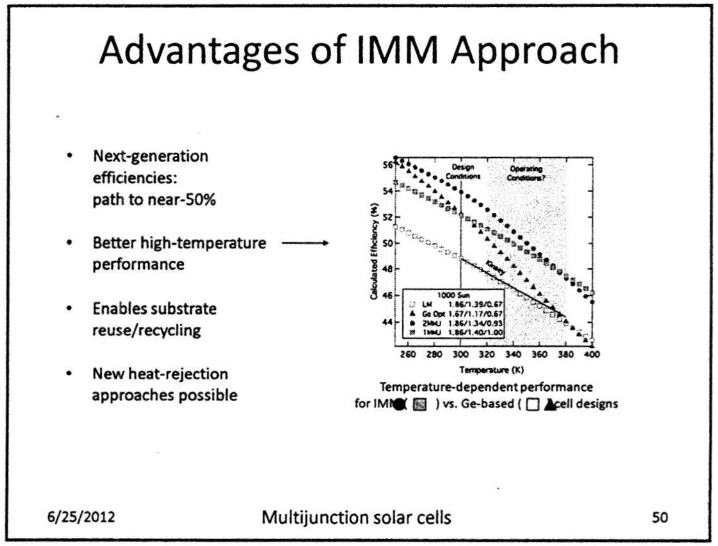
T4-



IMM Cell Bandgaps and Efficiency

Strain on GaAs:	
none	$Ga_{.5}In_{.5}P$ 1.83 eV
	grade
0.3%	$Ga_{.96}In_{.04}As$ 1.34 eV
	grade
2.5%	$Ga_{.37}In_{.63}As$ 0.9 eV

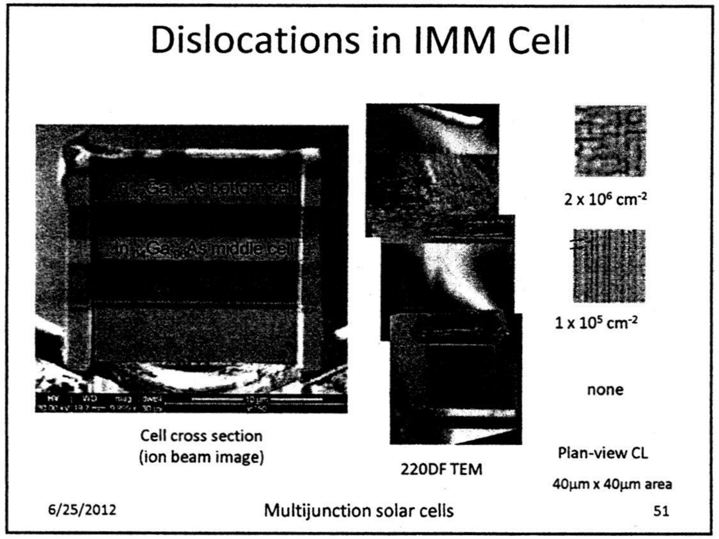
Targets the higher-bandgap efficiency lobe (Ge-based cells target the lower lobe)



Advantages of IMM Approach

- Next-generation efficiencies: path to near-50%
- Better high-temperature performance →
- Enables substrate reuse/recycling
- New heat-rejection approaches possible

Temperature-dependent performance
for IMM (● ▨) vs. Ge-based (□ ▲) cell designs



Dislocations in IMM Cell

Cell cross section
(ion beam image)

