INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR.704 - 17

Workshop on Materials Science and Physics of Non-Conventional Energy Sources

(30 August - 17 September 1993)

"Advances in Materials for PV Conversion"

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Compound semiconductors

by

F. Pfisterer and H.W. Schock

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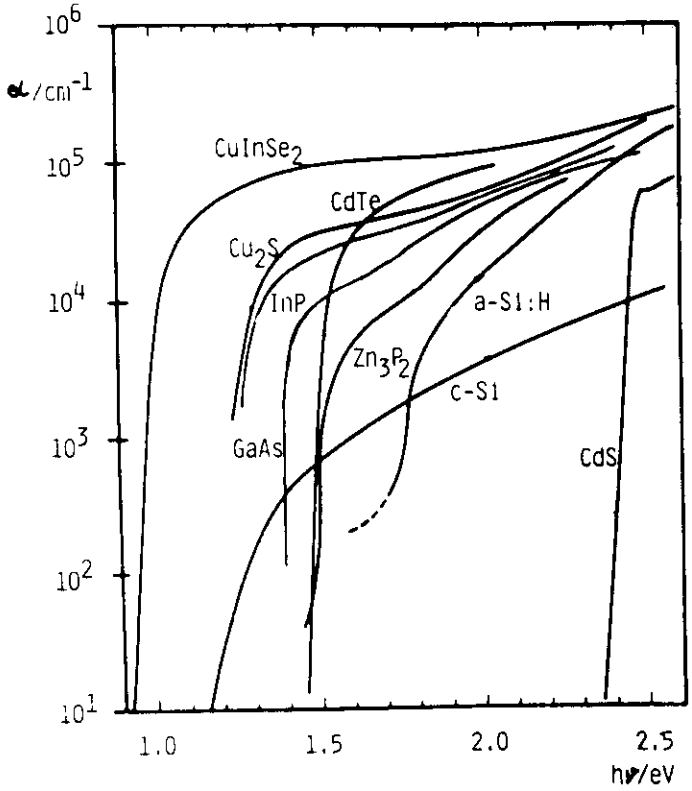
Why compound semiconductors?

- Variety of compounds available with superior photovoltaic properties.
- Mostly Chalcogenides.: Sulfides, Selenides, Tellurides

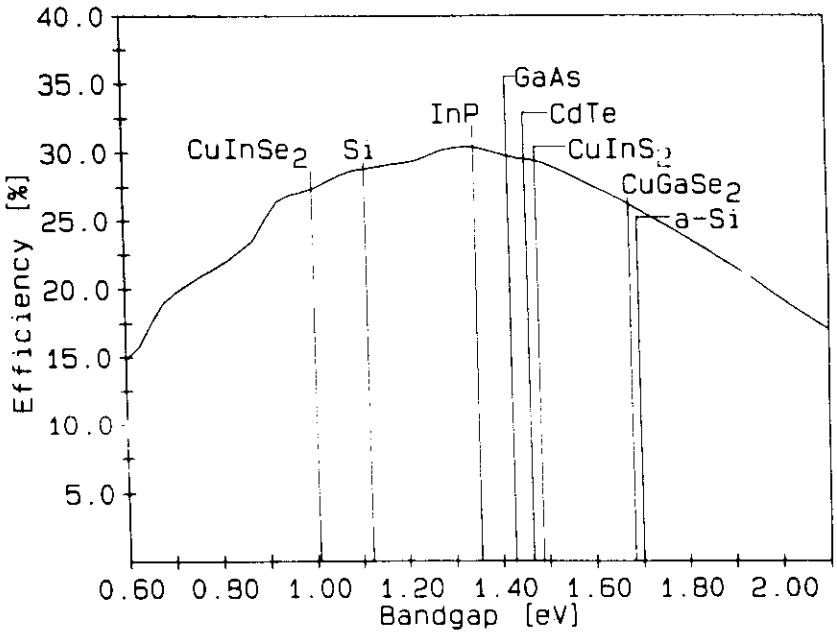
* high absorption coefficient (direct gap)
* defects not electronically active
* low surface recombination velocity
* high quality material at low deposition temperature and with various deposition processes
* Reaction with oxygen improves properties
* variable bandgap of alloys

Absorption Coefficients



Theoretical Efficiencies

- Interesting bandgap range for single junctions : 0.9 - 1.8 eV
- Maximum efficiency for E_g = 1.3 - 1.4 eV
- Broad maximum covering many materials



After Henry

Heterojunctions, window materials

What is the best design for the device?

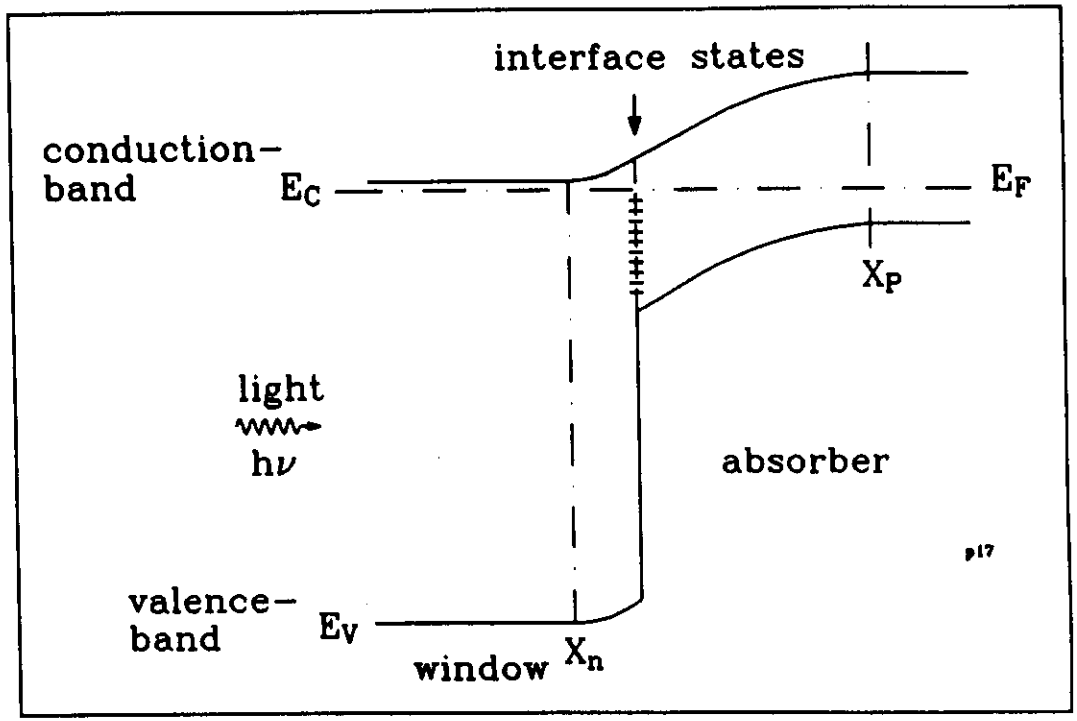
- absorb as much light as possible in the active part of the device
- realize a high barrier for the forward (bucking current)
- avoid recombination of photocurrent

But
- material dependent
- determined by the technology

a) "True" Heterojunction
space charge region and diffusion voltage drop mainly in the absorber

- photocurrent collection assisted by the field

- high field at the interface may reduce barrier (like in a Schottky barrier)
- doping of window and absorber have to be well balanced

