

# Fabrication and Material Design of Next-Generation Solar Cells

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# Outline

## ★ Introduction

- Why New-Generation solar cells are needed ?

## ★ Progress and Prospects of CIGS Solar Cells

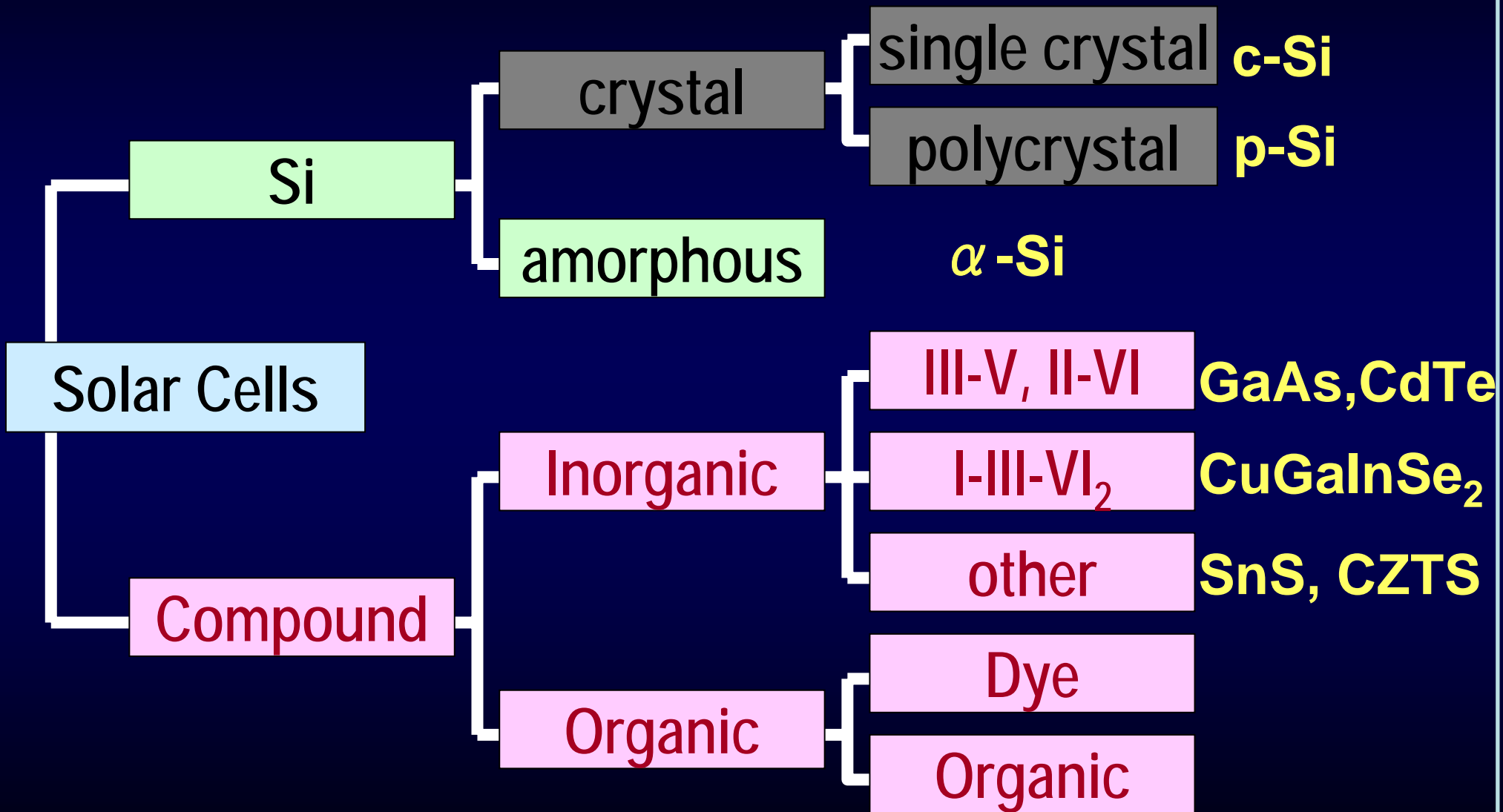
- Manufacturing Technologies

## ★ Progress and Prospects of New Materials

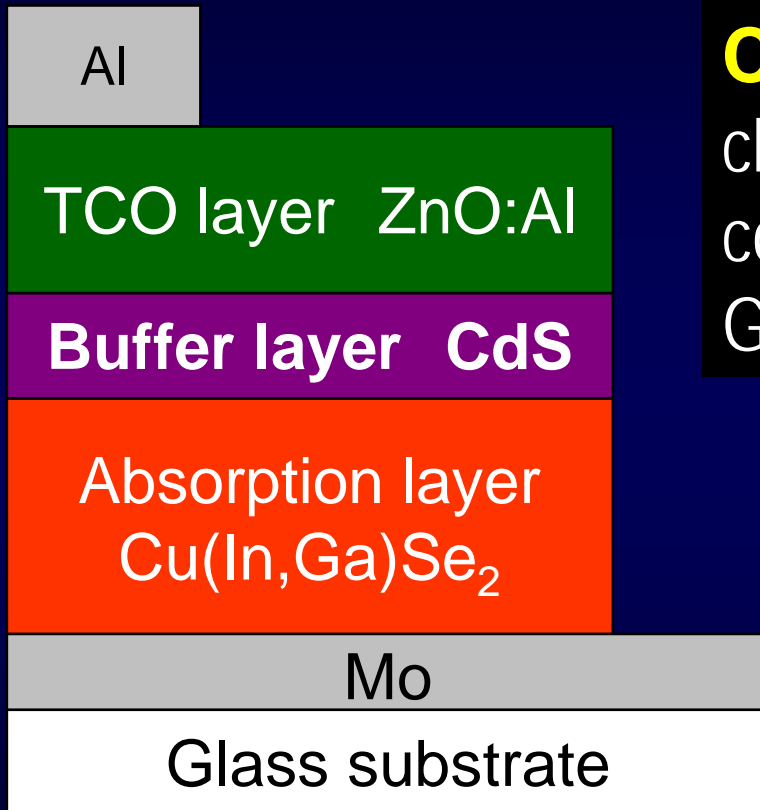
- Material Design of 3<sup>rd</sup> generation Solar Cells
- Material Design of Transparent Solar Cells

## ★ Summary

# Light absorbing materials



# What is CIGS-related solar cell ?



Typical structure of CIGS solar cell

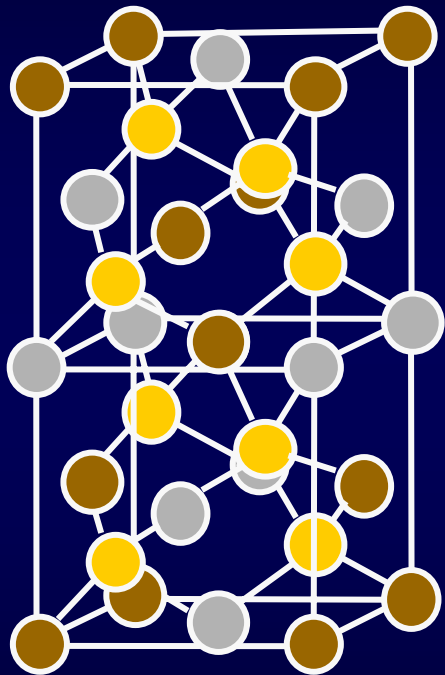
## CIGS:

chalcopyrite structured semiconductor composed of Copper (**Cu**), Indium (**In**), Gallium (**Ga**), and Selenium (**Se**).

## CIGS-solar cells:

Thin film solar cell using CIGS layer as a light absorption layer.

