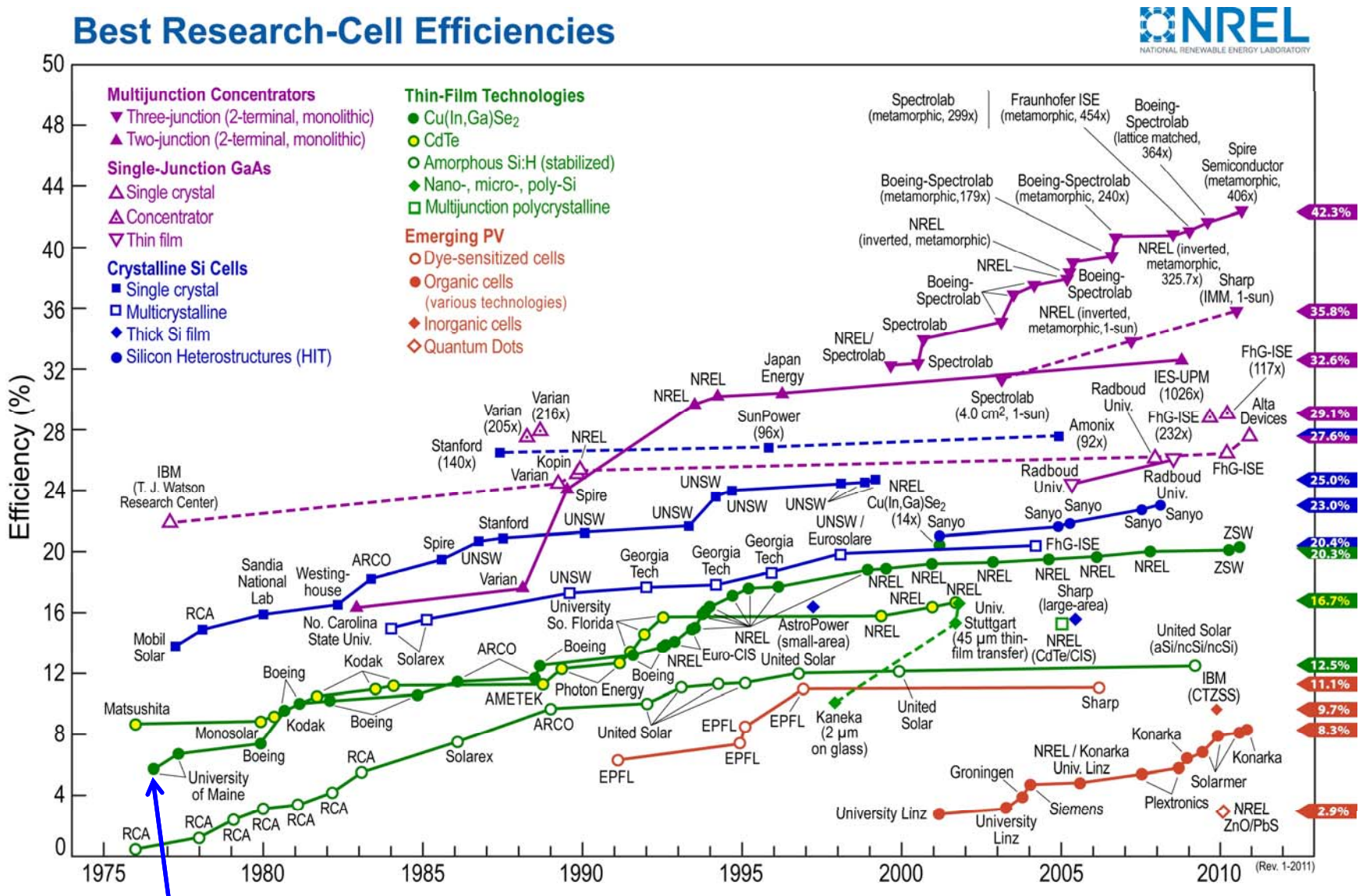
CIGS Photovoltaic Technology

- materials
- devices
- methods

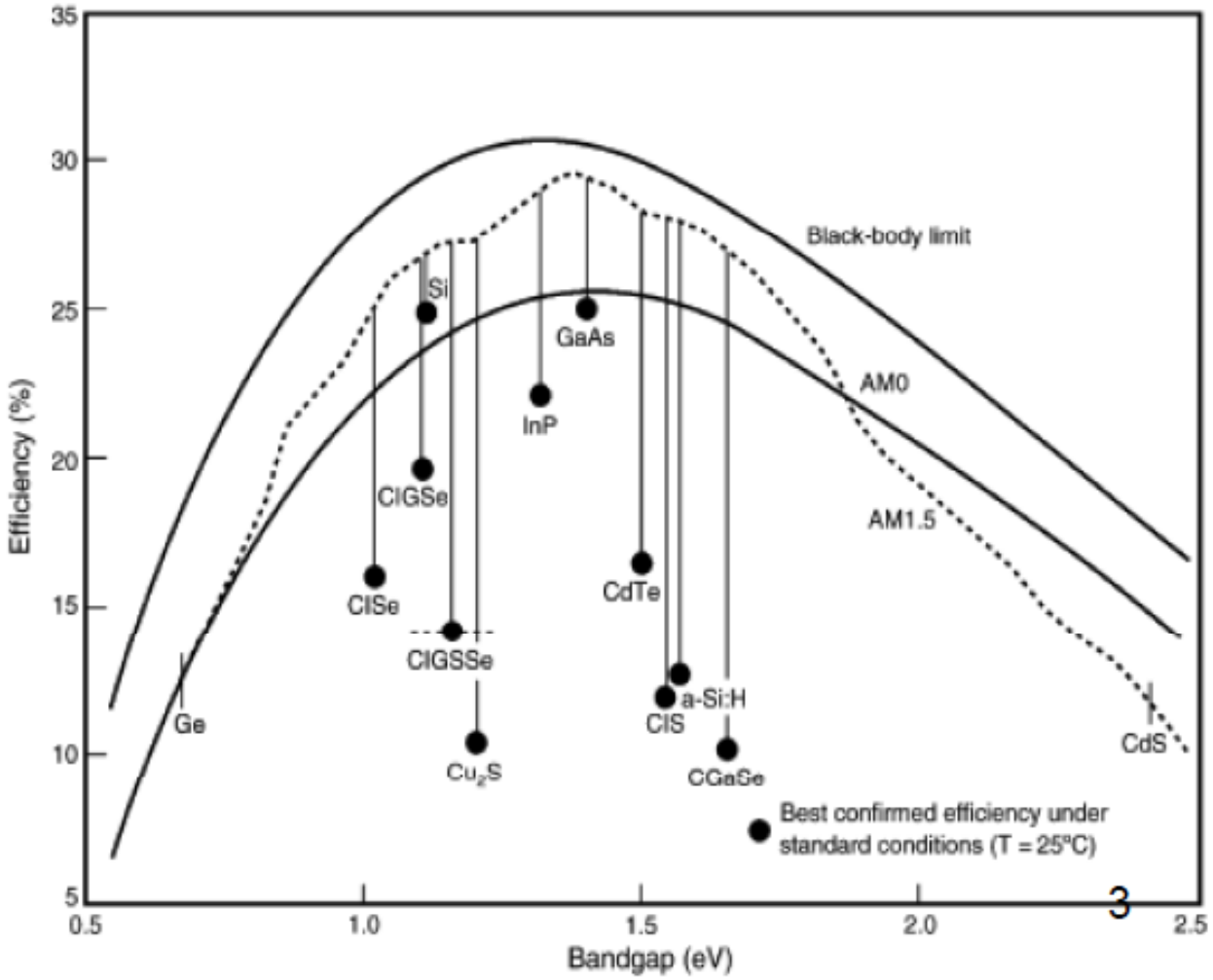


Cu (In,Ga) Se_2 ……i.e., Copper Chalcopyrites

Journal of Electron Spectroscopy and Related Phenomena 150 (2006) 105–135

Solar photovoltaics R&D at the tipping point: A 2005 technology overview

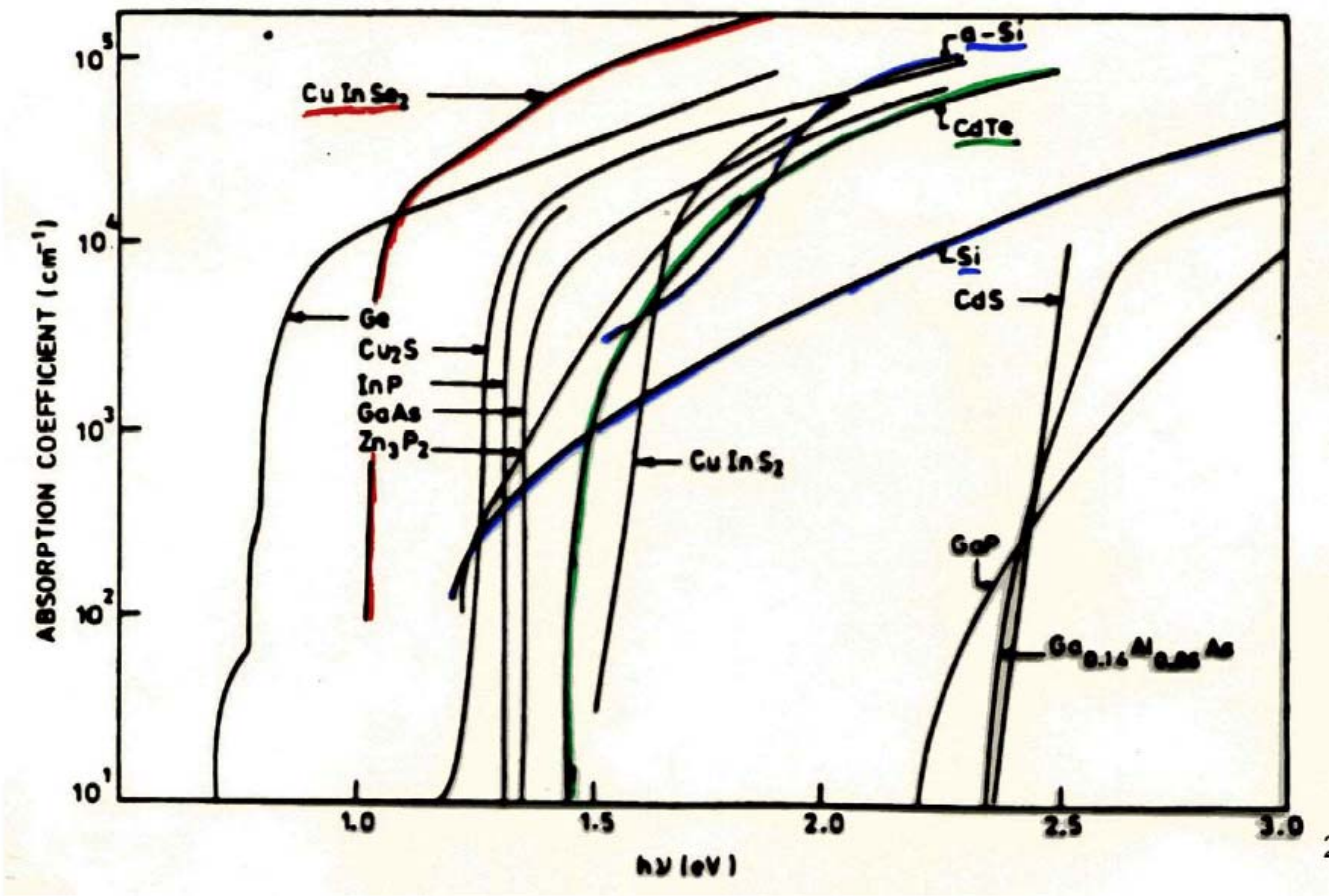
Lawrence L. Kazmerski



	Laboratory Cell Efficiency	Best in Class Production Module	Typical Production
CPV	~40%	~32%	~29%
c-Si	~25%	~20%	~18%
mc-Si	~20%	~17%	~14%
CIGS	~20%	~11%	~11%
CdTe	~16%	~11%	~11%
a-Si	~12%	~8%	~8%
OPV	~7%	~4%	~2%