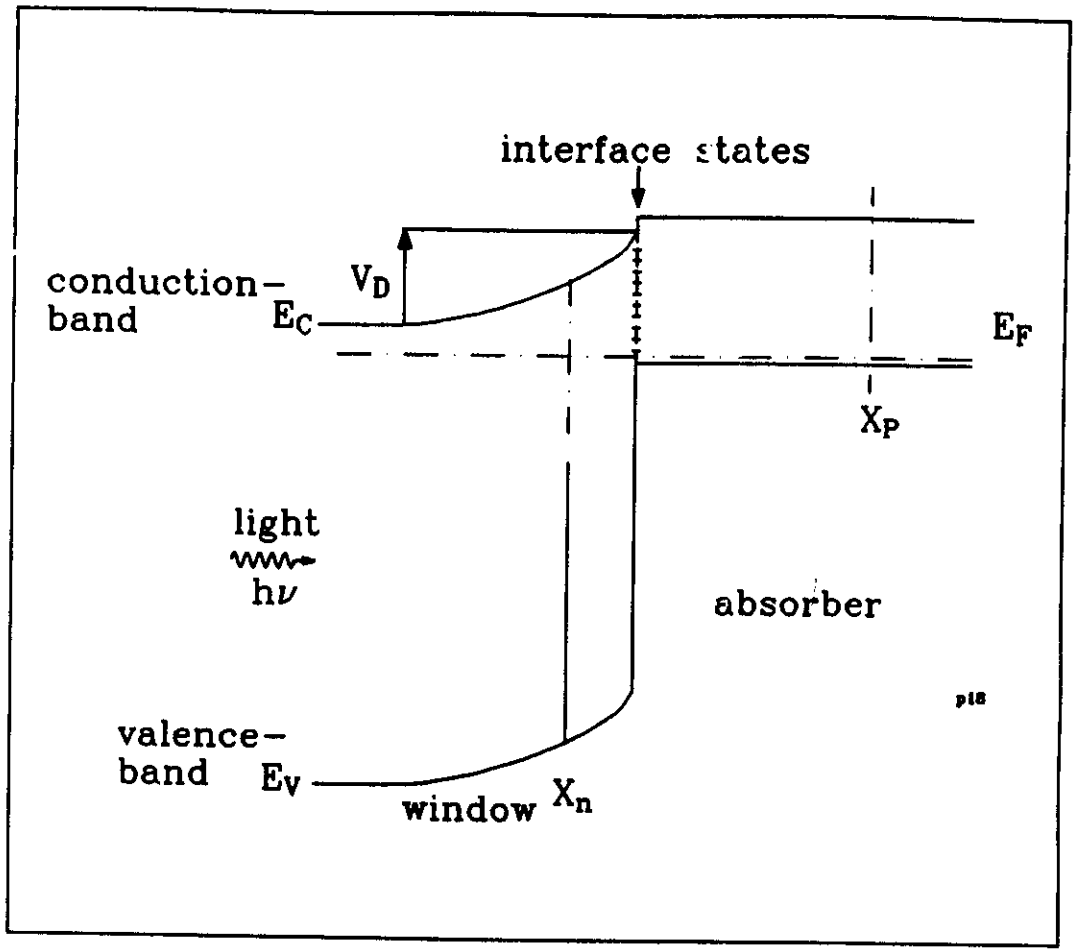


b) "Surface sensitization" of a wide gap material
(e.g. Cu_2S-CdS)

- **space charge region and diffusion voltage drop in the window**
- **interface controlled photocurrent.**

$j_{ph} = \mu F/(S_I + \mu F)$

A. Rothwarf

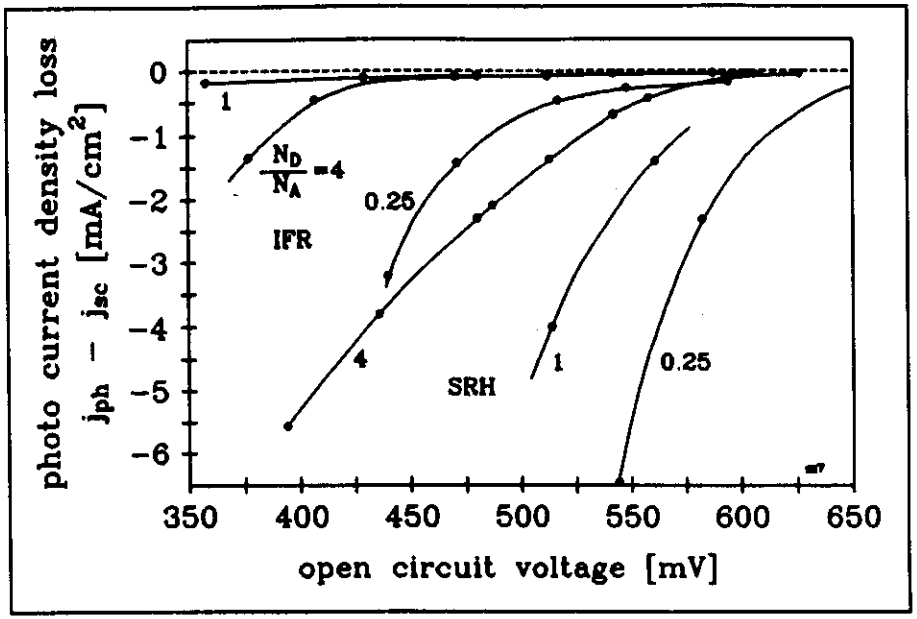


Results of Modelling:

Photocurrent loss and open circuit voltage depend differently on the recombination mechanism

simplified summary:

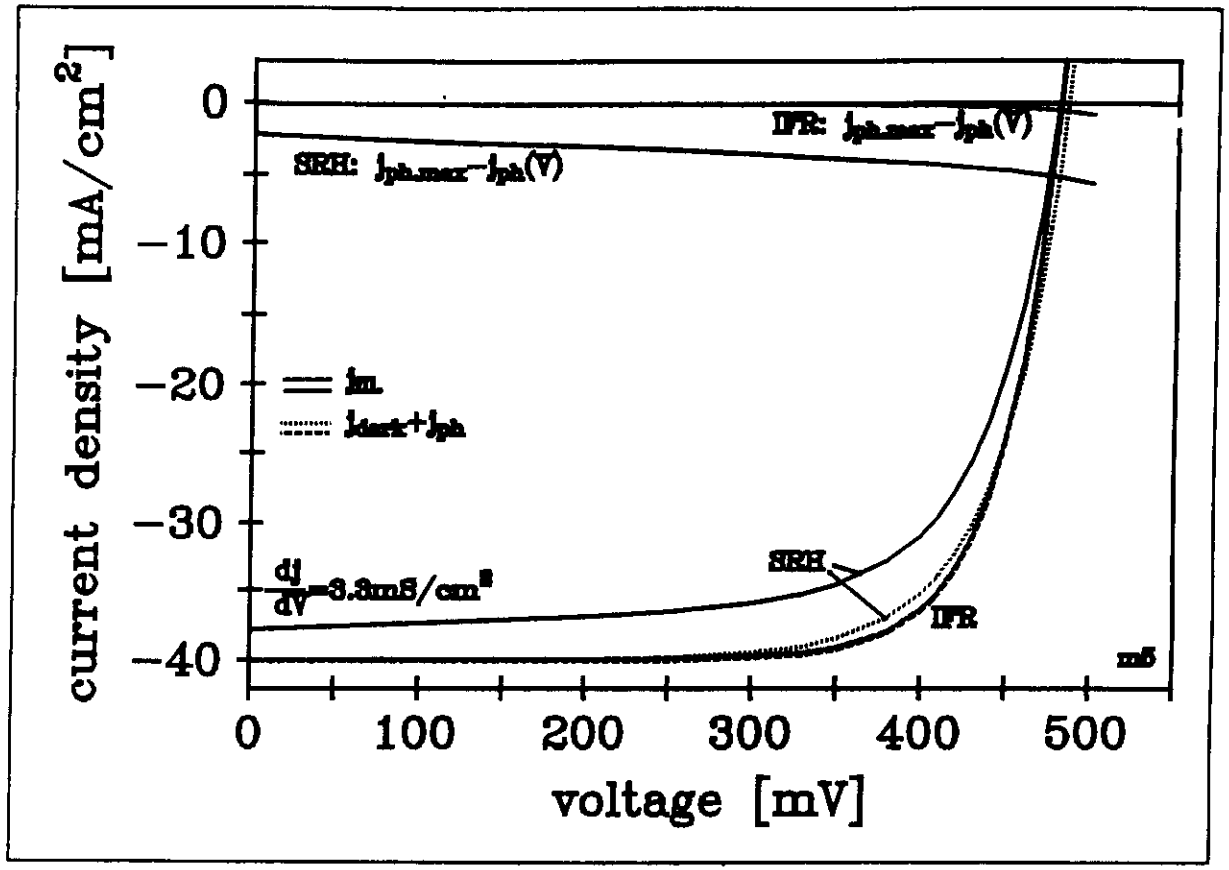
- **recombination in space charge region affects photocurrent**
- **interface recombination affect photvoltage**