220DF TEM

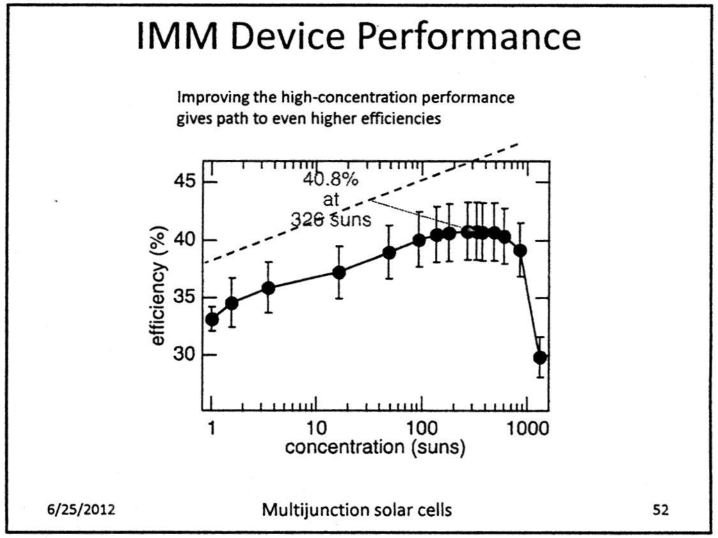
2 x 10^6 cm^{-2}

1 x 10^5 cm^{-2}

none

Plan-view CL

40μm x 40μm area



IMM Device Performance

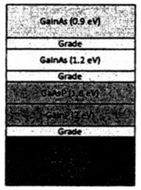
Improving the high-concentration performance
gives path to even higher efficiencies

Four Junctions

Going to four junctions: potential for further performance advances

1.86 eV	2.03 eV
1.34 eV	1.56 eV
0.93 eV	1.21 eV
	0.92 eV
optimal 3 junc. | =53%	optimal 4 junc. | =57%

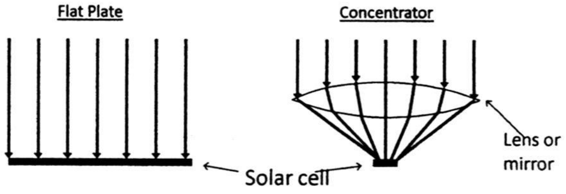
IMM approach gives a path to this goal



four-junc. IMM concept

Concentrator photovoltaics

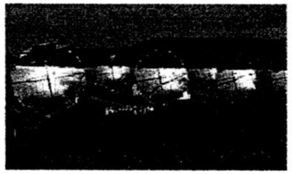
Use optics to reduce the equivalent cell area, by ~2 to 1000 times



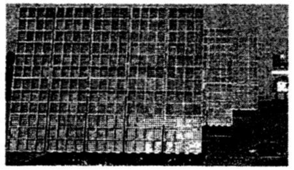
- Shifts the major system cost from the cell to the optics and tracking
- Can afford more efficient, expensive cells

… to Utilities (1–100 MW)

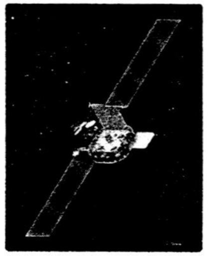
Mirror-based system
130 m² dish, 500 suns,
water cooled
24 kW with Si cells,
35 kW with multijunc.



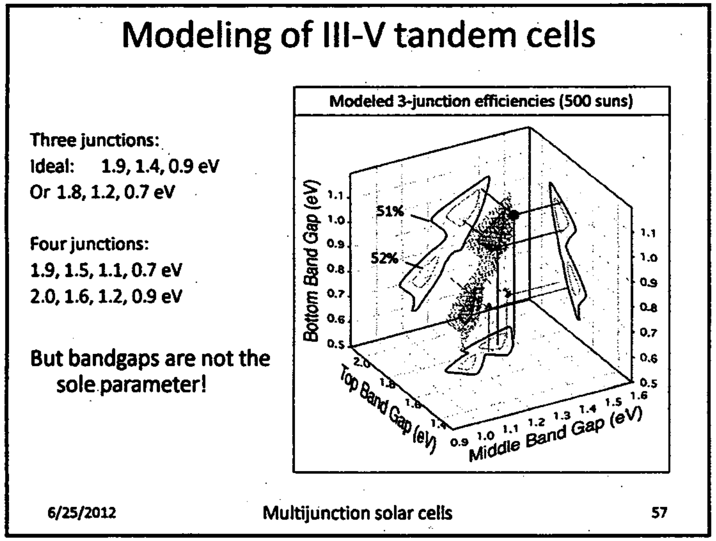
Lens-based system
25 kW units shown, at
Ariz. Public Service



Multijunctions also used in Space



T4-15



Modeling of III-V tandem cells

Three junctions:
Ideal: 1.9, 1.4, 0.9 eV
Or 1.8, 1.2, 0.7 eV

Four junctions:
1.9, 1.5, 1.1, 0.7 eV
2.0, 1.6, 1.2, 0.9 eV

But bandgaps are not the sole parameter!

Modeled 3-junction efficiencies (500 suns)

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