Presentation by John Lushetsky, DOE Solar Program, Grid Parity and Beyond –Challenges and Opportunities, *NIST Workshop for Advances in PV Technologies and Measurements,* May 12, 2010, Denver, CO

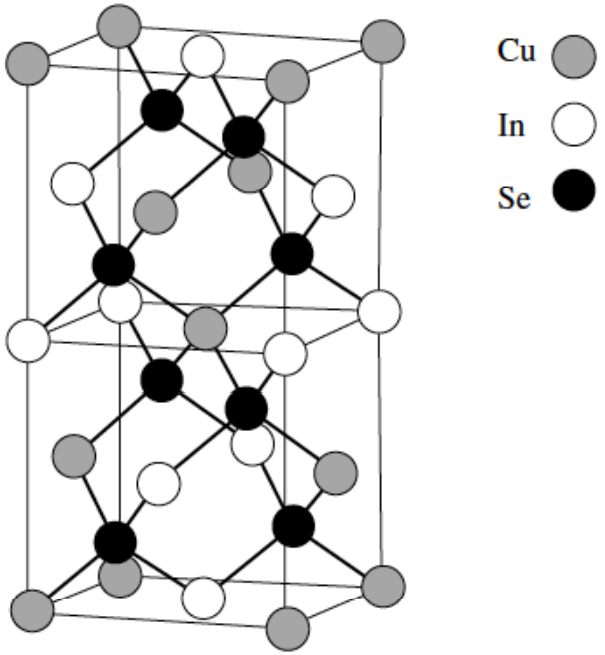
Absorption spectra of various semiconductors



Courtesy of Al Compaan

Crystal Structure

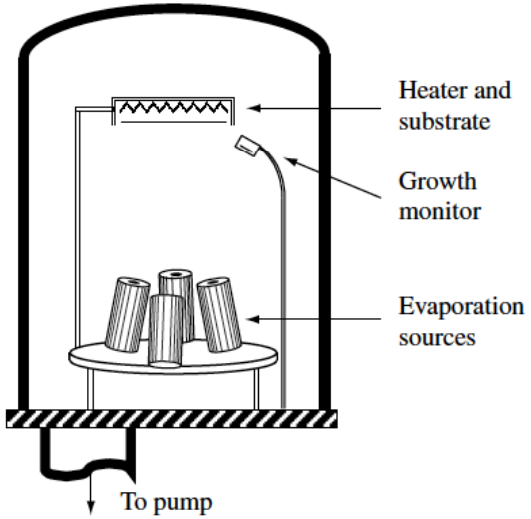
- $CuInSe_2$ and $CuGaSe_2$ have the chalcopyrite lattice structure.
- Diamond-like structure similar to the sphalerite (zincblende) structure but with an ordered substitution of the group I (Cu) and group III (In or Ga) elements on the group II (Zn) sites of sphalerite.
- Tetragonal unit cell, *c/a close to 2.*
- Deviation from *c/a = 2* due to different strengths for Cu–Se and In–Se, Ga–Se bonds.



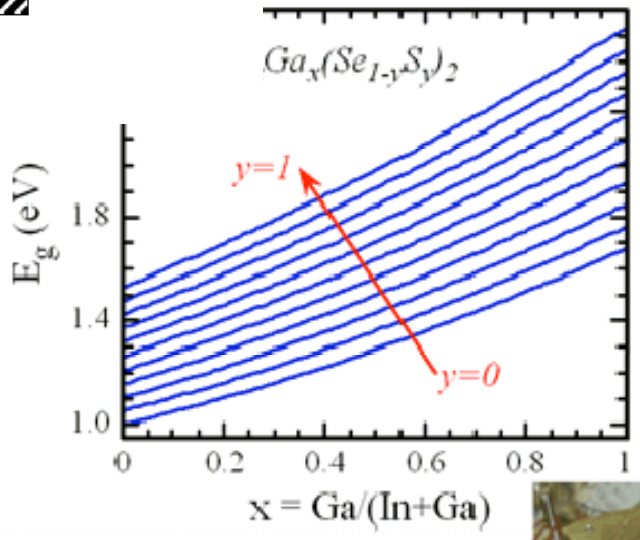
Group: I III VI

$$\begin{pmatrix}\mathrm{Cu}\\ \mathrm{Ag}\\ \mathrm{Au}\end{pmatrix}\begin{pmatrix}\mathrm{Al}\\ \mathrm{Ga}\\ \mathrm{In}\end{pmatrix}\begin{pmatrix}\mathrm{S}\\ \mathrm{Sc}\\ \mathrm{Te}\end{pmatrix}_2$$

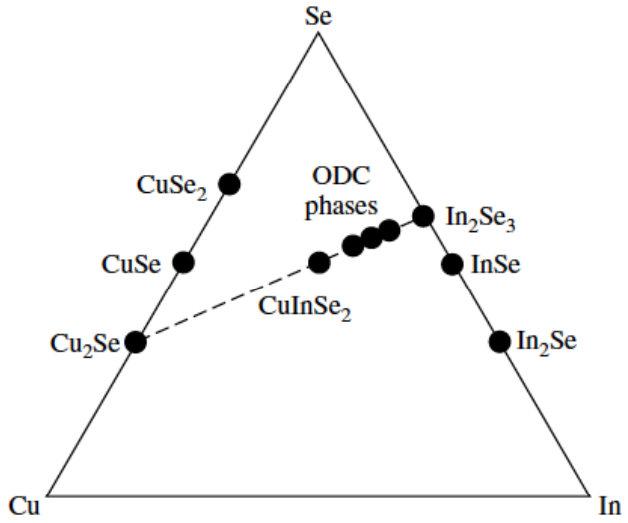
From "$Cu(InGa)Se_2$ Solar Cells", by Shafarman and Stolt, and *Wikipedia*



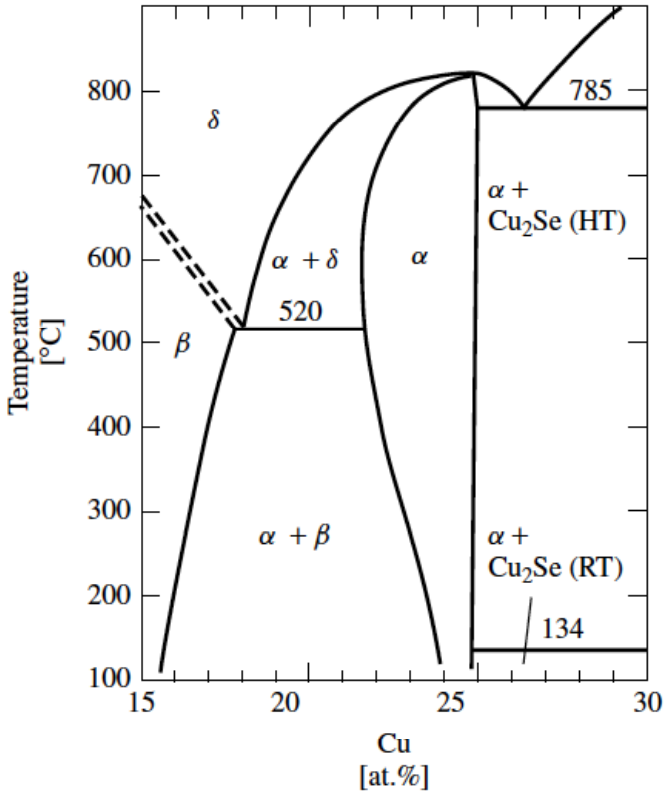
At IEC Cu(InGa)(SeS)$_2$ films are deposited by five source elemental evaporation (right) and by the reaction of Cu-Ga-In films in H_2Se and H_2S



http://www.udel.edu/iec/CIGS.html



Ternary phase diagram of the Cu–In–Se system. Thin-film composition is near the pseudobinary Cu_2Se–In_2Se_3 tie-line



Pseudobinary In2Se3–Cu2Se equilibrium phase diagram for compositions around the CuInSe2 chalcopyrite phase, denoted *α. The δ phase is the high-temperature sphalerite phase,* and the *β phase is an ordered defect phase (ODC). Cu2Se exists as a room-temperature (RT) or* high-temperature (HT) phase. (After G¨odecke T, Haalboom T, Ernst F, *Z. Metallkd.* ***91, 622–634*** (2000) [32])

From "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

History of CIGS

- $CuInSe_2$ was first synthesized and characterized in 1953 by Hahn et al.
- Solar cell-relevant work started at Bell Laboratories in the early 1970s. A wide selection of ternary chalcopyrite crystals were grown and characterized (structural, electronic, and optical properties).
- The first $CuInSe_2$ solar cells were made by evaporating *n-type CdS onto p-type single*
- crystals of CuInSe2 by Shay et al. in 1974. Potential as near-infrared photodetectors since their spectral response was broader and more uniform than Si photodetectors.
- Shay et al. in 1975, increased the solar cell efficiency to 12% as measured under outdoor illumination "on a clear day in New Jersey".
- Relatively little effort has been devoted to single-crystal $CuInSe_2$ devices since the early work, due to, at least in part, the difficulty in growing high-quality crystals.
- The first thin-film CuInSe2/CdS devices (~ 6 – 7%) were fabricated in 1976 by Kazmerski *et al.* using films deposited by evaporation of CuInSe2 powder along with excess Se.
- Thin-film CuInSe2 solar cells began to receive a lot of attention when 9.4%, cells were demonstrated by Mickelsen et al. from Boeing, in 1981.
- With this advance, interest in Cu2S/CdS thin-film solar cells waned due to problems related to electrochemical instabilities, and many of these researchers turned their focus to CuInSe2.