R. Menner and H.W. Schock, Proc. 11th EC Photov. Solar Energy Conf., Montreux, 1992.

Different recombination mechanisms can be estimated from the IV characteristics

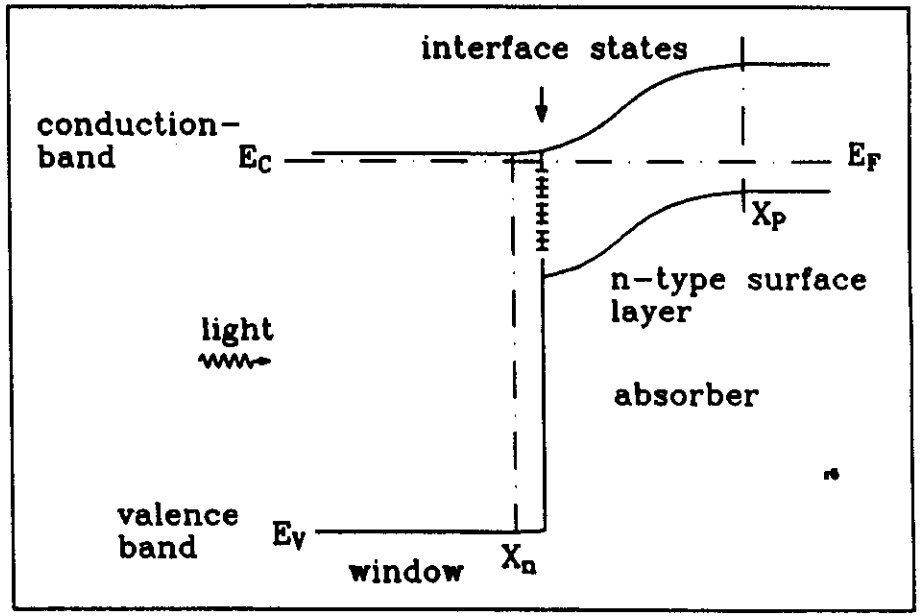
e.g photocurrent and thus fill factor is less affected by inter-face recombination



c) Heterojunction, buried homojunction.

Interface states affect only surface recombination at n-n junction

if junction is too deep, response to high energy photons is affected



Window materials:

Material	Energy gap [eV]	Remarks
In_2O_3	3.2	
SnO_2	3.3	
In_2O_3:SnO_2 (ITO)	3.2	
ZnS	3.2	Buffer layer
CdS	2.42	Buffer layer

Evaporated CdS, (Zn,Cd)S were commonly used window materials

Now:
Transparent conductive oxide + chemically deposited CdS

CHEMICAL BATH DEPOSITION OF CdS ON $CuInSe_2$

Advantage: surface coverage perfect a very small thickness

PROCEDURE :

-) GROWTH SOLUTION :

CdI_2 or $CdSO_4$: $1.4 \cdot 10^{-3}$ M
Ammonia (NH_3) : 1 M
Thiourea (NH_2CSNH_2) : 0.14 M

Sequence

1. Cd^{2+}
2. NH_3
3. NH_2CSNH_2
4. Insert CIS sample

In 3-4 min. at 60 °C the thickness of CdS film is 10-50 nm.

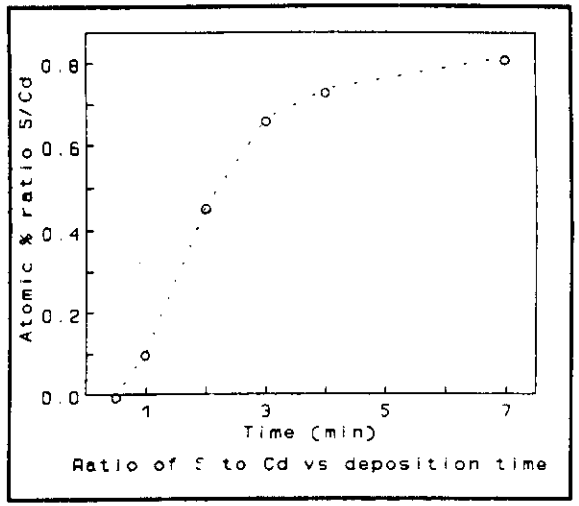
J. Kessler, K.O. Velthaus, M. Ruckh, R. Laichinger, H.W. Schock, D. Lincot, R. Ortega and J. Vedel, Proc. 6th Int. Photov. Sci. Eng. Conf. (PVSEC-6), New Delhi, 1992, 1005.

ETCHING EFFECTS AND GROWTH KINETICS

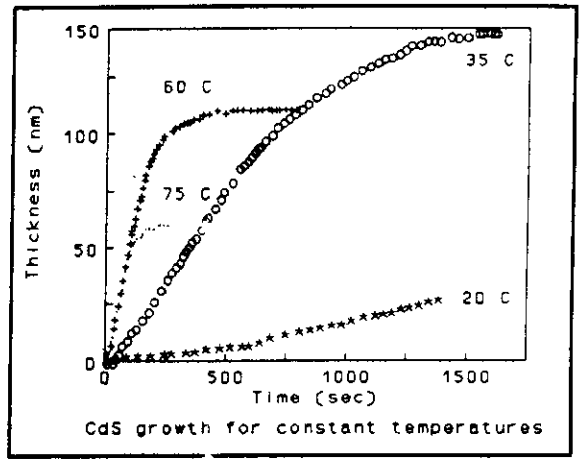
ANALYSIS TOOLS :

-) X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) →

* Surface composition
* Chemical states



Ratio of S to Cd vs deposition time



CdS growth for constant temperatures

-) QUARTZ MICROBALANCE (QMB) →

* CIS coated quartz oscillators : in situ mass exchange monitoring

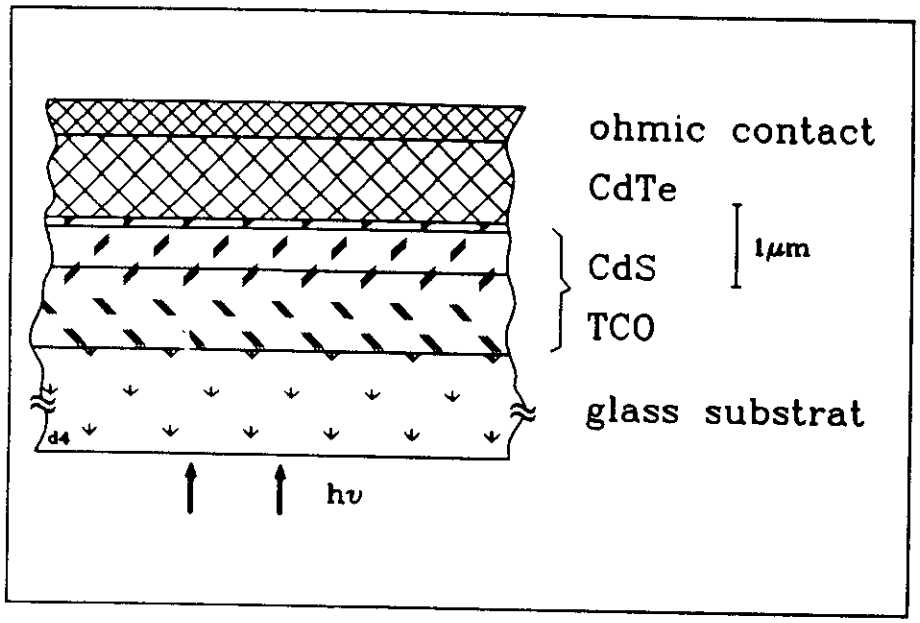
INTERFACIAL CHEMISTRY (on $CuInSe_2$ surface):

Use of "partial" bath conditions at 60°C with "fast" temperature profile.

-) precleaned CIS	: Indium oxide (Auger), SeO_2 (PE), Cu_xSe (Auger)
-) NH_3 alone	: Oxides removed, In ↘
-) NH_3 + Cd^{2+}	: Large Cd signal, Se ↗, Cu_xSe removed
-) NH_3 + NH_2CSNH_2	: S, C, N found but S/N ➢ 1
-) Cu rich/In rich CIS	: Qualitatively same results
-) Thermodynamic Considerations	: Show the possibility of ion exchange between Cd^{2+} and In in In_2Se_3 leading to the formation of CdSe.
	: Indicate the importance of oxygen in the etching effects. This point is confirmed by QMB experiments.