# Properties of CIGS Solar Cells



Chalcopyrite Structure

Group-I



Group-III



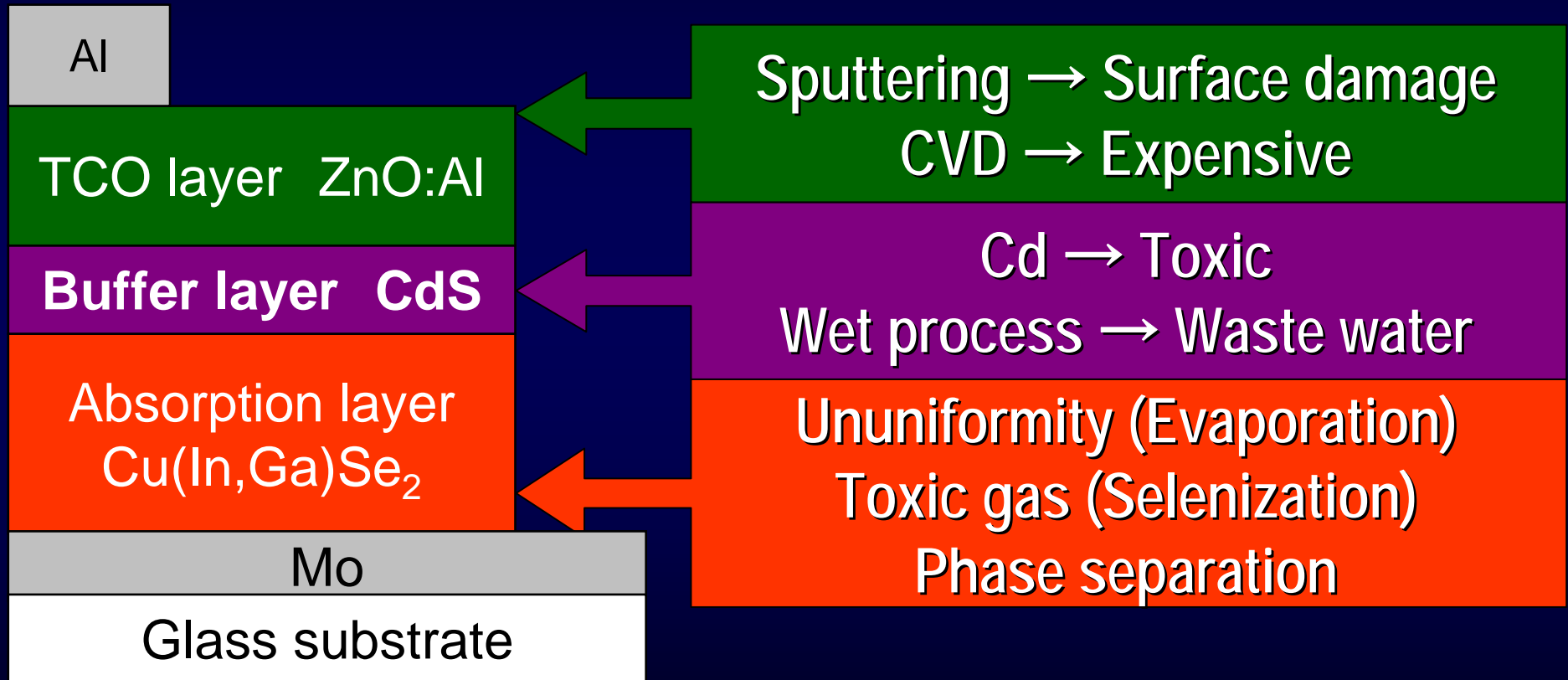
Group-VI



- ★ Highest efficiency  
(among the thin film solar cells)
- ★ High optical absorption coefficients
- ★ Long life, radiation resistant
- ★ Simple processes

**Rapid!, Cheap!, Good! Fabrication**

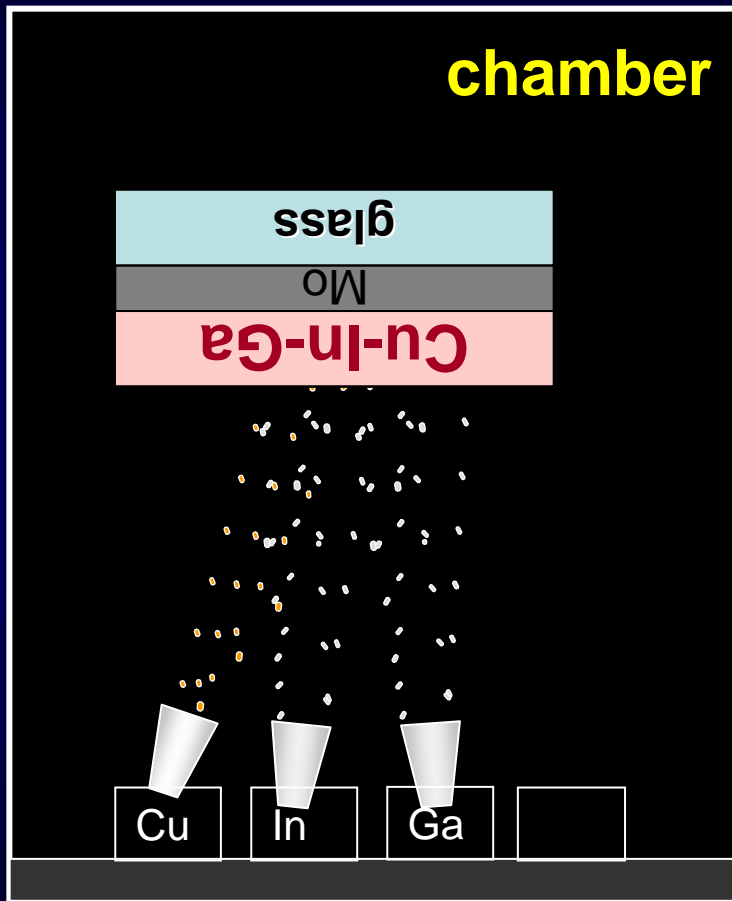
# Several problems of CIGS fabrication



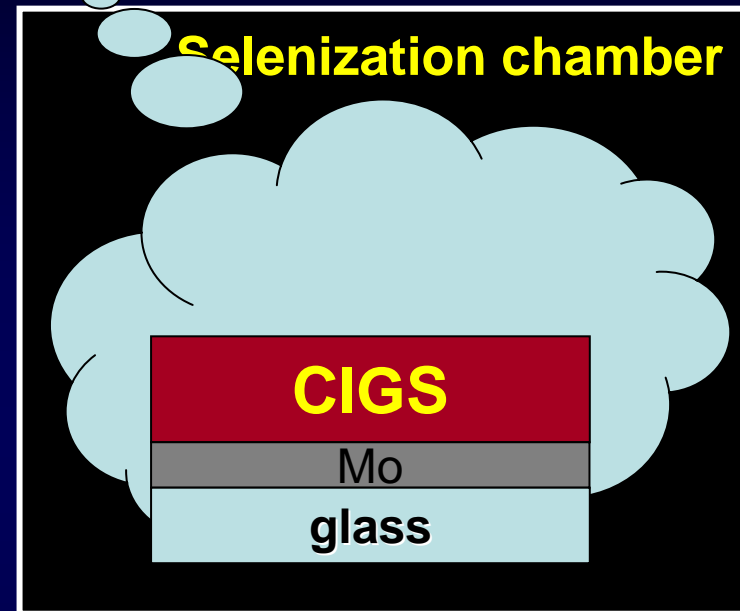
Typical structure of CIGS solar cell

# Selenization method

Se(Se vapor,  $H_2Se$ ) etc.