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

From its earliest development, CuInSe2 was considered promising for solar cells because of its favorable electronic and optical properties including its direct band gap with high absorption coefficient and inherent *p-type conductivity. As science and technology* developed, it also became apparent that it is a very forgiving material since:

(1) high efficiency devices can be made with a wide tolerance to variations in Cu(InGa)Se2 composition,

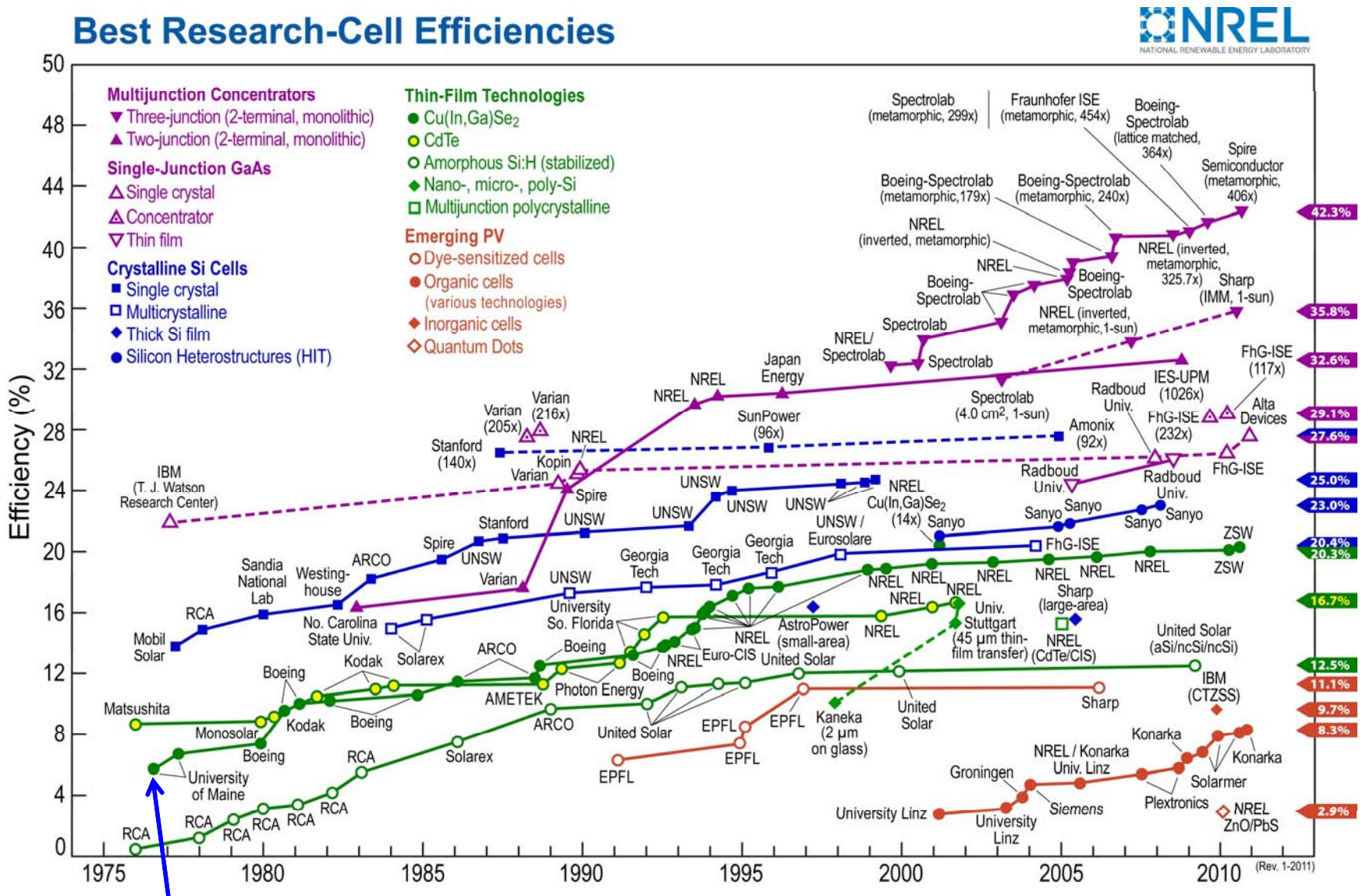
(2) grain boundaries are inherently passive so even films with grain sizes less than 1 μm can be used, and

(3) device behavior is insensitive to defects at the junction caused by a lattice mismatch or impurities between the Cu(InGa)Se2 and CdS. The latter enables high-efficiency devices to be processed despite exposure of the Cu(InGa)Se2 to air prior to junction formation.

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

- Boeing Devices:
  - CuInSe2 deposited by co-evaporation, i..e evaporation from separate elemental sources, onto ceramic substrates coated with a Mo back electrode.
  - Heterojunction partner formed by evaporation of CdS or (CdZn)S in two layers: undoped CdS followed by an In-doped CdS (to aid in current conduction)
- In 1980s, Boeing and ARCO Solar began to address the difficult manufacturing issues related to scale-up, yield, and throughput leading to many advancements in CuInSe2 solar cell technology.
- These two basic approaches to CuInSe2 deposition remain the most common deposition methods and produce the highest device and module efficiencies.
- Boeing focused on depositing Cu(InGa)Se2 by co-evaporation,
- ARCO Solar focused on a two-stage process of Cu and In deposition at a low temperature followed by a reactive anneal in H2Se.

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

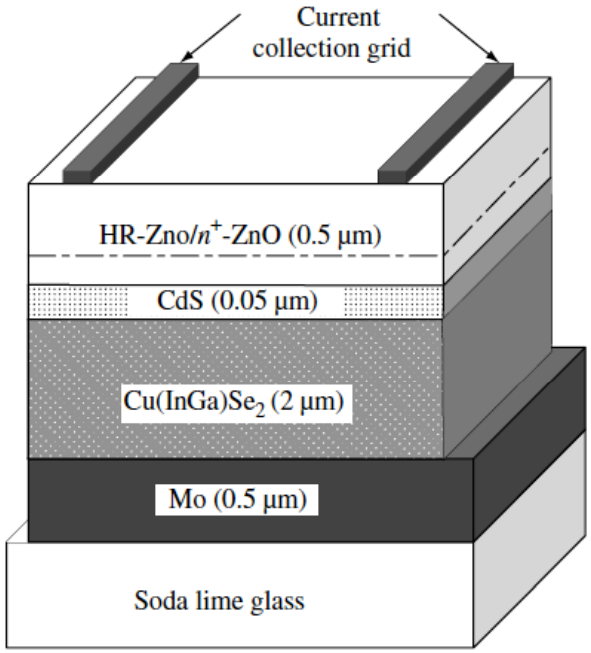


Cu (In,Ga) Se_2 ……i.e., Copper Chalcopyrites

All the solar cells have the same basic cell structure built around a Cu(InGa)Se2/CdS junction in a substrate configuration.

Soda lime glass substrate, coated with a sputtered Mo layer as a back contact.

After the Cu(InGa)Se2 deposition, the junction is formed by chemical bath–deposited CdS with thickness ≤5 0 nm. Then a high-resistance (HR) ZnO layer and a doped high-conductivity ZnO layer are deposited, usually by sputtering or chemical vapor deposition. Either a current-collecting grid or monolithic series interconnection completes the device or module, respectively.



Schematic cross section of a typical Cu(InGa)Se_2 solar cell

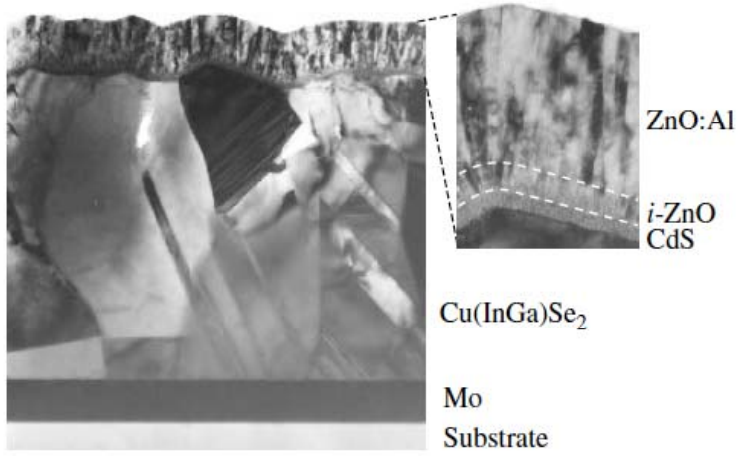
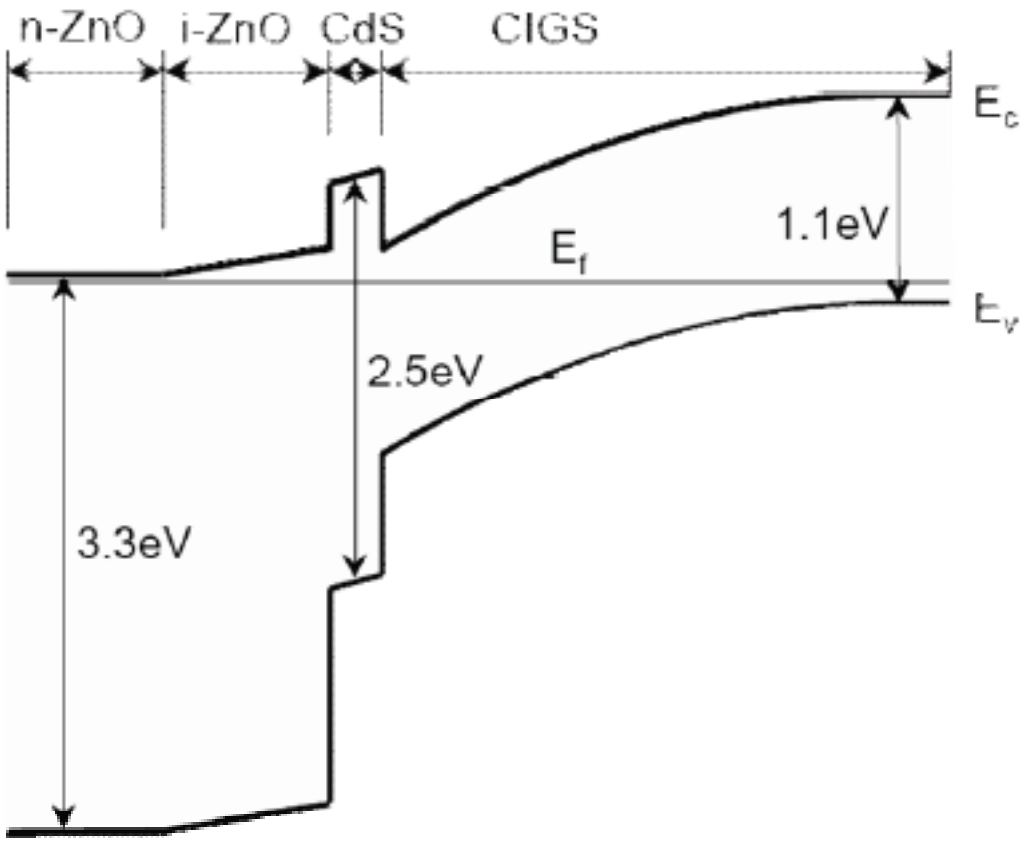


Figure 13.2 TEM cross section of a Cu(InGa)Se_2 solar cell

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*



http://www.tf.uni-kiel.de/matwis/amat/matwissem_en/kap_6/illustr/gerngross_reverey_paper_ws_08_1.pdf

The basic solar cell configuration implemented by Boeing provided the basis for a series of improvements that have lead to the high-efficiency device technology of today.

The most important of these improvements to the technology include the following:

(1) The absorber-layer band gap was increased from 1.02 eV for CuInSe2 to 1.1–1.2 eV by the partial substitution of In with Ga, leading to a substantial increase in efficiency [Chen et al., 1987].