CdTe based solar cells

structure



problem of contacting high work function material

Many different deposition processes possible

CdS should be thin to improve blue response

TCO with low sheet resistance

Specific properties of CdTe

* simple binary phase diagram
* congruent evaporation of the compound - easy to obtain stoichiometric material
* direct gap at 1.45 eV
* doping p and n-type possible
* sufficient lifetime
* low grain boundary recombination

Deposition processes for CdTe

Molecular beam epitaxy, evaporation,physical vapour deposition	MBE, PVD	evporation of elements or CdTe
Laser Ablation	LA	ablation of compound target
Close space sublimation, vapor transport	CSS CSVT	Sublimation of CdTe compound, carrier gas
Chemical vapour deposition, Metalorganic-	CVD, MOCVD	dissociation of compounds, metalorganic compounds on heated substrate
Atomic layer epitaxy	ALE	layer by layer growth from CVD, MOCVD precursors
Spray Pyrolysis	SPL	pyrolysis of compounds in solutions
Reaction of stacked Elemental layers	SEL	Annealing of stacks of elemental layers
Electrodeposition	ED	electrochemical deposition from solutions
Screen printing	SP	screen printing and sintering of elements or compounds in binder

Apparatus for tne deposition of CdTe by Close spaced sublimation

Deposition close to equilibrium
Small temperature difference between
source and substrate

T_s = 600 °C

High deposition rates

after Y.S. Tyan, Solar Cells, 23 (1988) 19

The $CdCl_2$ treatment

* important step for annealing of cells deposited at low temperature
* 620 °C
* increases grain size
* promotes interdiffusion of CdS/CdTe

R.W. Birkmire et al, Int. J. Solar Energy, 1992, Vol. 12, 145

Contacting p-CdTe Layers:

* one of the most difficult problems in these devices

Formation of ohmic contacts

- Te enrichment by etching
- Cu diffusion
- Au, C as contact material
- or other compounds HgTe, ZnTe

CdS-CdTe Junctions

* No real heterojunction in efficient devices

Interdiffusion of CdS and CdTe at the interface forms a buried, graded junction,

onset of spectral response at photon energies lower than the bandgap of CdTe

R.W. Birkmire et al, Int. J. Solar Energy, 1992, Vol. 12, 145

Results

Cell type	Depos.Process for absorber	V_{oc} [mV]	j_{sc} [mA/cm^2]	FF	Eff. [%]	Area [cm^2]	Ref./Lab.
MgF_2/glass/-SnO_2/CdS/CdTe	CSS	843	25.1	0.745	15.8	1.05	Univ. South Florida
Glass/SnO_2/CdS/CdTe	ED	819	23.5	0.74	14.2	0.02	BP Solar
Glass/SnO_2/CdS/CdTe	ALE	804	23.8	0,73	14.0	0.12	Microchemistry
Glass/ITO/CdS/CdTe	ED	720	27.9	0.65	13.1	0.02	Univ. Queensland
SnO_2/CdS/CdTe	SPL	783	25	0.67	12.3	0.31	Photon Energy
CdS/CdTe	SP	797	21.1	0.67	11.3	1.02	Matsushita
(Zn,Cd)S/CdTe	SP	870	23.6	0.61	12.5	0.3	Korea Adv. Inst.
Glass/SnO_2/CdTe	CSVT	663	28.1	0.56	10.5	4	ARCO Solar
SnO_2/CdS/CdTe/ZnTe	ED	767	22.4	0.7	11.2	1.07	AMETEK
glass/TO/ CdS/CdTe	CSS	745	22.6	0.65	11.0	0.4	Battelle Inst.

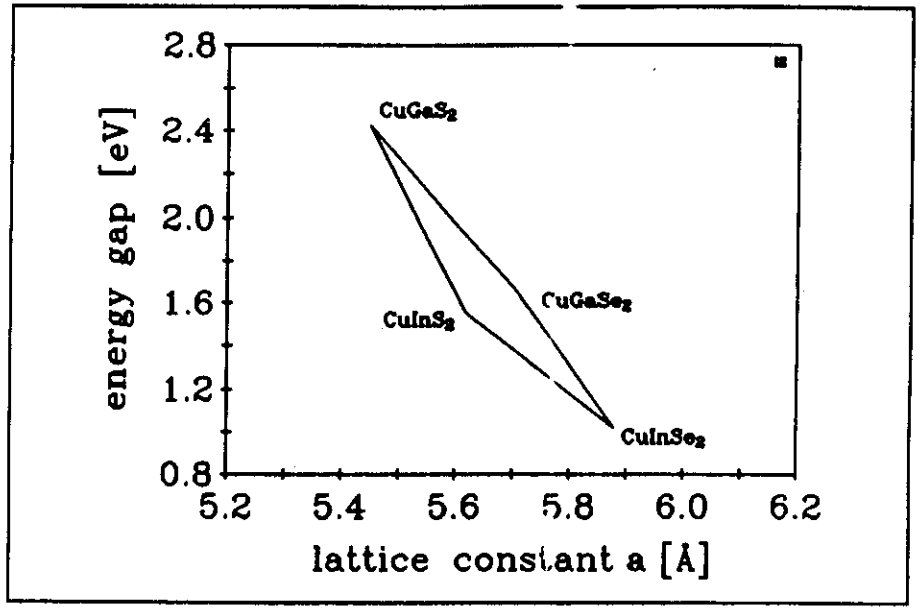
ED electrodeposition, SPL spray pyrolysis, SP screen printing, CSVT close spaced vapour transport, CSS close spaced sublimation

CuInSe2 and related alloys

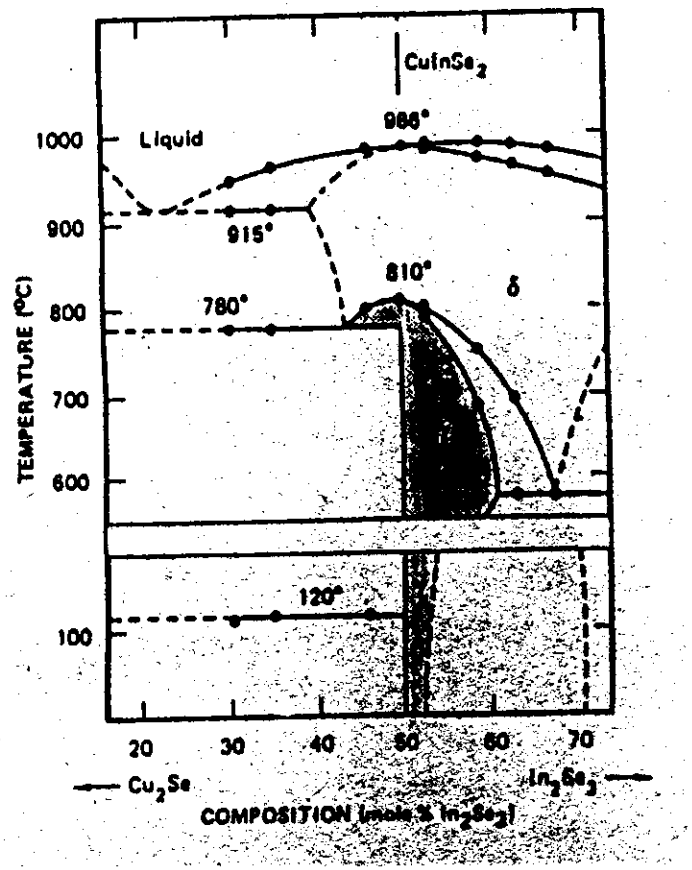
* Direct gap semiconductors
* high absorption coefficient
* long diffusion lenght

* growth can be controlled through binary phases
* Wide range of bandgaps available with alloys