Sputter, Printing,  
Spin-Coating and so on



- Large area uniformity
- Simple equipments
- × Phase separation between CIS and CGS
- × Toxic gas ( $H_2Se$ )

# CBD(chemical bath deposition) method

## Fabrication of CdS buffer layer

Substrate

$\text{CdI}_2$

$\text{CS}(\text{NH}_2)_2$

$\text{NH}_4\text{OH}$

Typical condition

Growth temperature  $70^\circ\text{C}$

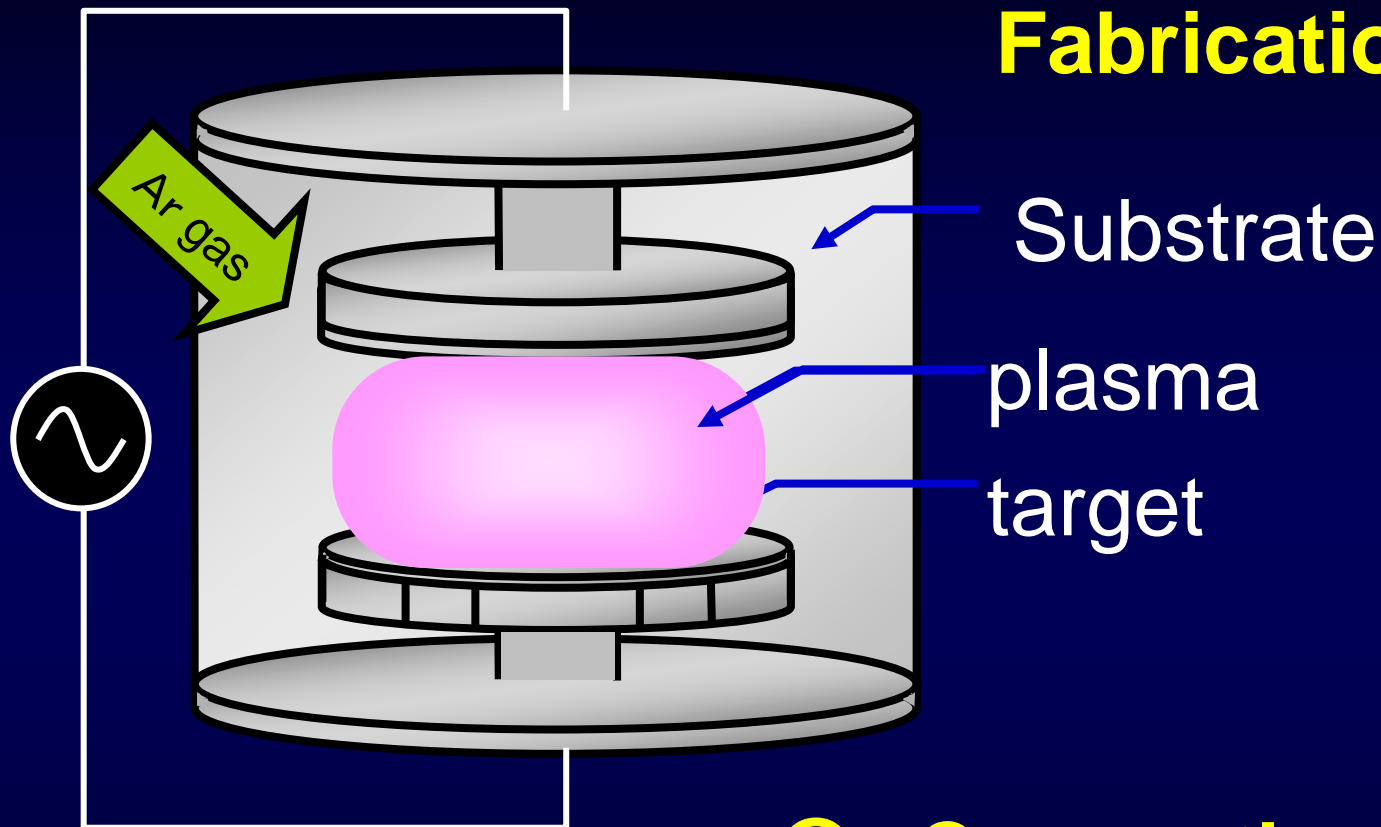
$\text{CdI}_2$	0.001M
$\text{CS}(\text{NH}_2)_2$	0.05M
$\text{NH}_4\text{OH}$	1M

heater



# Sputtering method

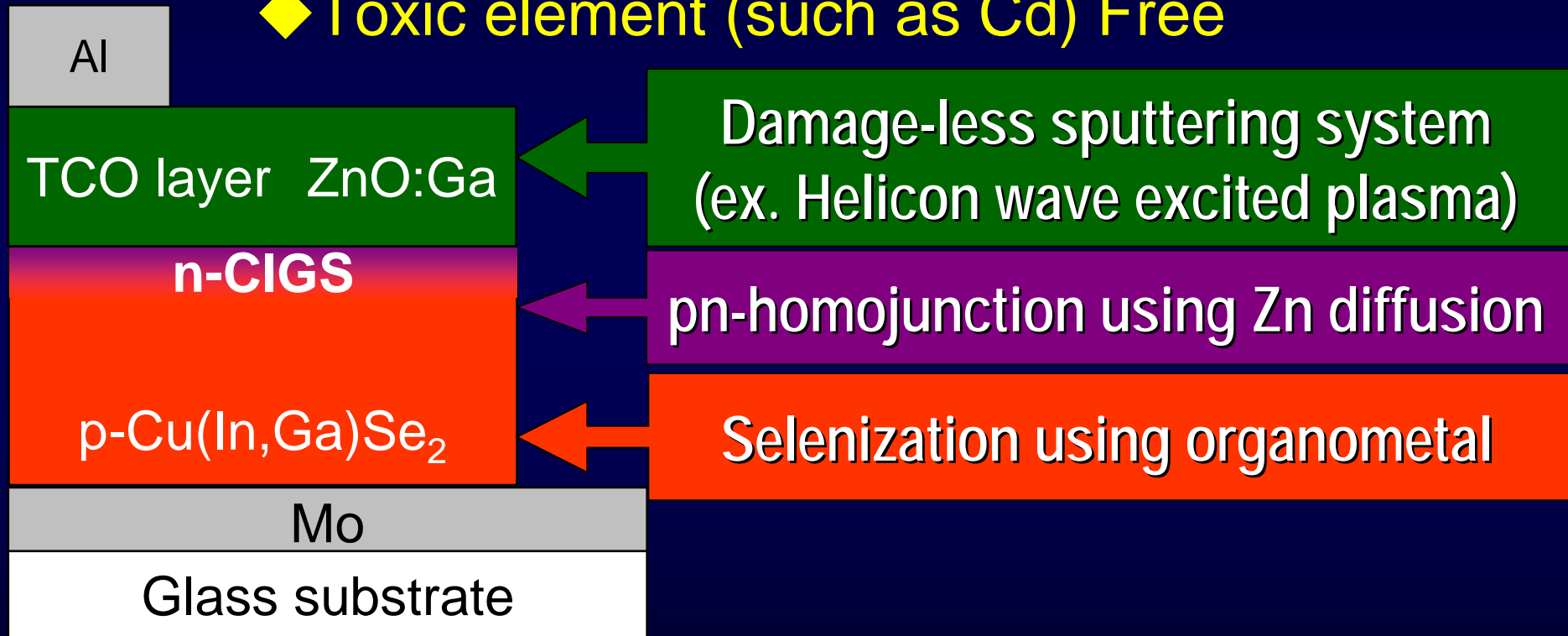
## Fabrication of ZnO layer



- Conventional technique
- Not so expensive
- × plasma damage for cell

## For the future ... (in my case)

- ◆ All dry process
- ◆ Reduction of the number of the processes
- ◆ Toxic element (such as Cd) Free