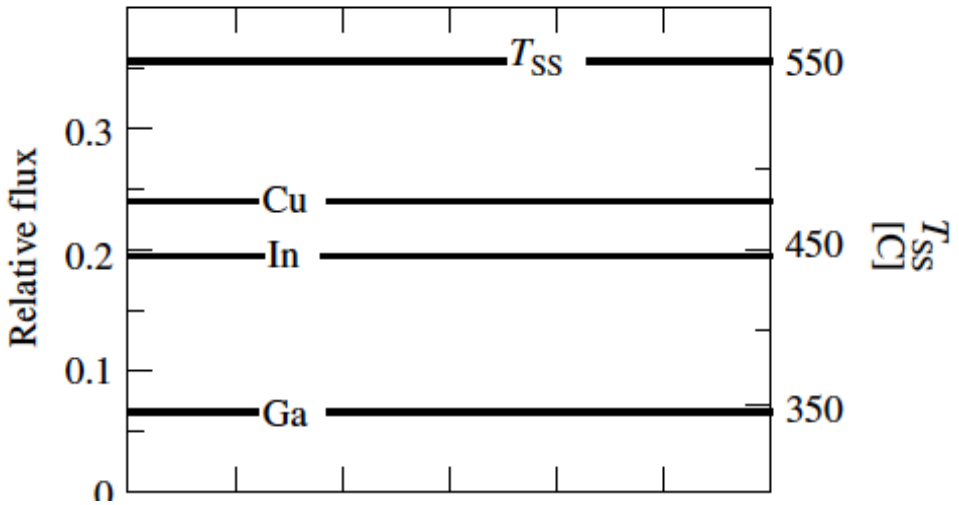
(2) The 1- to 2-µm-thick doped (CdZn)S layer was replaced with a thin, ≤50 nm, undoped CdS and a conductive ZnO current-carrying layer [Potter, 1986]. This increased the cell current by increasing the short wavelength (blue) response.

(3) Soda lime glass replaced ceramic or borosilicate glass substrates. Initially, this change was made for the lower costs of the soda lime glass and its good thermal expansion match to CuInSe2. However, it soon became clear that an increase in device performance and processing tolerance resulted primarily from the beneficial indiffusion of sodium from the glass [Hedstrom, *1993).*

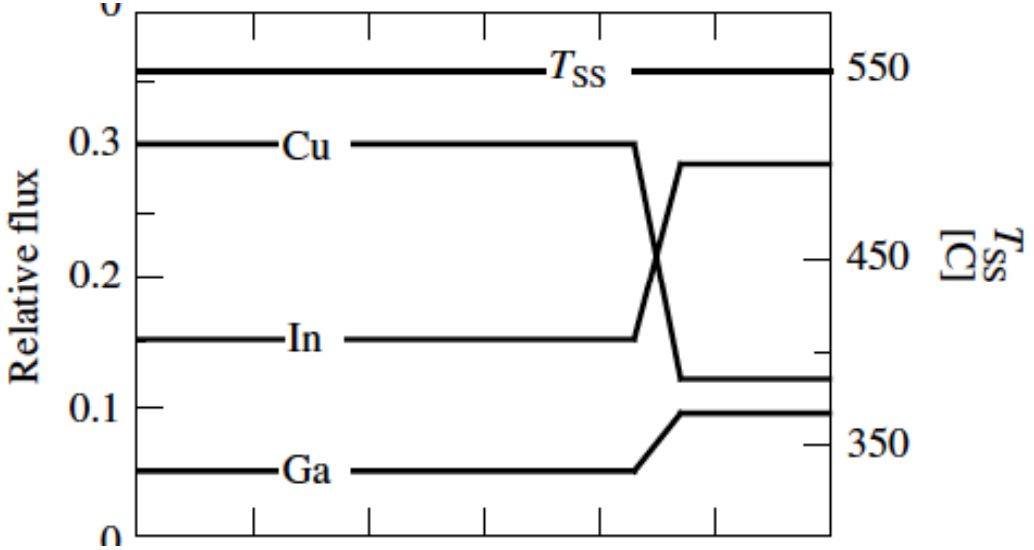
(4) Advanced absorber fabrication processes were developed that incorporate band gap gradients that improve the operating voltage and current collection [Gabor, 1996, Tarrant, 1993].

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

Simplest stationary process: all fluxes are constant.



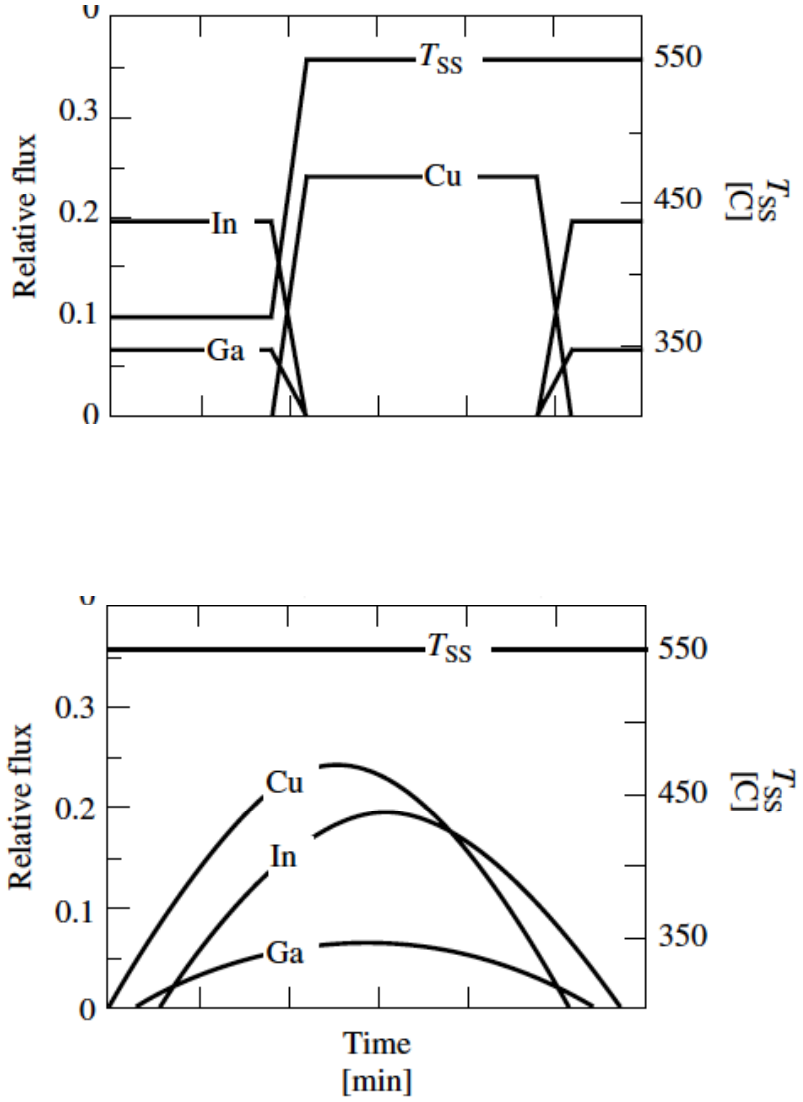
"the Boeing process" - the bulk of the film is grown to be Cu rich in overall composition so that it contains a Cu*xSe phase in addition to Cu(InGa)Se2.* The fluxes are then adjusted to finish the deposition with In- and Ga-rich flux so that the final film composition has the desired Cu-deficient composition.



After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

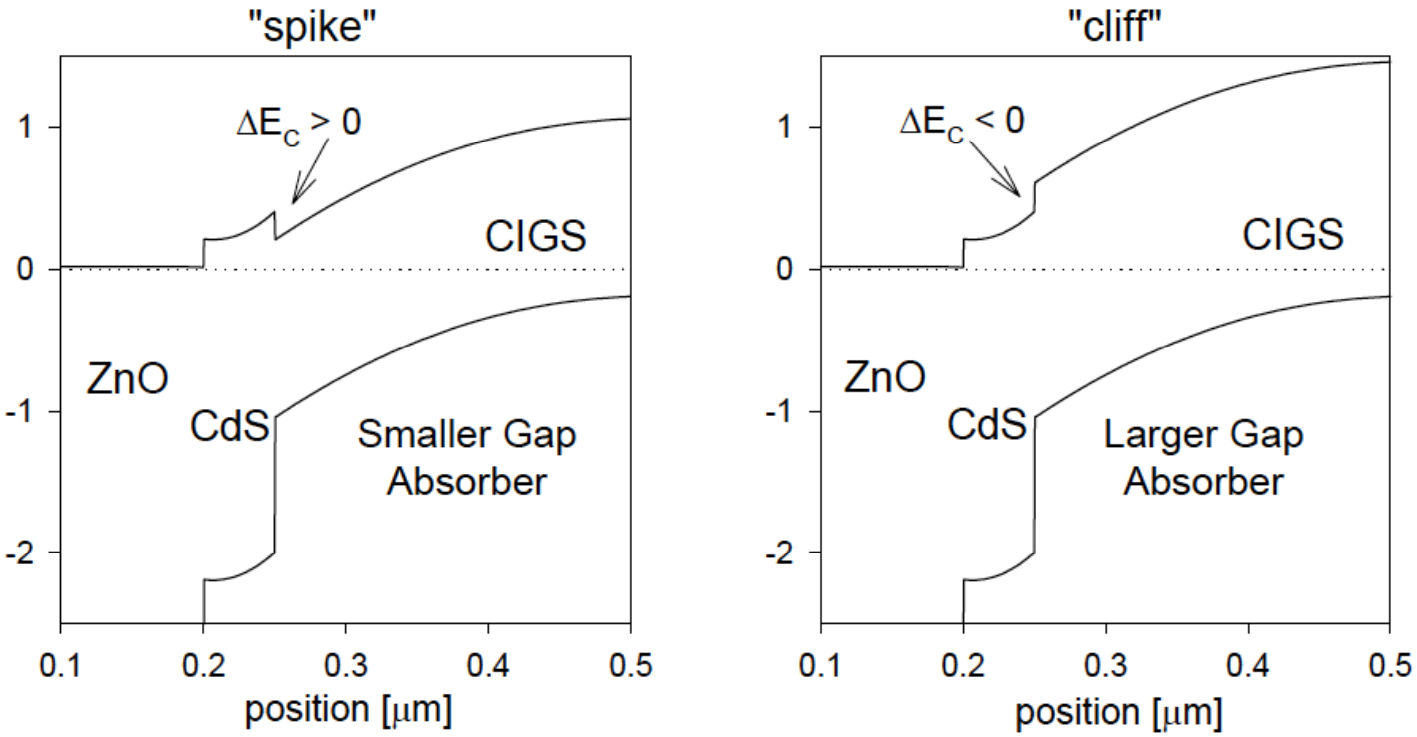
In and Ga are deposited separately initially to form a an (InGa)*xSey compound, followed by the deposition of Cu and* Se until the growing film reaches the desired composition. The layers interdiffuse to form the Cu(InGa)Se2 film. Gabor *et al. allowed the Cu flux to reach a*n overall Cu-rich composition. Then a third step is added to the process in which In and Ga, again in the presence of excess Se, are evaporated to bring the composition back to Cu-deficient. The metals interdiffuse, forming the ternary chalcopyrite film. This process produces the highest efficiency, due band gap grading and improved crystallinity.