Energy gap and lattice constants



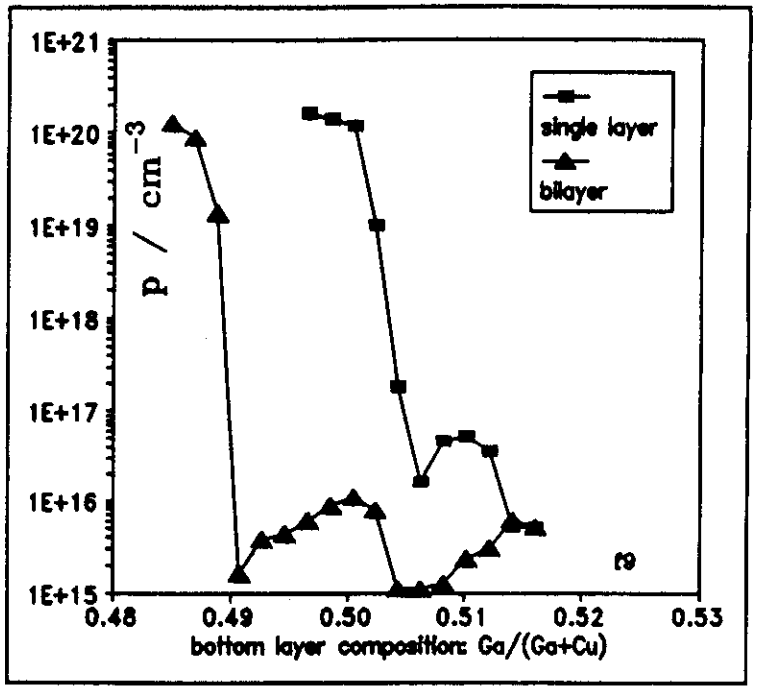
Phase diagram of $CuInSe_2$



after Fearheiley, Solar Cells 16 (1986) 91

Conductivity of Cu-rich films dominated by Cu_xSe for example $CuGaSe_2$

Carrier conc. vs film composition



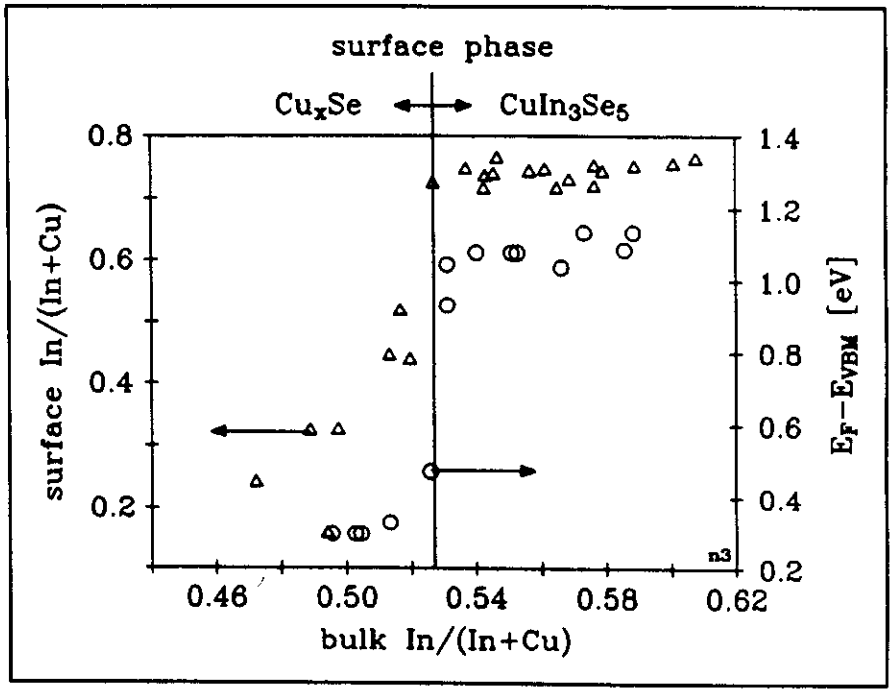
R. Klenk, R. Mauch, R. Schäffler, D. Schmid and H.W. Schock, Conf. Rec. 22nd IEEE Photov. Spec. Conf., Las Vegas, 1991, (IEEE, New York, 1991), 1071.

Specific property of the material

Surface composition changes abruptly with bulk composition

Cu-rich bulk - Cu_xS like surface

In-rich bulk - $CuIn_3Se_5$ like surface



B. Dimmler, F. Grunwald, D. Schmid and H.W. Schock, Conf. Rec. 22nd IEEE Photov. Spec. Conf., Las Vegas, 1991, (IEEE, New York, 1991), 1088.

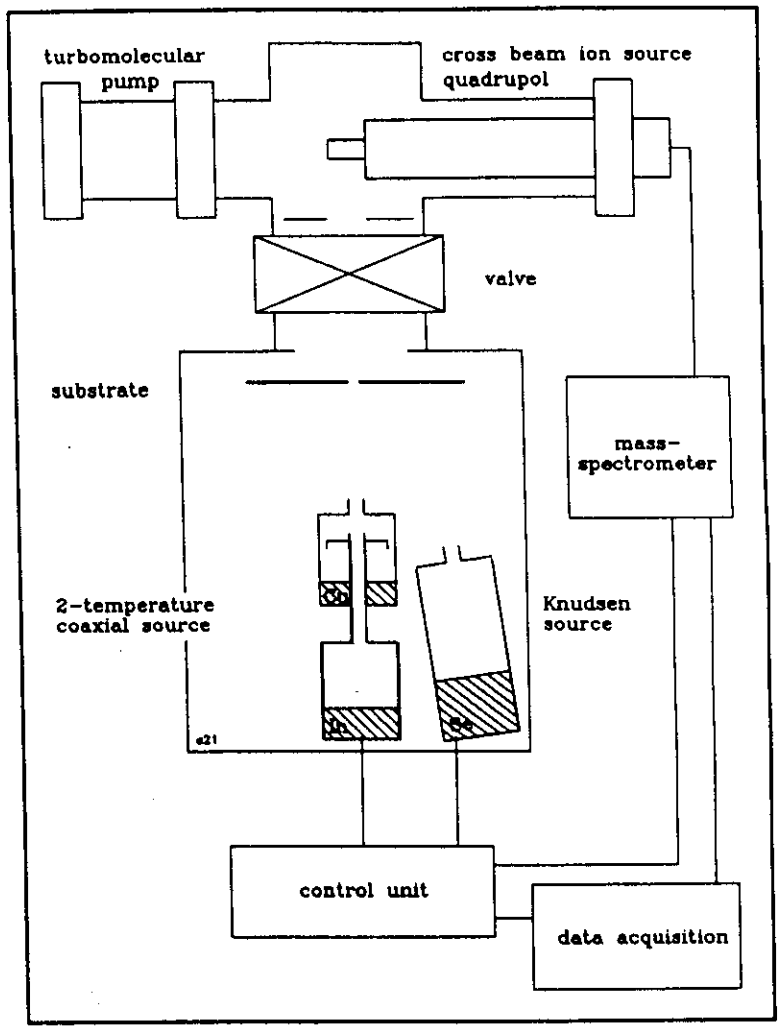
M. Ruckh, F. Grunwald and H.W. Schock, to be published in J.Appl.Phys.

Deposition Processes for $CuInSe_2$ and $Cu(Ga,In)(Se,S)_2$ films.

Process	features of the process	Comments
coevaporation	small gradient of Cu/In ratio during deposition	suitable for multinary, graded films, small grains
modified coevaporation	large gradient of Cu/In, selenium deficiency, high substrate temperature	Crystallization enhanced by quasi liquid secondary phases films
stacked layer annealing	locally large compositional gradients	homogenisation inhibited by $CuInSe_2$ interlayers
selenisation (Se)	very strong gradients of Cu/In	difficult to control morphology
screen printing	- presynthesized material + additional flux	flux important for formation of dense films
electrodeposition	codeposition of the elements, small gradients	difficult to obtain large grains
laser ablation of CuInSe2 targets	codeposition of different species, no thermal equilibrium	well oriented small grains, smooth film

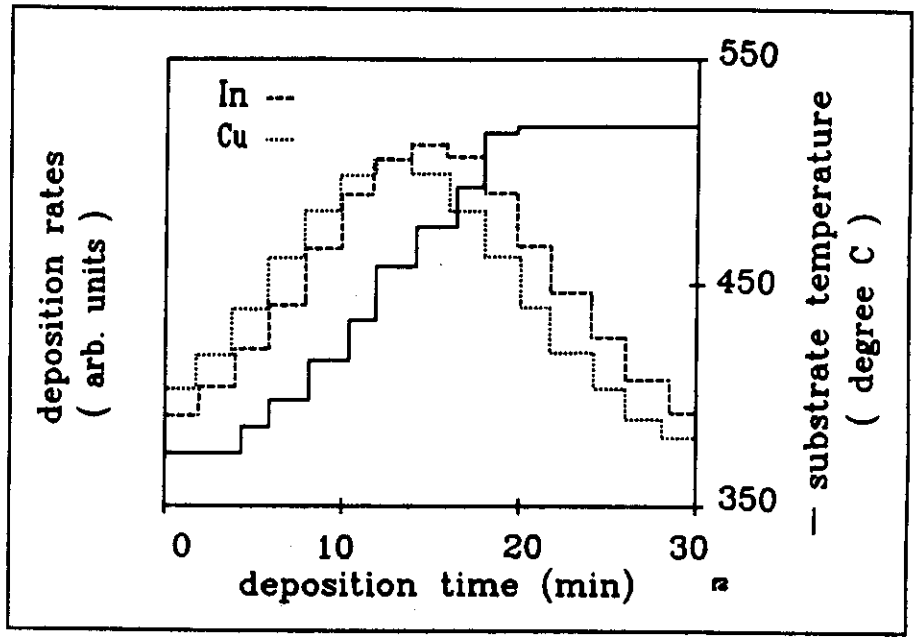
Schematic view of an evaporation system for $CuInSe_2$ - films