**Rapid!, Cheap!, Good! Fabrication**

# How to fabricate CIGS

films

## *CIGS growth*

### Co-evaporation method

- ◎  $\eta = 19.5\%$  (small cell)
- △ Scaling up → Difficult

### Selenization method

- ◎ Simple process
- ◎ Scaling up → Large cell

## *Se source for Selenization*

H<sub>2</sub>Se

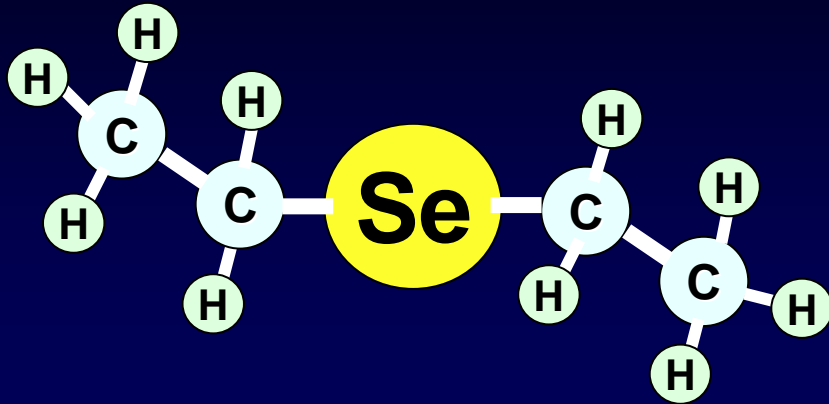
Toxic, High pressure, ....

Elemental Se

Low efficiency, .....

**DESe**

# Selenization using Diethylselenide (DESe)



Diethylselenide  
(DESe)

*Liquid at RT*

*Normal organometal*

*Safety*

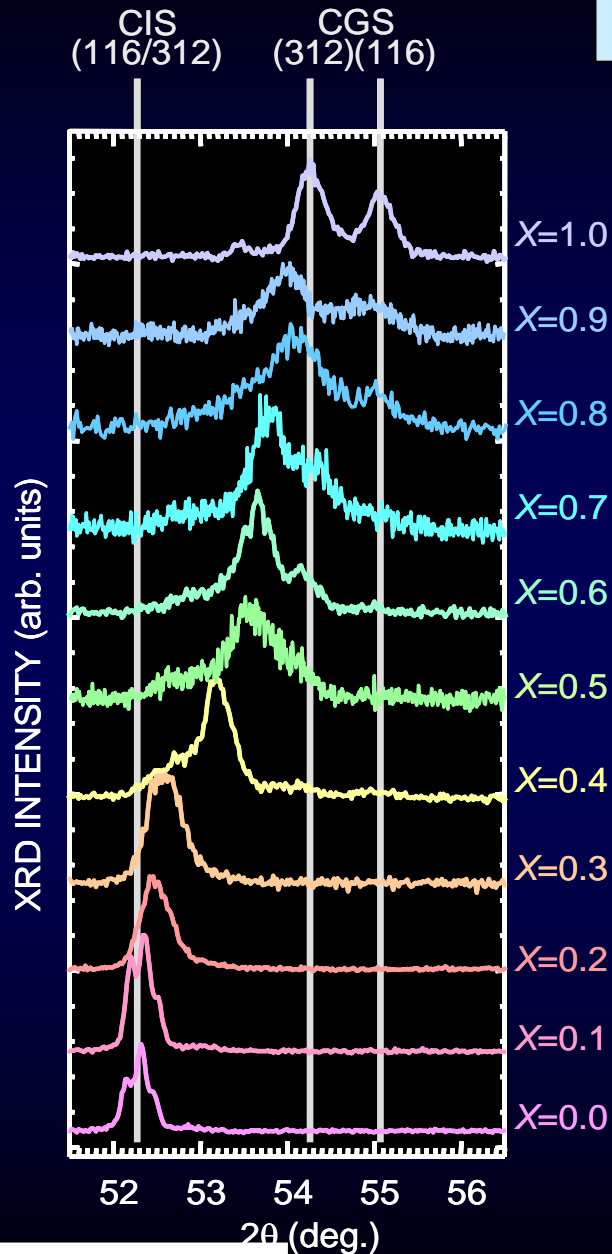
*NOT so expensive*

*Easy to handle*

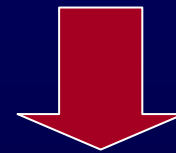
## *CIS growth using DESe*

- ◆ S.F.Chichibu *et al.* J.Cryst Growth, 243 (2002) 404.
- ◆ T.Yamamoto *et al.* J.Phys. & Chem. Solids, 64 (2003) 1855.