Process on moving belt



After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

Sign Convention for ∆E_C



Spike can impede photoelectrons (may be bad)

Cliff slows forward electrons in interfacial-recombination region (also may be bad)

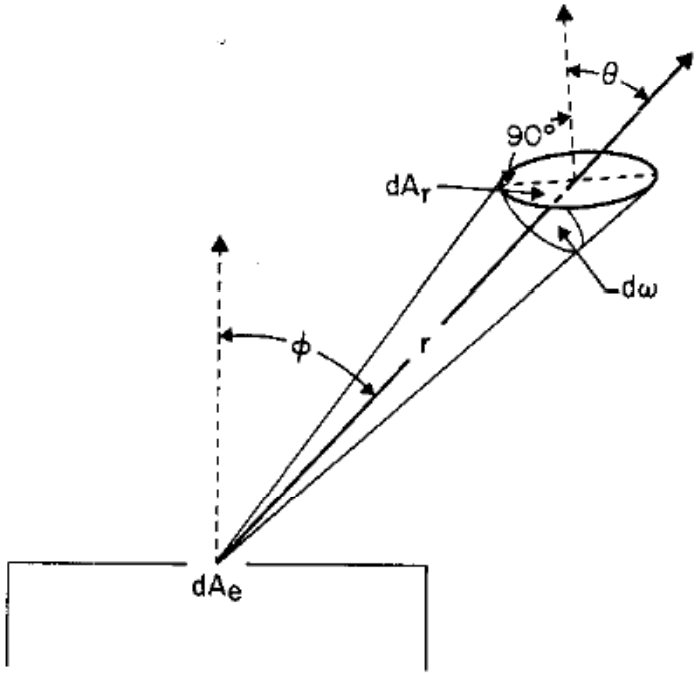
Some consensus on ∆E_C magnitudes between theory, experiment, and numerical simulations of J-V curves

http://www.physics.colostate.edu/groups/photovoltaic/PDFs/EMRS04.pdf

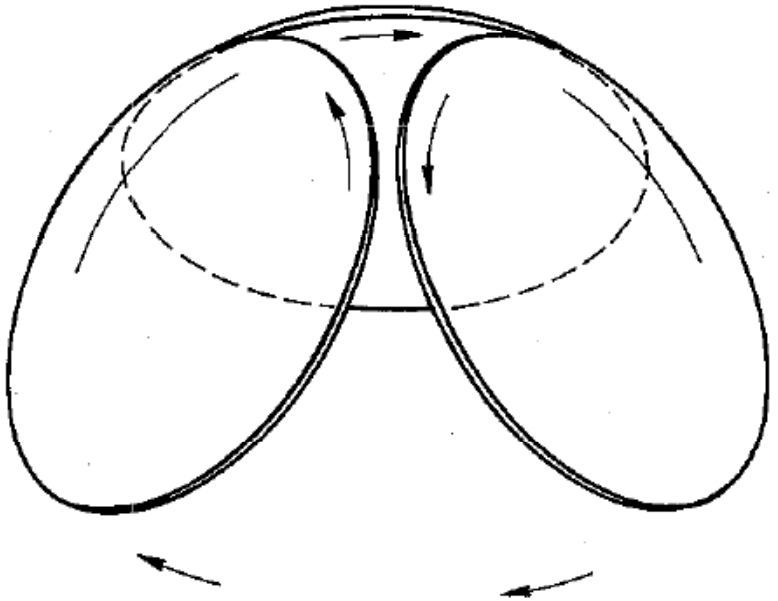
- *EC's in-line evaporation system for the deposition of Cu(InGa)Se2 on a moving substrate can be used with flexible web (plastic or metal foil) in a roll-to-roll configuration or with glass substrates.*

http://www.udel.edu/iec/CIGS.html

Evaporation Control



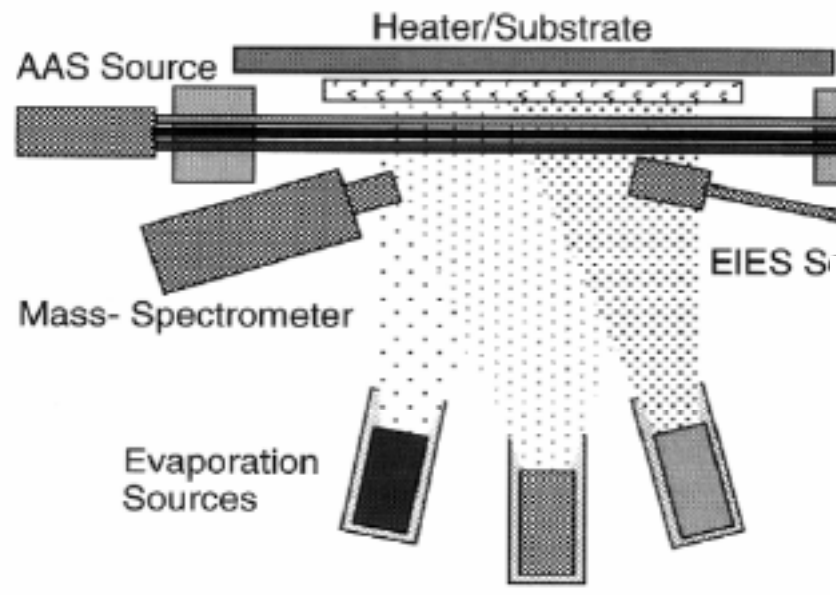
Evaporation Geometry



Substrate Motion

Sze, Figs. 4, 5, p. 394-95

http://www.seas.harvard.edu/crozier/PDFs/ES174_06_Microfabrication_L5.pdf



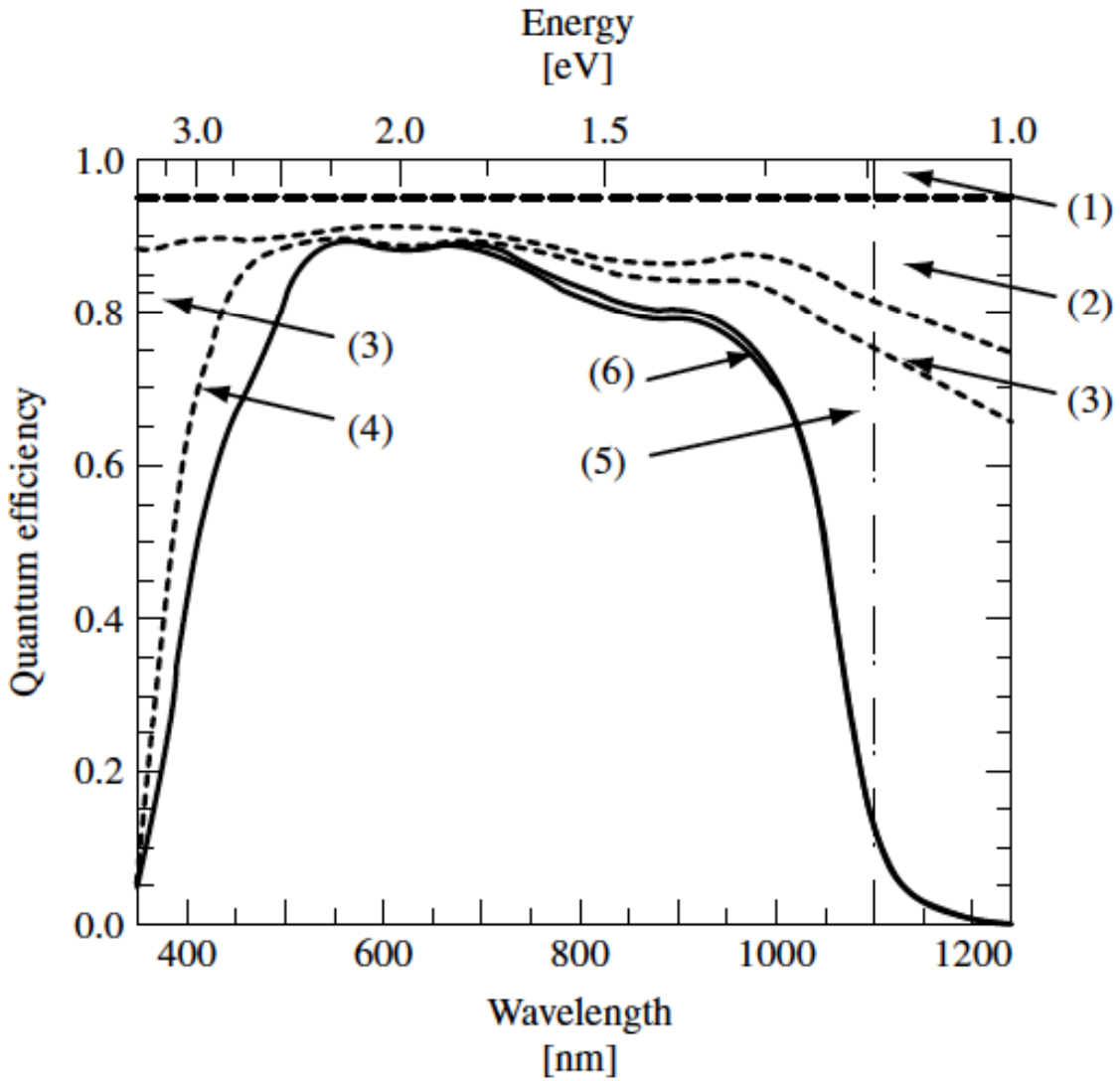
http://www.tf.uni-kiel.de/matwis/amat/matwissem_en/kap_6/illustr/gerngross_reverey_paper_ws_08_1.pdf

Table 1. Summary of Process Monitors Currently Used in CIGS Co-Evaporation

Method	Probe	Features	System	Cost	Commercially Available
TC	Source Temperature	Rate of One Element	Lab, Industry	$	Yes
QCM	Quartz Crystal	Rate of One Element	Lab	$$	Yes
QMS	Mass Ion	Flux of Multiple Elements	Lab	$$$	Yes
TC	Heat Radiation	Composition	Lab	$	Yes
TC Pyrometer	Heat Radiation	Composition, Thickness	Lab	$$	Yes Yes
Infrared Monitor	Heat Radiation	Composition, Thickness	Lab	$$	Yes
SLS	White Light	Composition, Thickness, Surface Structure, Band gap	Lab	$$$	No
SE	Polarized Light	Composition, Thickness, Surface Structure, Band gap	Lab, Industry	$$$	No
EIES	Atomic Emission	Flux of Multiple Elements	Lab	$$$	Yes
AA	Atomic Absorption	Flux of Multiple Elements	Lab, Industry	$$$	Yes
XRF	X-ray	Composition, Thickness	Lab, Industry	$$$	Yes

From CHINESE OPTICS LETTERS / Vol. 8, Supplement / April 30, 2010
In situ optical monitor system for CIGS solar cell applications, Fan and Nagai

Losses in the spectral response of the device (current losses



After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

Current losses

1. Shading from a collection grid used for most devices. In an interconnected module this will be replaced by the area used for the interconnect, as discussed in Section 13.6.2.

2. Front surface reflection. On the highest-efficiency devices this is minimized with an antireflection layer for which an evaporated MgF2 layer with thickness ~100 nm is commonly used. However, this is not practical in a module in which a cover glass is typically required.