- Rate control by mass spectrometer
- concentric source for Cu and In
- effusion source for Se



B. Dimmler and H.W. Schock, Proc. 9th EC Photov. Solar Energy Conf., Freiburg, 1989, (Kluwer, Dordrecht, 1989), 160.

Element rates for deposition of high quality films



R.H. Mauch, M. Ruckh, J. Hedström, D. Lincot, J. Kessler, R. Klinger, L. Stolt, J. Vedel and H.W. Schock, Proc. 10th EC Photov. Solar Energy Conf., Lisboa, 1991, (Kluwer, Dordrecht, 1991), 1415.

Modified Coevaporation/ Selenization

Combination of Coevaporation and Selenization

B. Dimmler, D. Schmid and H.W. Schock, Proc. 6th Int. Photov. Sci. Eng. Conf. (PVSEC-6), New Delhi, 1992.

film preparation

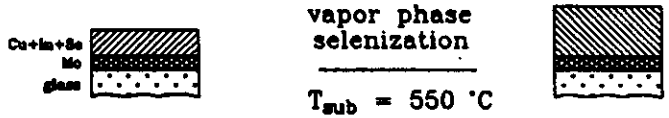
① standard bilayer $CuInSe_2$ (BL)

1^{st} layer Cu-rich
T_{sub} = 350 °C

+

2_{nd} layer In-rich
T_{sub} = 450 °C

② single layer $CuInSe_2$ (SL)



vapor phase selenization

T_{sub} = 550 °C

precursor
Cu+In+Se in deficiency
T_{sub} = 300 °C

③ $CuGaSe_2$: coevaporation of Cu+Ga+Se as bilayer and gradient layer
T_{sub} = 550 – 650 °C

Selenization

Different methods

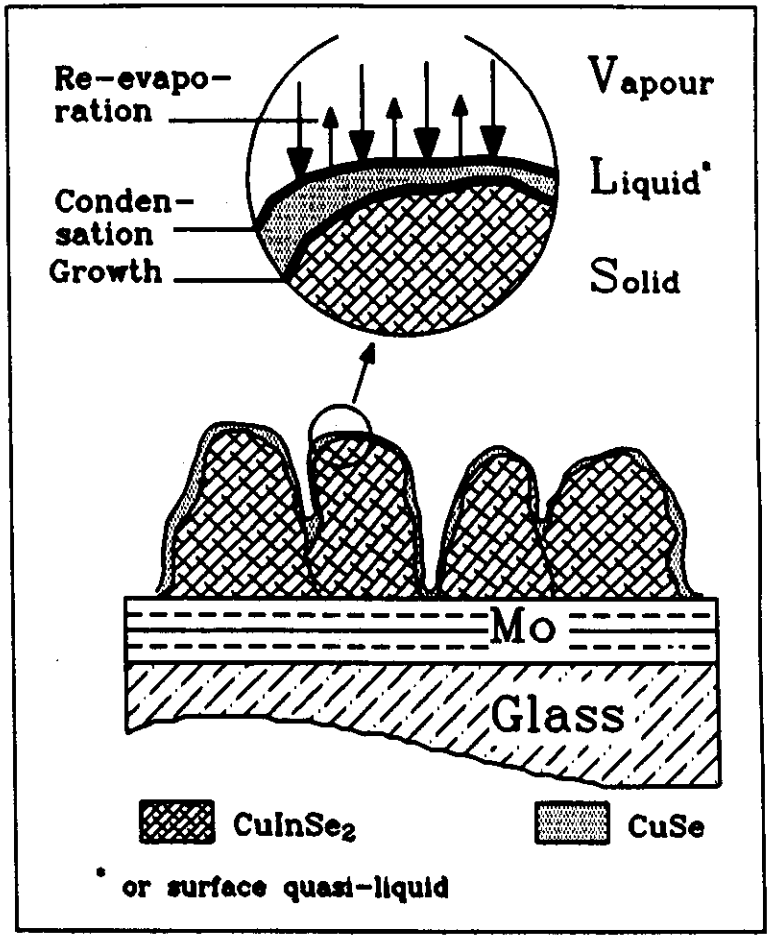
* Cu/In precursours
  separate layers
  prealloyed films

* Selenization process

  - H_2Se
  - Se vapor
  - Se film

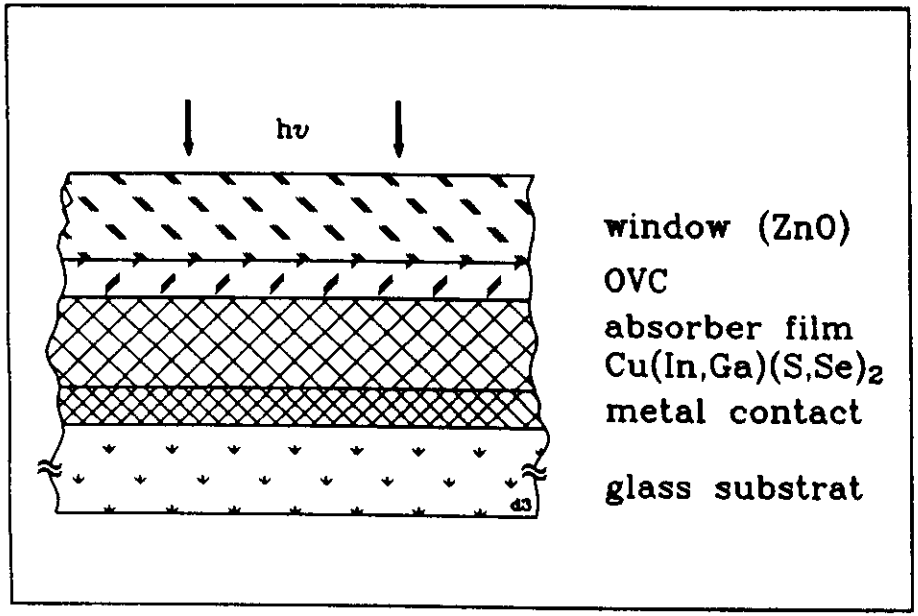
* Improvement of sticking: Ga or Tellurium at the Molybdenum surface

Growth mechanisms of Cu-rich films by evaporation vapour-liquid -solid growth provides good crystallinity



R. Klenk, T. Walter, H.W. Schock, and D. Cahen, Adv. Mater. 1993, 5, No. 2, 114

schematic structure of a $Cu(In,Ga)(S,Se)_2$ solar cell



ZnO deposition processes should not affect $CuInSe_2$ surface

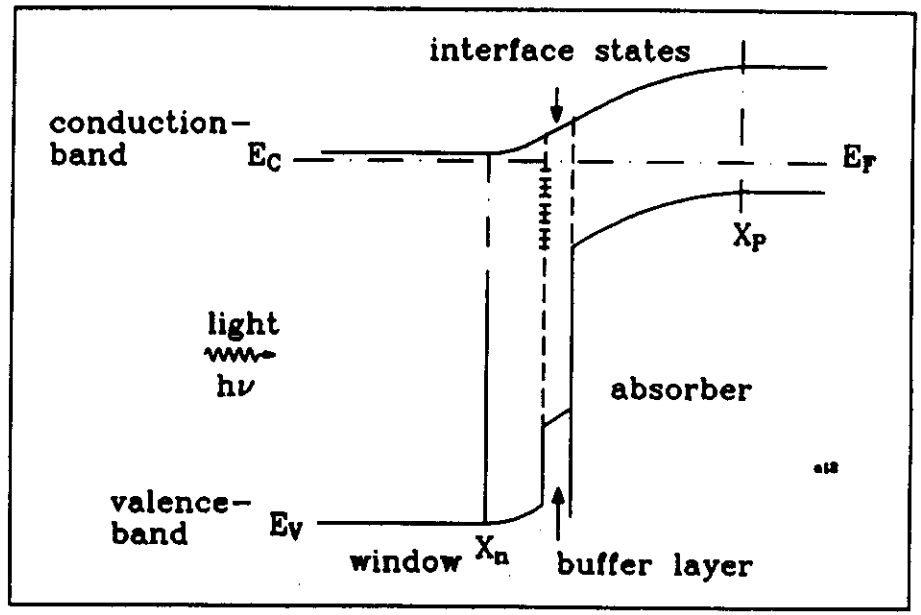
Ordered vacancy compound serves as n-type surface layer