# XRD pattern of CIGS films

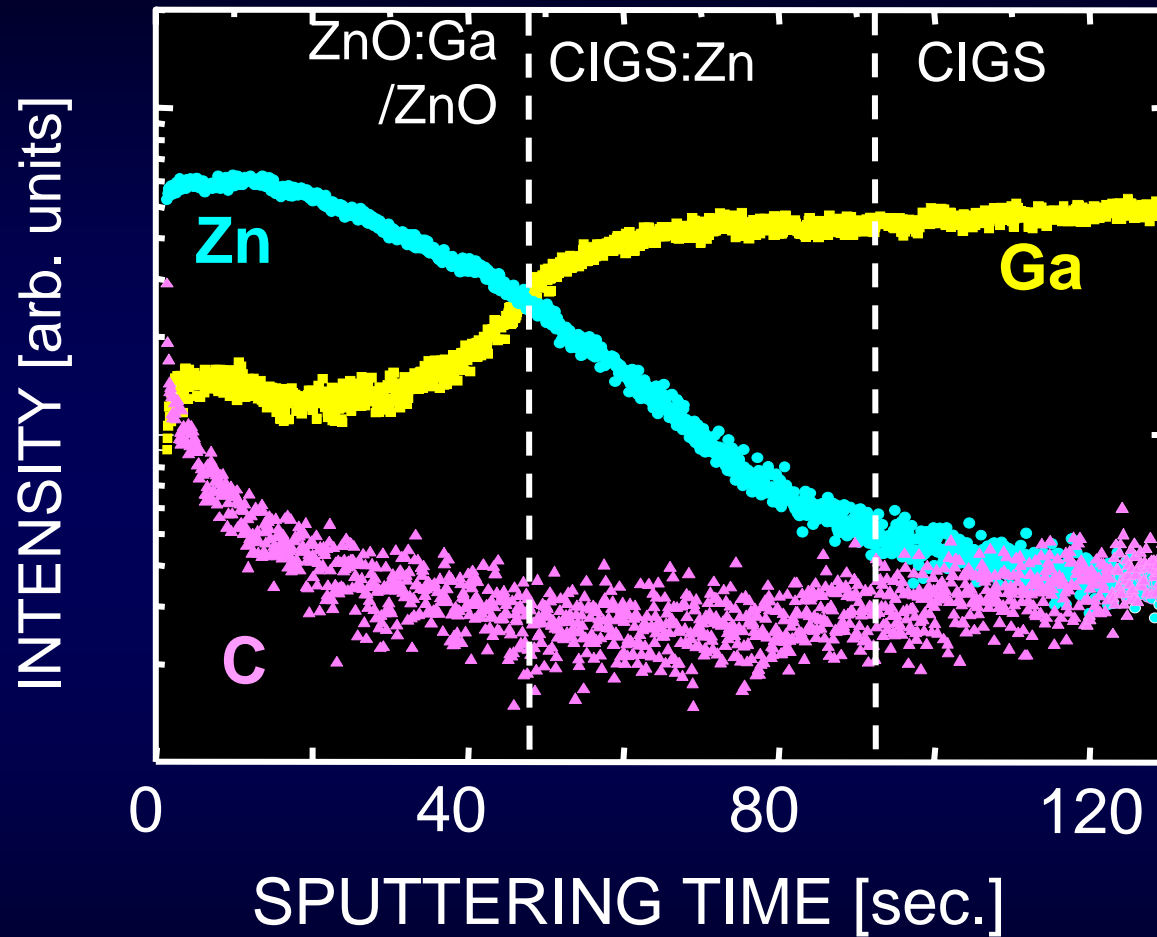


○ Simple **EQUIPMENT**  
○ Simple **PROCESS**



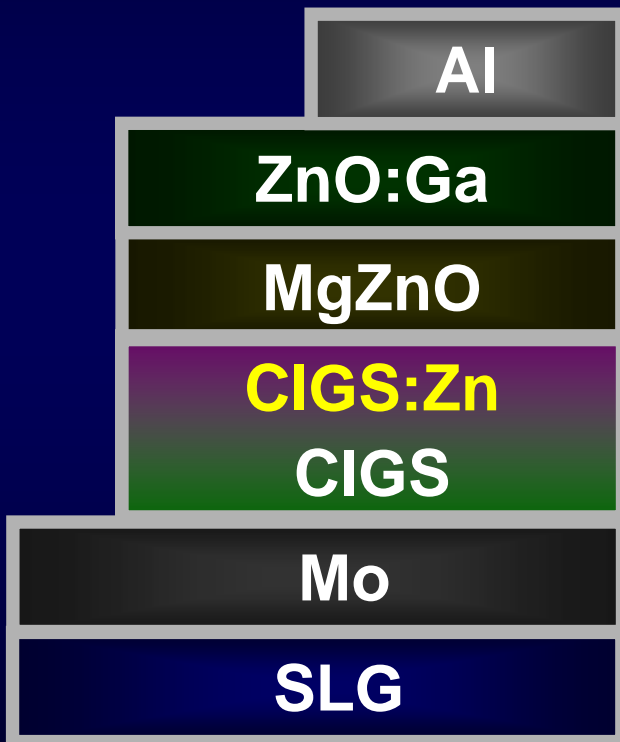
**Highly advantageous  
for the development  
of low-cost solar modules**

# Depth profile of carbon in the cell



***WITHOUT Carbon contamination!***

# CIGS solar cell structure



## CBD-CdS

- ✗ **TOXIC** element (Cd)
- ✗ Fabricated by **WET PROCESS**



## pn-homojunction (by Zn-doping)

- **AVOID** carrier recombination at the physical interface
- Fabricated by **DRY PROCESS**
- **SAFE** element (Zn, Cu, In etc.)

# Experiment

1st step

preparation of **CIGS films**

[\*] Thin Solid Films 515 (2007) 5867.

Selenization method using **Diethylselenide** [\*]

or  
3 stage method

2nd step

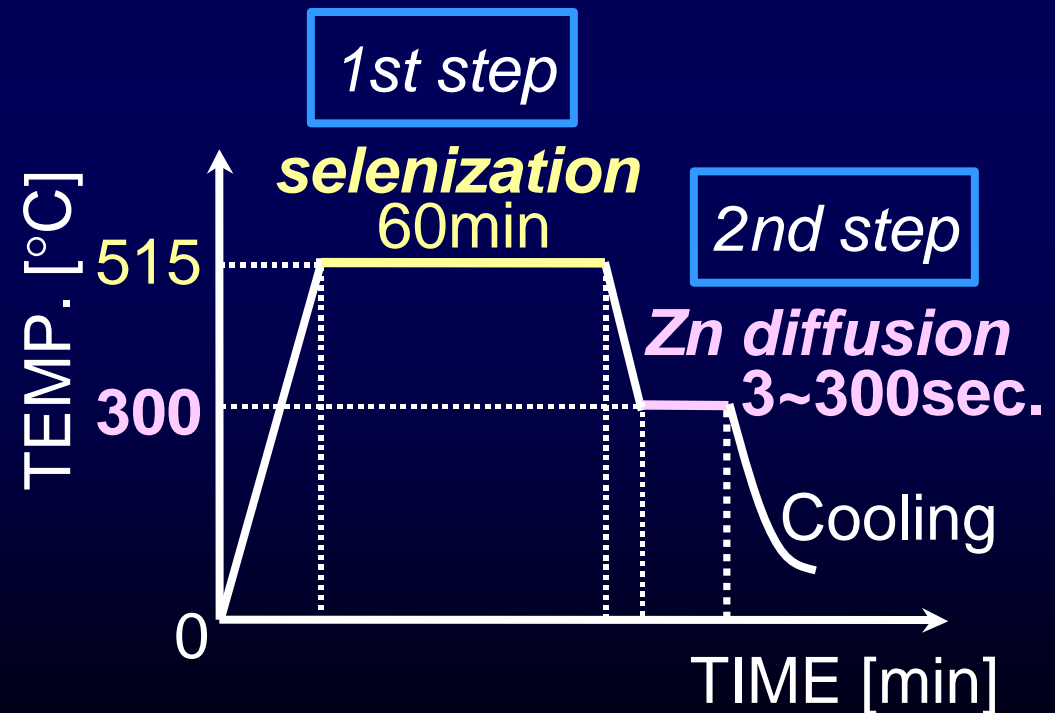
**Zn-diffusion**

@Atmospheric pressure

Dimethylzinc :  $60\mu\text{mol}/\text{min}$

$[(\text{CH}_3)_2\text{Zn} : \text{DMZn}]$

+  $\text{N}_2$  carrier gases:  $2\text{L}/\text{min}$





# Experiment

3rd step

*Fabrication of solar cells*

**ZnO:Ga/MgZnO/CIGS:Zn**

Deposition by *helicon-wave-excited-plasma sputtering (HWPS) method*

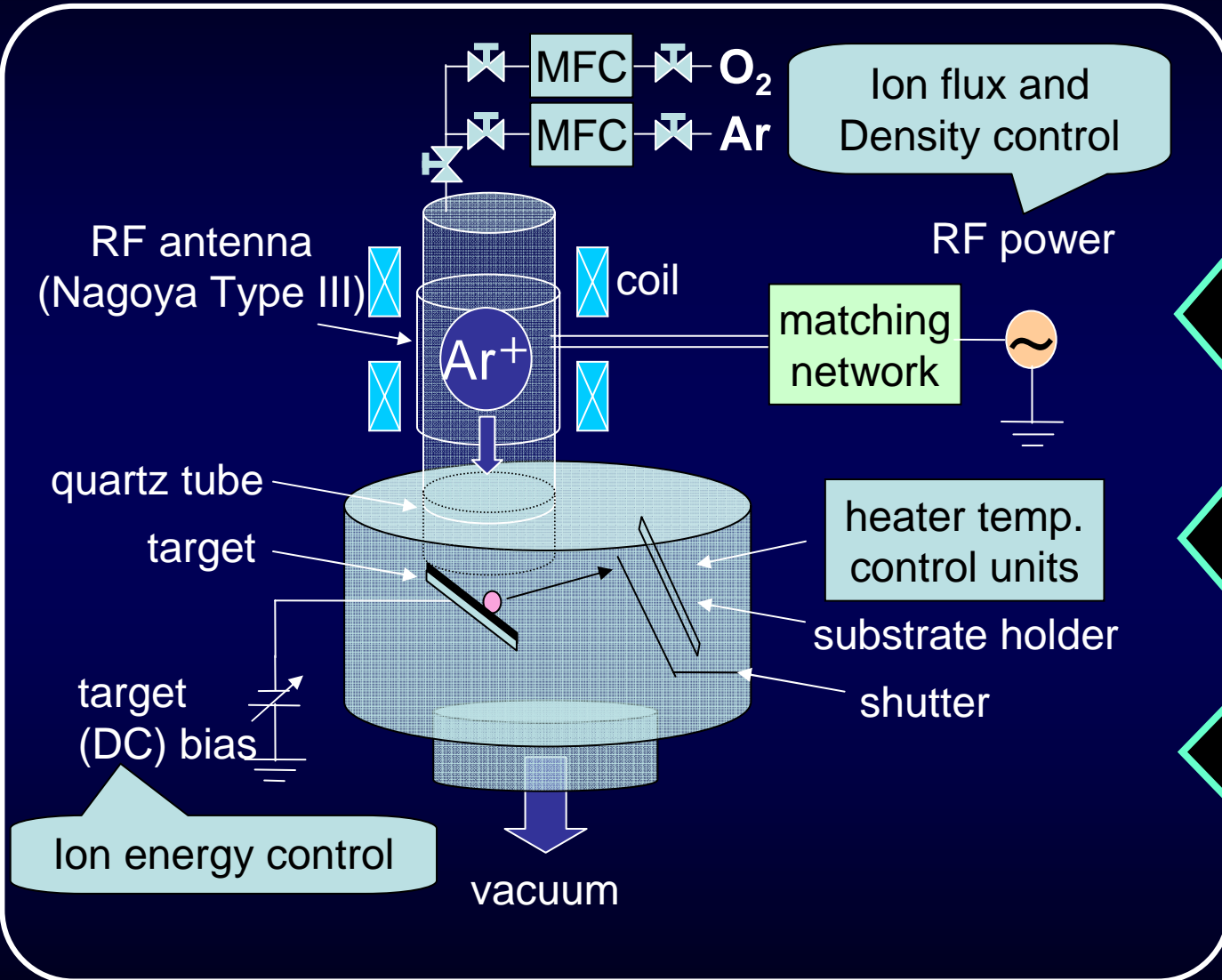
Appl. Phys. Lett. **72** (1998) 235.  
We reported yesterday.