3. Absorption in the TCO layer. Typically, there is 1 to 3% absorption through the visiblewavelengths, which increases in the near IR region, *λ > 900 nm, where free-carrier* absorption becomes significant, and for *λ < 400 nm near the ZnO band gap.*

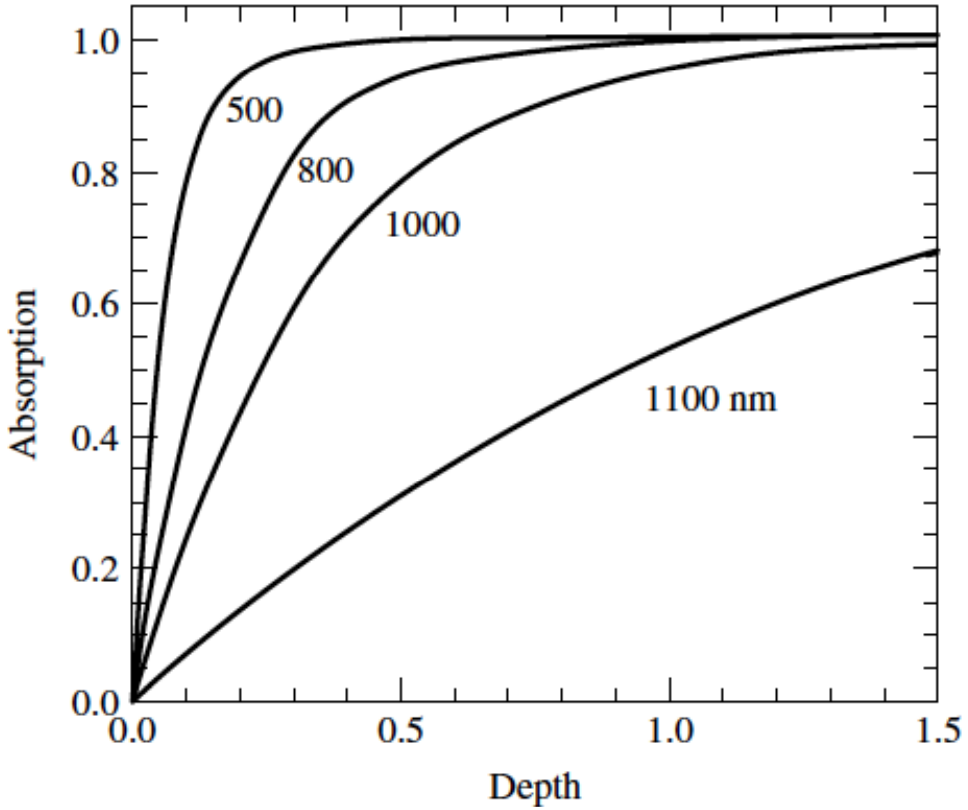
4. Absorption in the CdS layer. This becomes appreciable at wavelengths below ~520 nm corresponding to the CdS band gap 2.42 eV. The loss in *QE for λ < 500 nm is* proportional to the CdS thickness since it is commonly assumed that electron–hole pairs generated in the CdS are not collected. Figure 13.14 shows a device with a ~30 nm-thick CdS layer. In practice, the CdS layer is often thicker and the absorption loss greater.

5. Incomplete absorption in the Cu(InGa)Se2 layer near the Cu(InGa)Se2 band gap. Band gap gradients, resulting from composition gradients in many Cu(InGa)Se2 films, also affect the steepness of the long-wavelength part of the *QE curve. If the Cu(InGa)Se2 is* made thinner than ~1*.0 μm, this loss becomes significant [163] because of insufficient* absorption at long wavelengths.

$$QE_{\text{ext}}(\lambda, V) = [1 - R(\lambda)][1 - A_{\text{ZnO}}(\lambda)][1 - A_{\text{CdS}}(\lambda)]\, QE_{\text{int}}(\lambda, V)$$

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

Depletion width losses in thin cells



Absorption of light with different wavelengths in $Cu(InGa)Se_2$ with $x = 0.2$

After "$Cu(InGa)Se_2$ Solar Cells", by Shafarman and Stolt, and *Wikipedia*

Current losses

Table 13.4 Current loss, ΔJ, for $E > 1.12$ eV due to the optical and collection losses illustrated in Figure 13.14 for a typical Cu(InGa)Se_2/CdS solar cell

Region in Figure 13.14	Optical loss mechanism	ΔJ [mA/cm^2]
(1)	Shading from grid with 4% area coverage	1.7
(2)	Reflection from Cu(InGa)Se_2/CdS/ZnO	3.8
(3)	Absorption in ZnO	1.8
(4)	Absorption in CdS	0.8
(5)	Incomplete generation in Cu(InGa)Se_2	1.9
(6)	Incomplete collection in Cu(InGa)Se_2	0.4

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*

CIGS – other deposition approaches

- Co-evaporation and the 2-step process have been identified as potential low-cost alternatives for manufacturing, and have been dominant in recent research.
- Other techniques that have been explored:
- Reactive sputtering
- Hybrid sputtering in which Cu, In, and Ga are sputtered while Se is evaporated
- Closed space sublimation (CSS)
- Chemical bath deposition (CBD)
- Laser evaporation
- Spray pyrolosis (heat treatment / annealing in the presence of a reducing gas such as hydrogen).

Cu(InGa)Se_2 Solar Cells, by William N. Shafarman[1] and Lars Stolt[2]
[1]*University of Delaware, Newark, DE, USA,* [2]*Uppsala University, Uppsala, Sweden*
Handbook of Photovoltaic Science and Engineering. Edited by A. Luque and S. Hegedus
2003 John Wiley & Sons, Ltd ISBN: 0-471-49196-9

Roll-to-roll processing from solution source (e.g., Nanosolar)

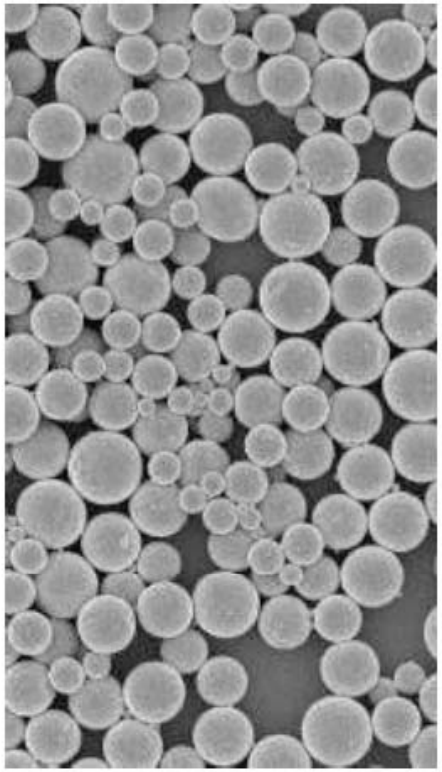


Figure 6 and 7: A laboratory sample of our nanoparticle ink. Nanoparticles shown to the right are an average of 20nm in diameter.

from NanoSolar white paper

Roll-to-roll processing from solution source (e.g., Nanosolar)

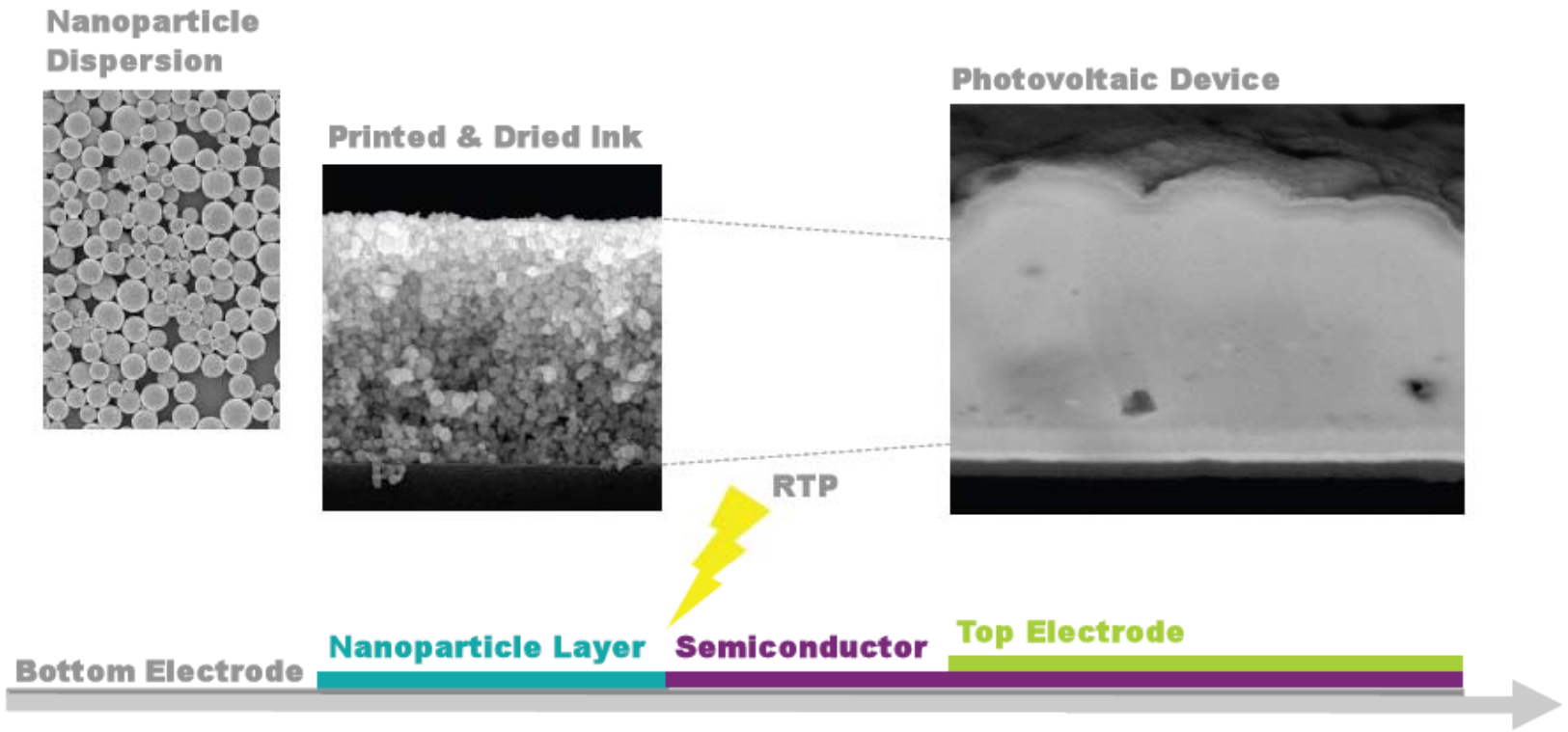


Figure 8: The basic process sequence consists of creating a high-quality dispersion of nanoparticles suitable for high-quality wet coating and converting the printed layer into a high-quality semiconductor using Rapid Thermal Processing (RTP). The art consists of doing so in a way that the resulting semiconductor is indistinguishable in electronic and crystalline quality from one deposited with far more expensive high-vacuum deposition techniques.

from NanoSolar white paper

Roll-to-roll processing from solution source (e.g., Nanosolar)