$CuInSe_2$ deposited by various process, best coevaporation and selenization

Mo till now most suitable back contact

$ZnO/CdS/CuInSe_2$ Heterojunction

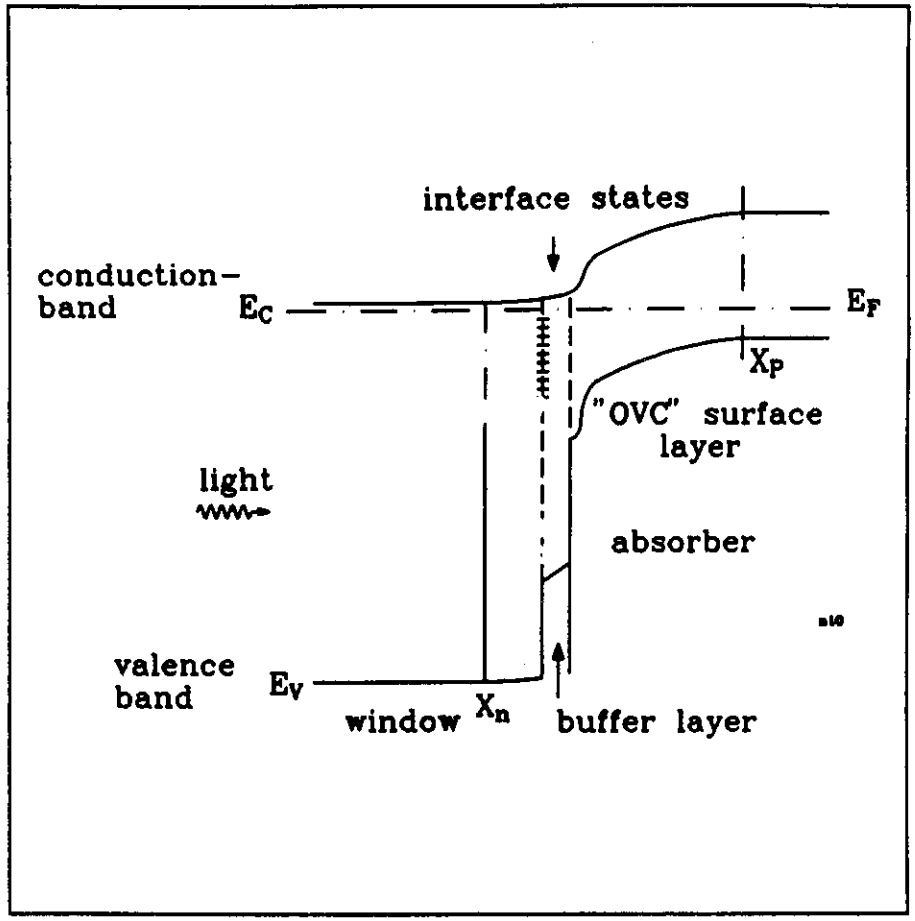
Original model of the junction



"Ordered vacancy compound (OVC)" Heterojunction

n-type surface phase forms
"intrinsic" buried junction with graded gap

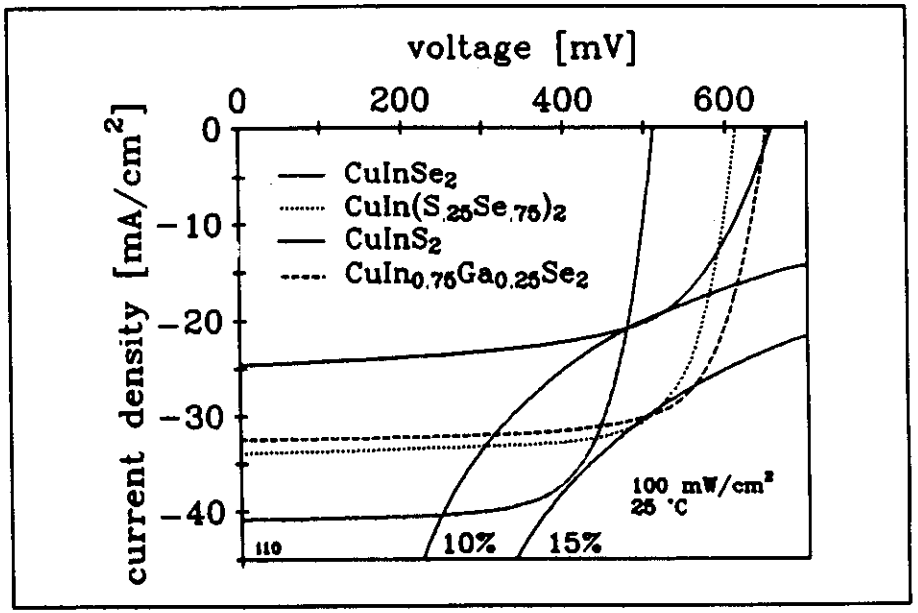
metallurgical junction represents surface of pn junction



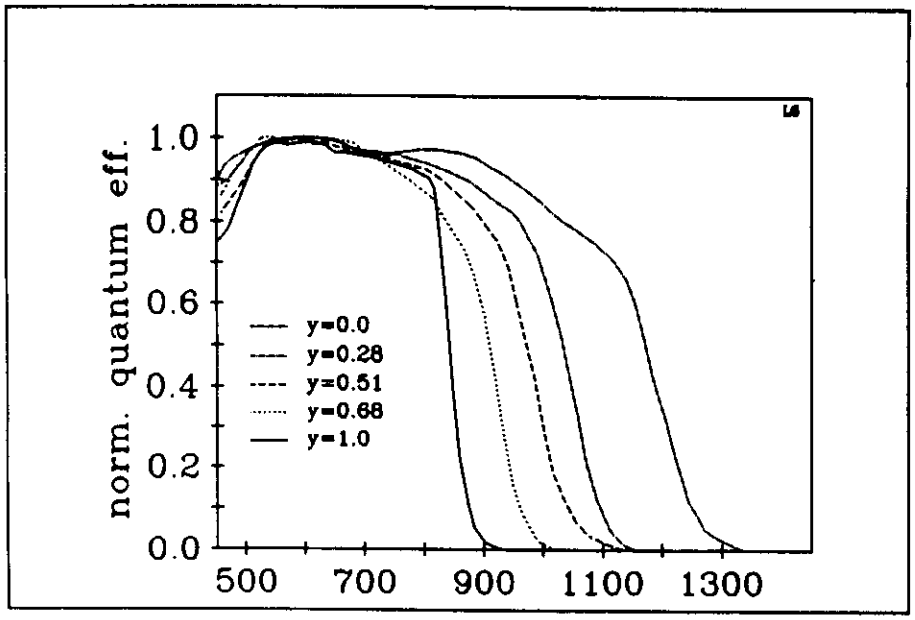
IV characteristics of $Cu(In,Ga)(S,Se)_2$ solar cells