**Characterization**

**Zn doped CIGS films: XRD, GDOES, PL, I-V, C-V**

**Zn doped CIGS cells: I-V**

# Helicon-Wave-Excited-Plasma Sputtering (HWPS) Method



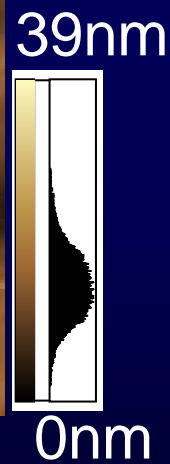
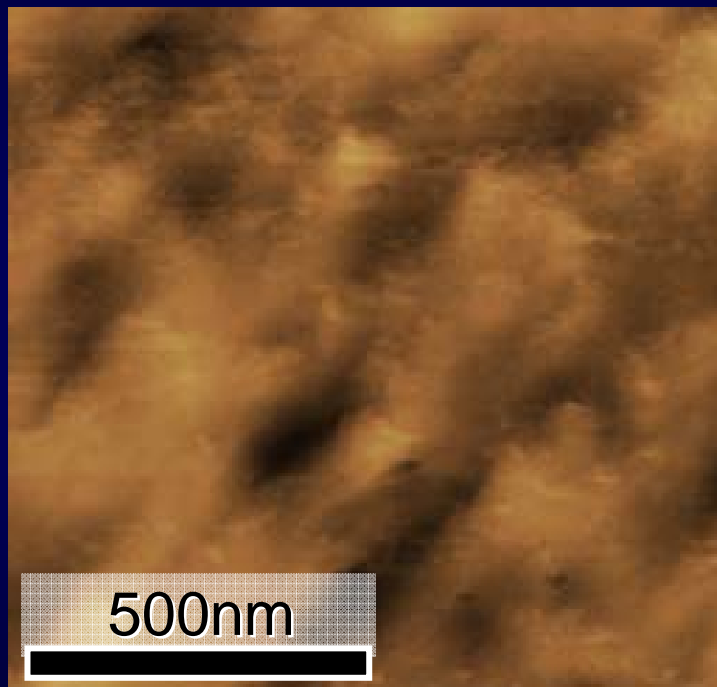
- Remote plasma  
Low damage on surface
- Independent control  
of ion flux and energy
- Low pressure  
Long mean free path

Appl. Phys. Lett. 72 (1998) 235.

# Surface Morphology of ZnO:Ga

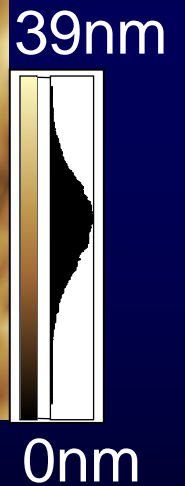
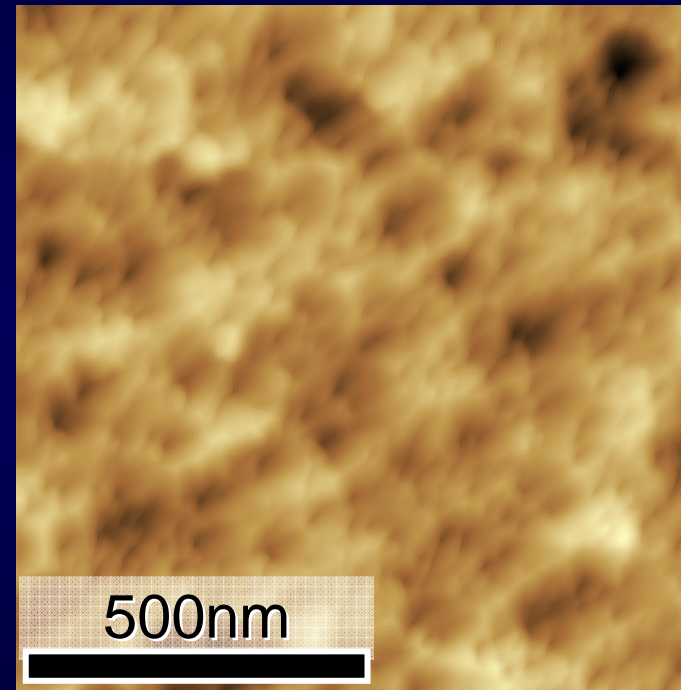
## *AFM images*