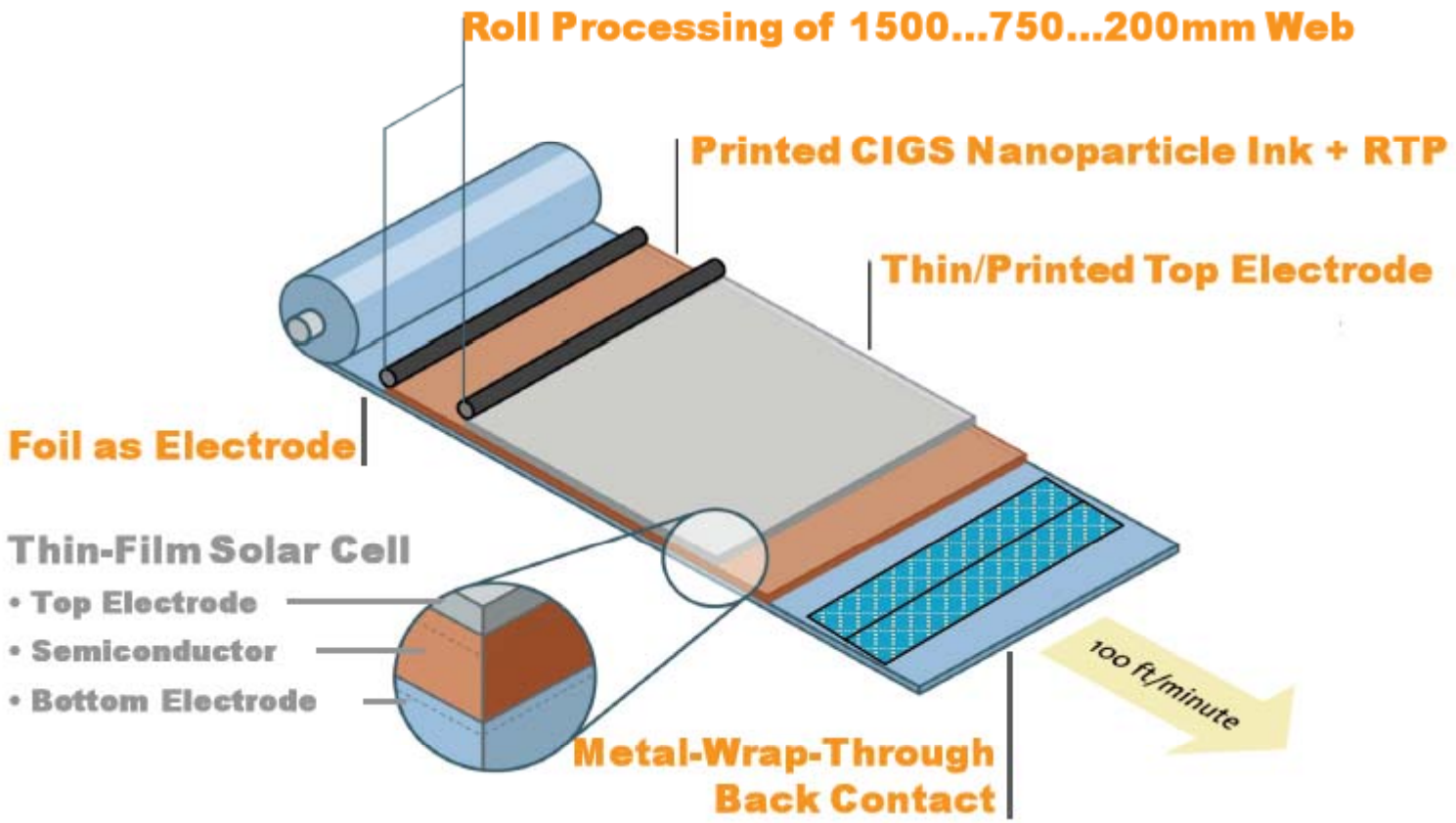


Figure 1: Nanosolar combines a host of innovations to deliver a distinct overall cost reduction.

from NanoSolar white paper

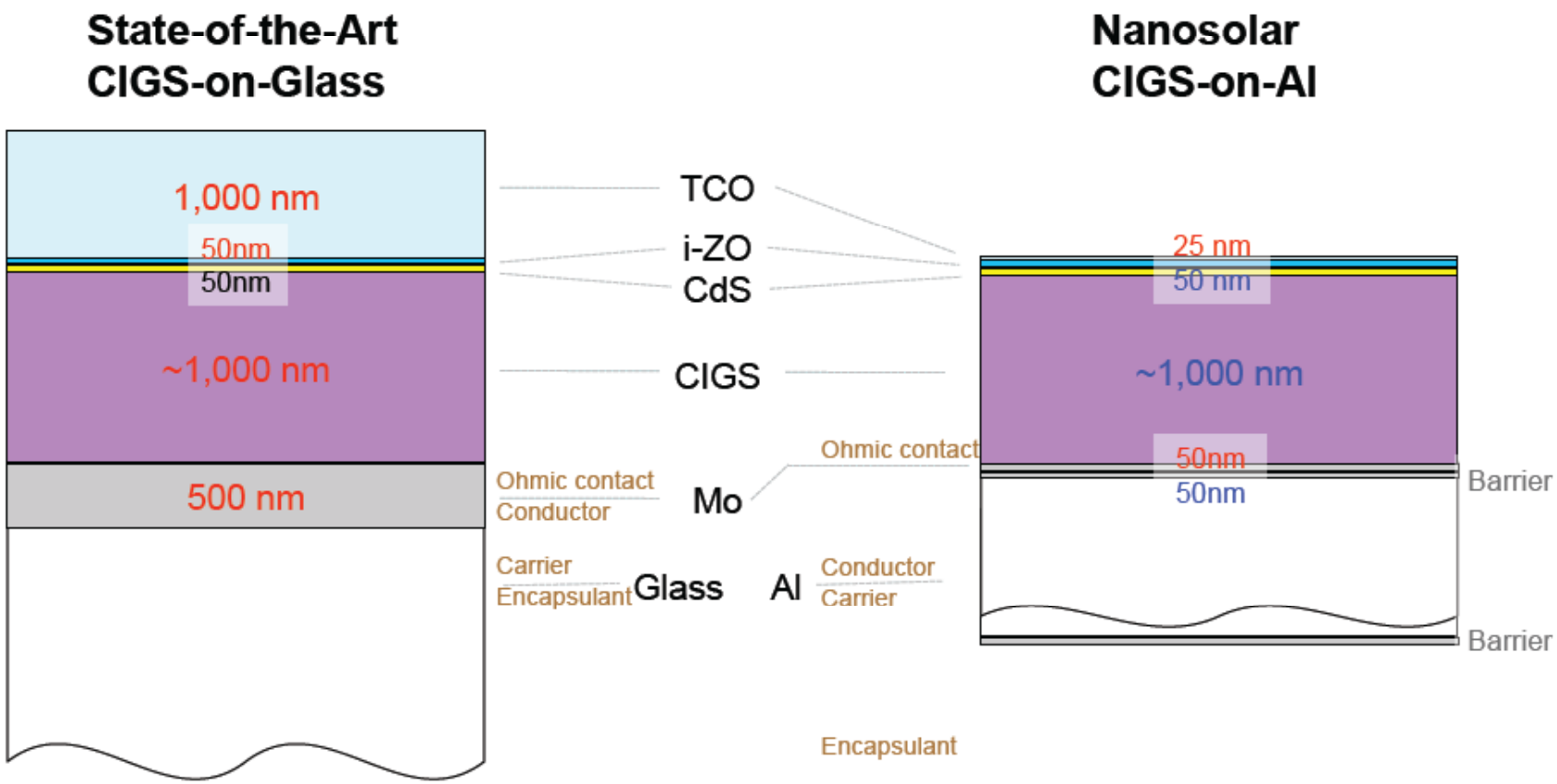


Figure 4: Comparison of State-of-the-Art CIGS versus Nanosolar's CIGS-on-Aluminum. Thickness numbers in red indicate depositions using a high-vacuum deposition technique. The state-of-the-art stack requires close to 3000nm of high-vacuum processing whereas Nanosolar's stack requires less than a tenth of that.

from NanoSolar white paper

Figure 9: A Nanosolar roll-to-roll processing tool for rapid semiconductor formation, San Jose, California.

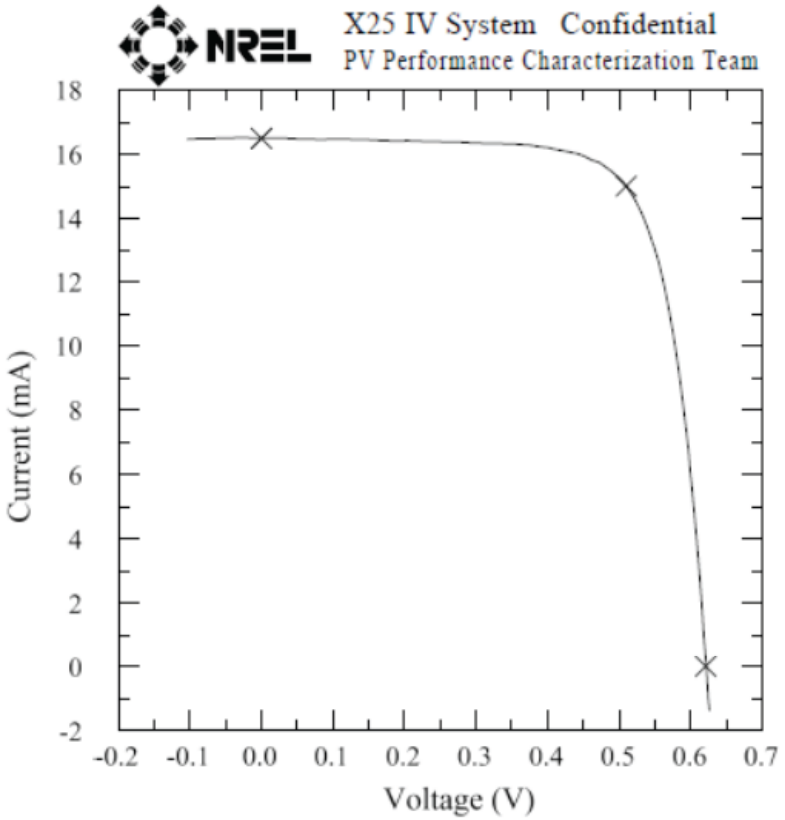
from NanoSolar white paper

Nanosolar

$CdS/Cu(In,Ga)Se_2$ Cell

Device ID: H09B071-01C #2
Apr 09, 2009 12:31
Spectrum: ASTM G173 global

Device Temperature: 24.0
Device Area: 0.5000 cm^2
Irradiance: 1000.0 W/m^2



V_{oc} = 0.6214 V	I_{max} = 15.010 mA
I_{sc} = 16.490 mA	V_{max} = 0.5101 V
J_{sc} = 32.980 mA/cm^2	P_{max} = 7.6540 mW
Fill Factor = 74.70 %	Efficiency = 15.31 %