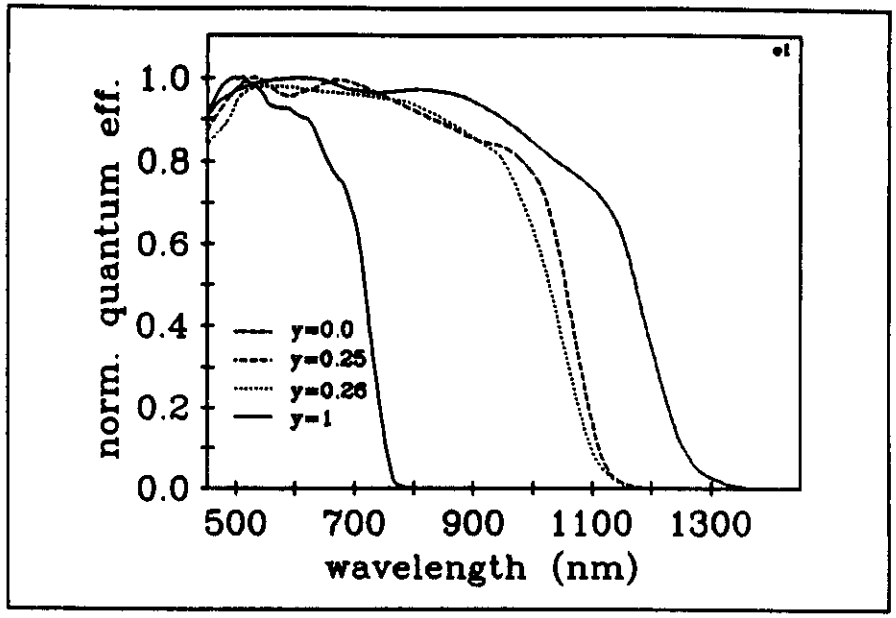
Efficiencies around 15% achieved with pure $CuInSe_2$ or alloys with Ga or S

Increase of energy gap helps to increase efficiency



spectral quantum efficiencies of $Cu(In,Ga)(S,Se)_2$





$CuInS_ySe_{1-y}$

$CuGa_yIn_{1-y}Se_2$

High blue sensitivity due to ZnO/thin CdS window

Performance of $CuInSe_2$ based solar cells

Solar Cell Type	V_{oc} [mV]	j_{sc} [mA/cm^2]	FF	Effi. [%]	Area [cm^2]	Lab.
MgF_2/ZnO/CdS/$CuInSe_2$	513	40.4	0.72	14.8	0.33	IM/RIT Stockh. IPE Uni Stuttgart
ZnO/CdS/Cu$In(Ga)Se_2$	508	41.0	0.68	14.1	3.5	ARCO/Siemens Solar
ZnO/CdS/$CuInSe_2$	486	39.8	0.72	13.9	0.25	IPE Uni Stuttgart
ZnO/CdS/$CuInSe_2$	483	38.3	0.67	12.4	0.93	ISET
ZnCdS/$CuInSe_2$	440	41.0	0.69	12.4	0.96	Boeing
ZnO/$CuInSe_2$	477	39.5	0.70	13.3	3.5	Siemens Solar Ind.
ZnO/BF*/$CuInSe_2$	443	37.7	0.62	10.3	0.25	IPE Uni Stuttgart
ZnO/ZnSe/$CuInSe_2$	391	40.1	0.64	10.0	3.5	Siemens Solar Ind.

* Cd - free Buffer layer BF), 100 mW/cm^2 Illumination at 25°C, power output of some samples have been confirmed at National Renewable Energy Laboratory

Performance of Chalcopyrite alloys based solar cells obtained

Solar Cell Type	Energy Gap	V_{oc} [mV]	j_{sc} [mA/cm^2]	FF	Effi. [%]	Area [cm^2]	Lab.
MgF_2/ZnO/CdS/CuIn(Ga)Se_2	1.17	646	32.2	0.74	15.4	0.35	IM/RIT Stockh. IPE Uni Stuttgart
MgF_2/ZnO/CdS/CuIn(S,Se)$_2$	1.12	613	33.5	0.74	15.2	0.15	IPE Uni Stuttgart
ZnO/CdS/CuIn(Se)S_2	1.45	655	24.5	0.64	10.3	0.25	IPE Uni Stuttgart
MgF_2/ZnO/CdS/CuInSSe	1.27	667	28.8	0.74	14.2	0.08	IPE Uni Stuttgart
ZnO/CdS/$CuIn_{0.71}Ga_{0.29}Se_2$	1.20	583	29.6	0.71	12.2	0.25	IPE Uni Stuttgart
ZnCdS/$CuIn_{0.63}Ga_{0.37}Se_2$	1.27	658	28.0	0.68	12.4	0.38	IPE Uni Stuttgart

* Cd - free Buffer layer (BF), 100 mW/cm^2 illumination at 25°C, power output of some samples have been confirmed at National Renewable Energy Laboratory

Future prospects

What are issues which have to be considered in the future

- **New Materials, is there a need to look for new materials and what do we expect (non toxic, abundant, properties for more efficient cells) e.g. WSe2, FeS2, FeSi2,**

- **New structures (are there new device stuctures to be developed ?)**

Toxicity

Studies are carried out considering problems of

Hazards during
- fabrication
- operation of the system
- recycling

see e.g. Workshop Report on Recycling of Cadmium and Selenium compounds from photovoltaic modules and manufacturin wastes. P.D. Moskowitz, K. Zweibel eds., Golden, March 1992, BNL 47787 Informal report

Availability

Elements are available in sufficient quantities

changes in purchases could affect the prices significantly

In-prices on the world market

From H. Keppner

New structures

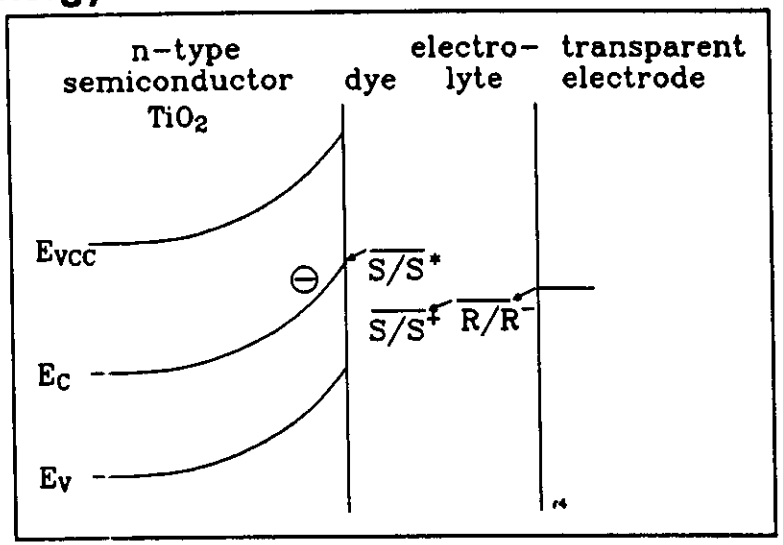
What improvements are possible with new device designs?

- Reduce junction area (thin film point contact cells)
- Increase length of optical path
- Cells with very short path for minority carrier transport

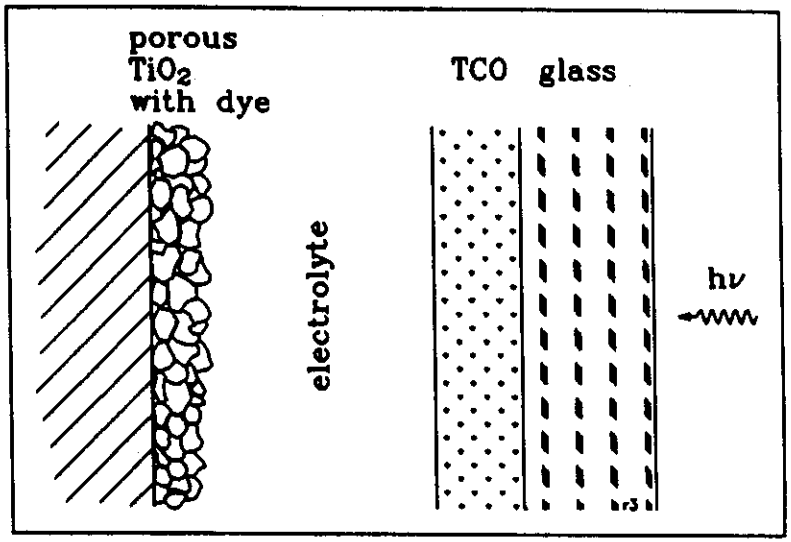
Can these improvements be compatible with low cost thin film solar cells?

The dye sensitized photoelectrochemical Cell

Energy band Scheme



Schematic structure of the cell



Efficiency up to 10 % at AM 1.5, higher at low illumination level
- issues: stability of dye, electrodes
After B. O'Regan and M. Grätzel, Nature, Vol 353, 24 Oct. 1991