**200°C, 1.5 wt.%**



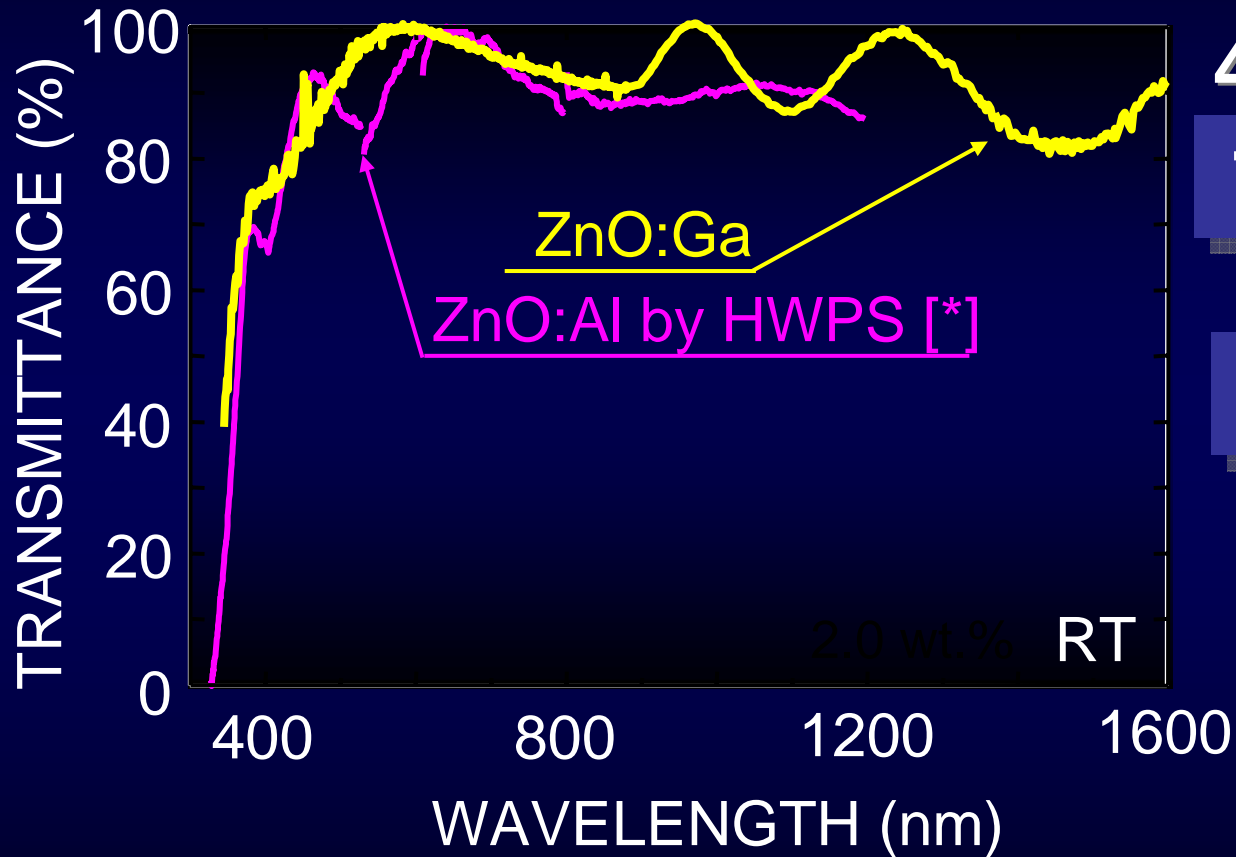
**RMS = 4 nm**

**400°C, 1.5 wt.%**



**RMS = 5 nm**

# Optical Transmittance Spectrum



400–1600 nm

Transmittance  $\geq$  80%

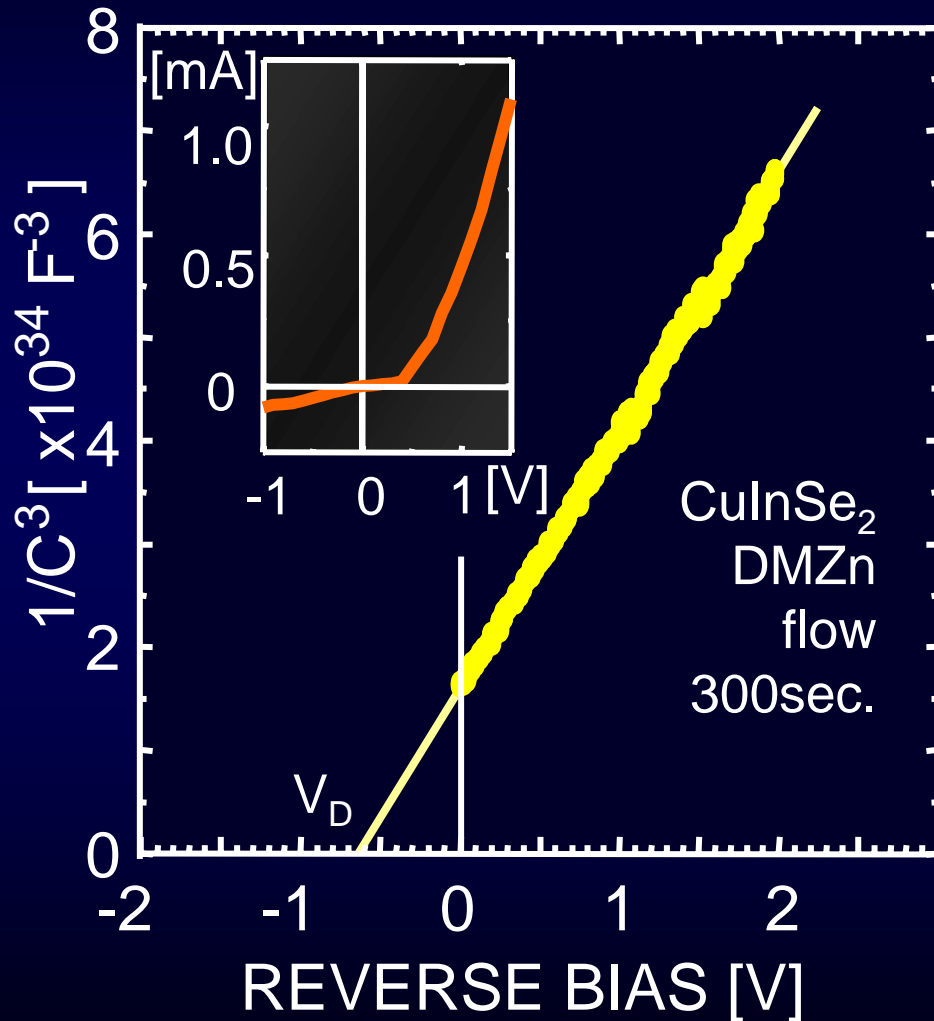
Multiple interference



Smooth surface

[\*] Appl. Phys. Lett. 72 (1998) 235.