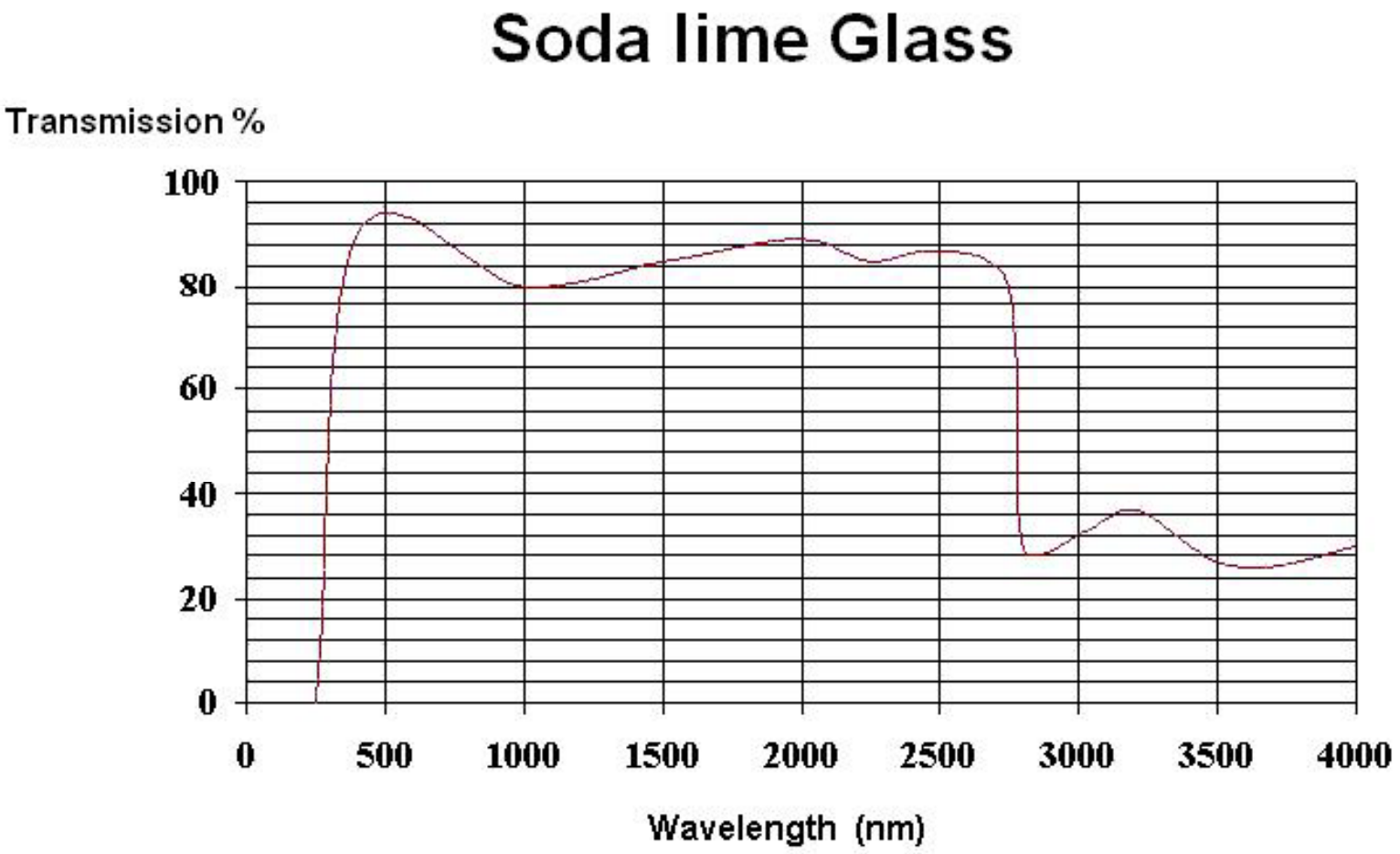
from NanoSolar white paper

Substrate considerations for CIGS (key issues)

- Earlier CIS or CIGS devices were fabricated on borosilicate glass. Switching to less-expensive soda lime glass, the solar cells worked better (i.e., higher efficiency).
- *Why does soda lime glass work well for CIS / CIGS*?
- **Coefficient of thermal expansion**: deposition done at a substrate temperature T_{SS} > 350 °C and as high as T_{SS} ~ 550 °C (close to the glass transition temp of ~564 °C). Subsequent cooling of the substrate introduces significant strain if coefficient of thermal expansion differ for the thin film and the substrate. Fortuitously, soda lime glass has a value for the thermal expansion coefficient of 9.5 (ppm/K); the value for CIS is ~8 ppm/K. In contrast, borosilicate glass has a value of 4.6 ppm/K.
- Soda lime glass includes oxides such as Na_2O, K_2O, and CaO, which provide **sources of alkali impurities** which diffuse into the Mo and Cu(InGa)Se_2 films resulting in beneficial defect effects.
- Alkalai impurities are better introduced through a controlled source, so now the glass is coated with a Na diffusion barrier such as SiO_x or Al_2O_3.
- "The chalcopyrite phase field is increased by the addition of Ga or Na." This means that the desirable phase of CIS (or CIGS) is more easily achieved in the presence of Na.

Cu(InGa)Se_2 Solar Cells, by William N. Shafarman[1] and Lars Stolt[2]
[1]*University of Delaware, Newark, DE, USA,* [2]*Uppsala University, Uppsala, Sweden*
Handbook of Photovoltaic Science and Engineering. Edited by A. Luque and S. Hegedus
2003 John Wiley & Sons, Ltd ISBN: 0-471-49196-9

Soda lime glass transmission



http://en.wikipedia.org/wiki/File:Soda_Lime.jpg

Soda lime glass properties

Properties	**Soda-lime glass for windows**
Chemical composition, (wt%)	73 SiO_2, 14 Na_2O, 9 CaO, 4 MgO, 0.15 Al_2O_3, 0.03 K_2O, 0.02 TiO_2, 0.1 Fe_2O_3
Glass transition temperature, T_g, °C	564
Coefficient of thermal expansion, ppm/K, ~100-300°C	9.5
Refractive index, n_D at 20°C	1.520
Heat capacity at 20°C, J/(mol·K)	*48*

http://en.wikipedia.org/wiki/Soda-lime_glass

CIGS back contact (molybdenum, Mo)

- All high-efficiency CIS and CIGS devices use Mo as the back contact.
- Typically deposited DC sputtering.
- Cell or module configuration determines required thickness (1 µm gives a sheet resistance of 0.1 to 0.2 Ω /□, *a factor of 2 to 4 higher resistivity* than bulk Mo.
- Sputter deposition requires careful control of the pressure to control stress in the film, to avoid adhesion.
- During Cu(InGa)Se_2 deposition, a $MoSe_2$ layer forms at the interface, with properties influenced by the Mo film (less $MoSe_2$ forms on dense Mo). Metals other than Mo have been investigated with limited success.

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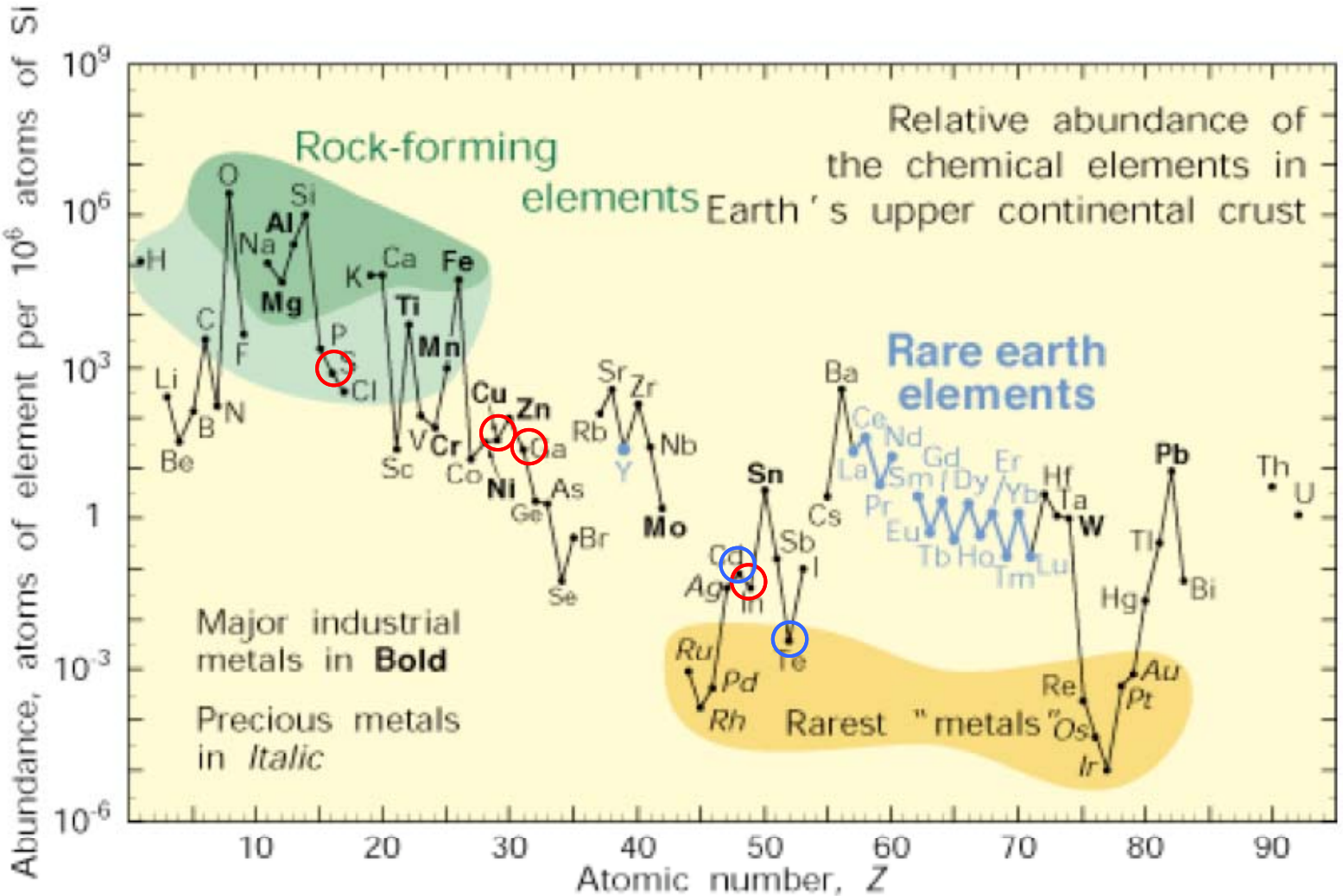

Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. Many of the elements are classified into (partially overlapping) categories: (1) rock-forming elements (major elements in green field and minor elements in light green field); (2) rare earth elements (lanthanides, La–Lu, and Y; labeled in blue); (3) major industrial metals (global production >~$3x10^7$ kg/year; labeled in bold); (4) precious metals (italic); and (5) the nine rarest "metals"—the six platinum group elements plus Au, Re, and Te (a metalloid)

Gordon B. Haxel, James B. Hedrick, and Greta J. Orris, Rare Earth Elements—Critical Resources for High Technology, U.S. Geological Survey Fact Sheet 087-02

http://pubs.usgs.gov/fs/2002/fs087-02/

State of Commercialization, as of 2003

Several companies worldwide are pursuing the commercial development of Cu(InGa)Se2-based modules. The most advanced, having demonstrated excellent reproducibility in its module manufacturing using the two-stage selenization process for Cu(InGa)(SeS)2 deposition is Shell Solar Industries (SSI) in California, which was formerly ARCO Solar and then Siemens Solar. They are now in production with 5-, 10-, 20-, and 40-W modules that are commercially available.

In Germany, Wurth Solar is in pilot production using an in-line coevaporation process for Cu(InGa)Se2 deposition and has also reported large area modules with *>12% efficiency. In the USA, several* companies are in preproduction or pilot production: Energy Photovoltaics, Inc. (EPV) is using its own in-line evaporation process, International Solar Electric Technology (ISET) is developing a particle-based precursor for selenization, and Global Solar Energy (GSE) is pursuing a process for roll-to-roll coevaporation onto a flexible substrate. In Japan, Showa Shell, using a two-stage selenization process, and Matsushita, using coevaporation for Cu(InGa)Se2 deposition, are also in production development stages.

Despite the level of effort on developing manufacturing processes, there remains a large discrepancy in efficiency between the laboratory-scale solar cells and minimodules, and the best full-scale modules. In part, this is due to the necessity for developing completely new processes and equipment for the large-area, high-throughput deposition needed for manufacturing thin-film photovoltaics. This is compounded by the lack of a comprehensive scientific base for Cu(InGa)Se2 materials and devices, due partly to the fact that it has not attracted a broader interest for other applications. This lack of a science base has been perhaps the biggest hindrance to the maturation of Cu(InGa)Se2 solar cell technology as most of the progress has been empirical. Still, in many areas a deeper understanding has emerged in the recent years.

After "Cu(InGa)Se_2 Solar Cells", by Shafarman and Stolt, and *Wikipedia*