# 1/C<sup>3</sup>-V curves of the Zn-diffused CIS/Mo/SLG



• Surfaces of the films → **n-type**

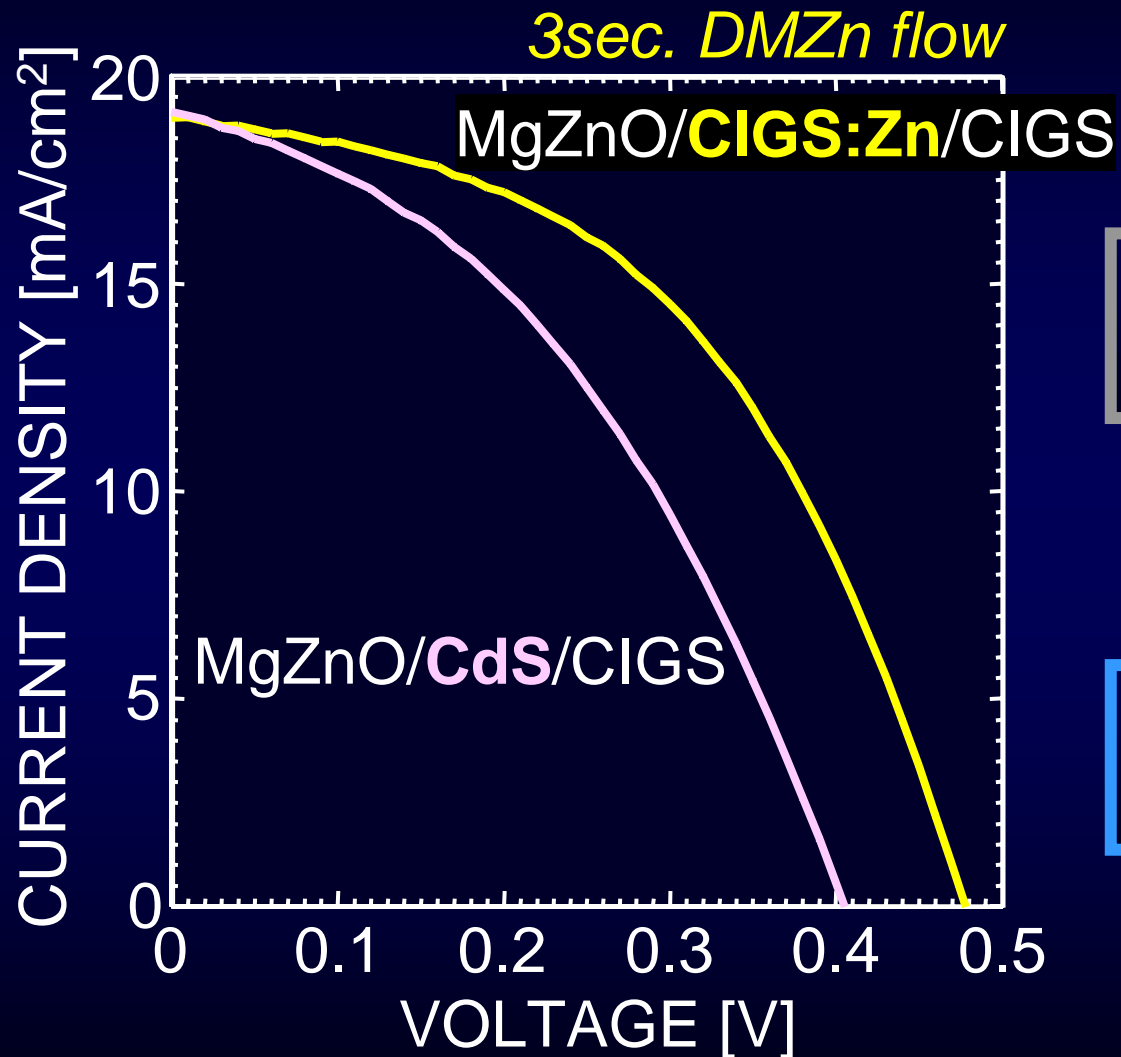
• I-V → **rectification property**

values of 1/C<sup>3</sup>  
change linearly

**linearly graded  
junction**

**pn-homojunction  
fabricated by thermal diffusion**

# Impact of introducing Zn-diffusion



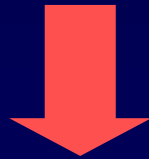
By 3 sec. DMZn flow  
instead of CBD-CdS

Voc is improved  
approximately by 20 %

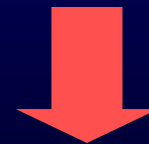
# Issues of CIGS growth

at  $E_g > 1.2\text{eV}$

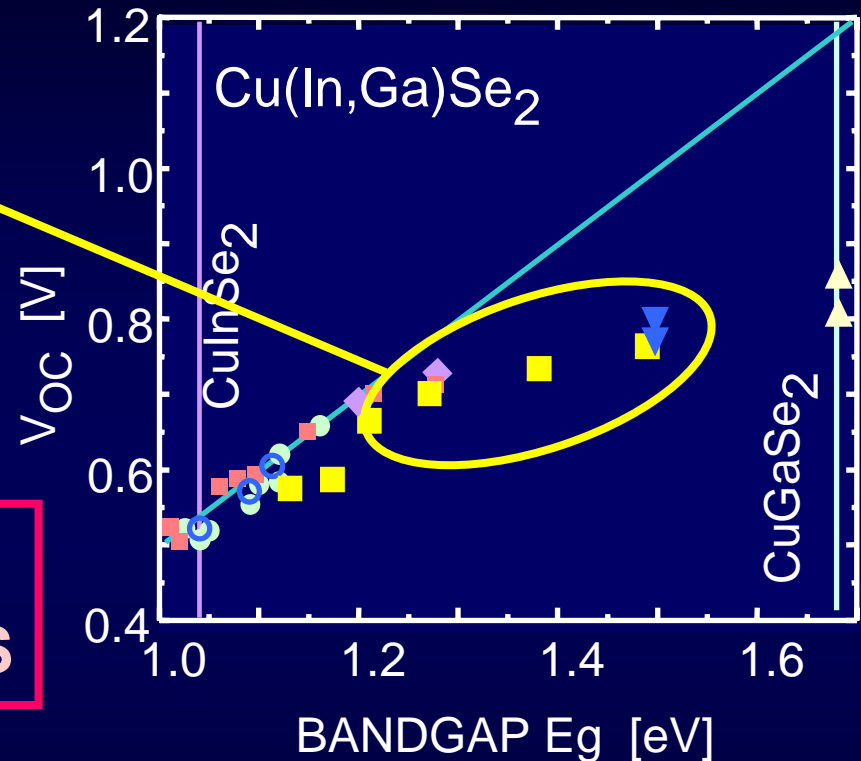
Crystal quality ↓  
Device performance ↓



Due to the difference in the  
reaction rates of the CIS and CGS



**Cu(In,Al)Se<sub>2</sub> (CIAS)**



R. Herberholz et al. Sol. Energy Mater.  
Sol. Cells 49 (1997) 227.

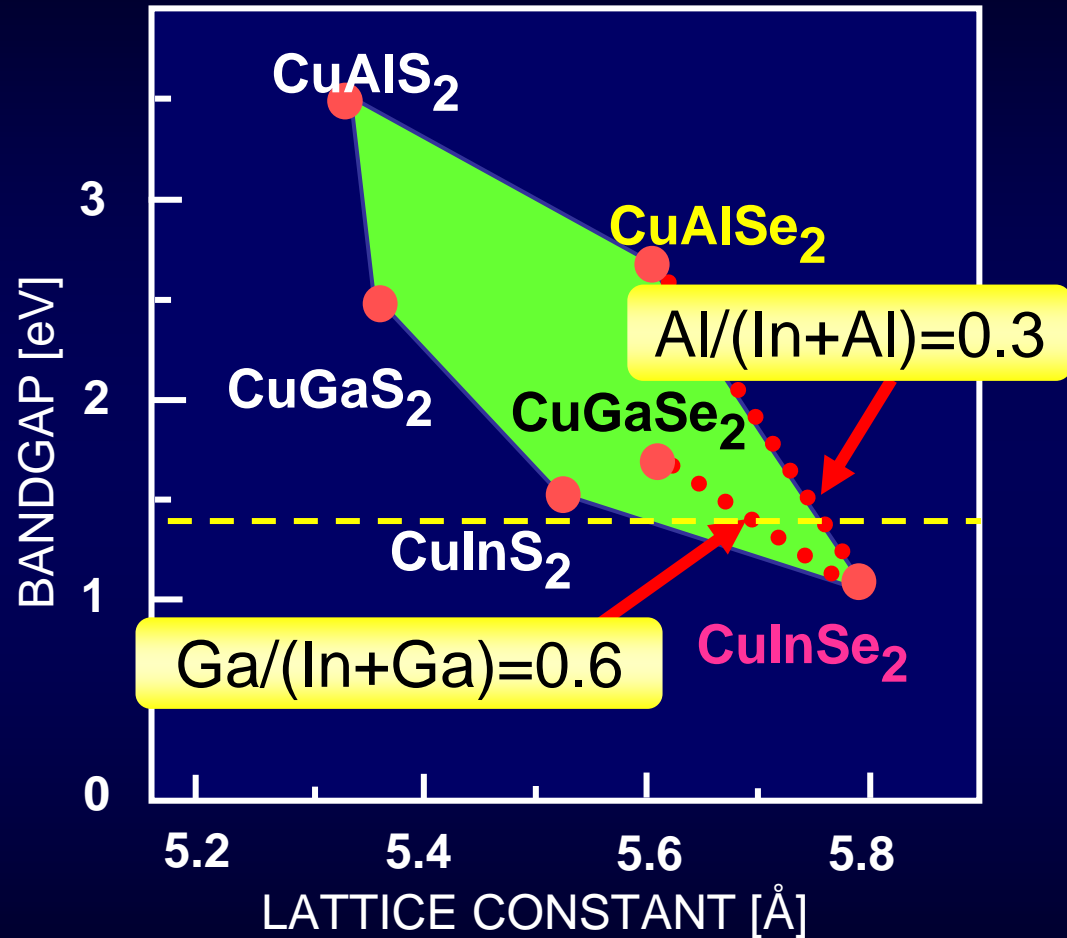
# Issues of Cu(In,Al)Se<sub>2</sub> growth

E<sub>g</sub> of CIAS  
1.0~2.7eV  
(CIS) (CAS)

CIAS

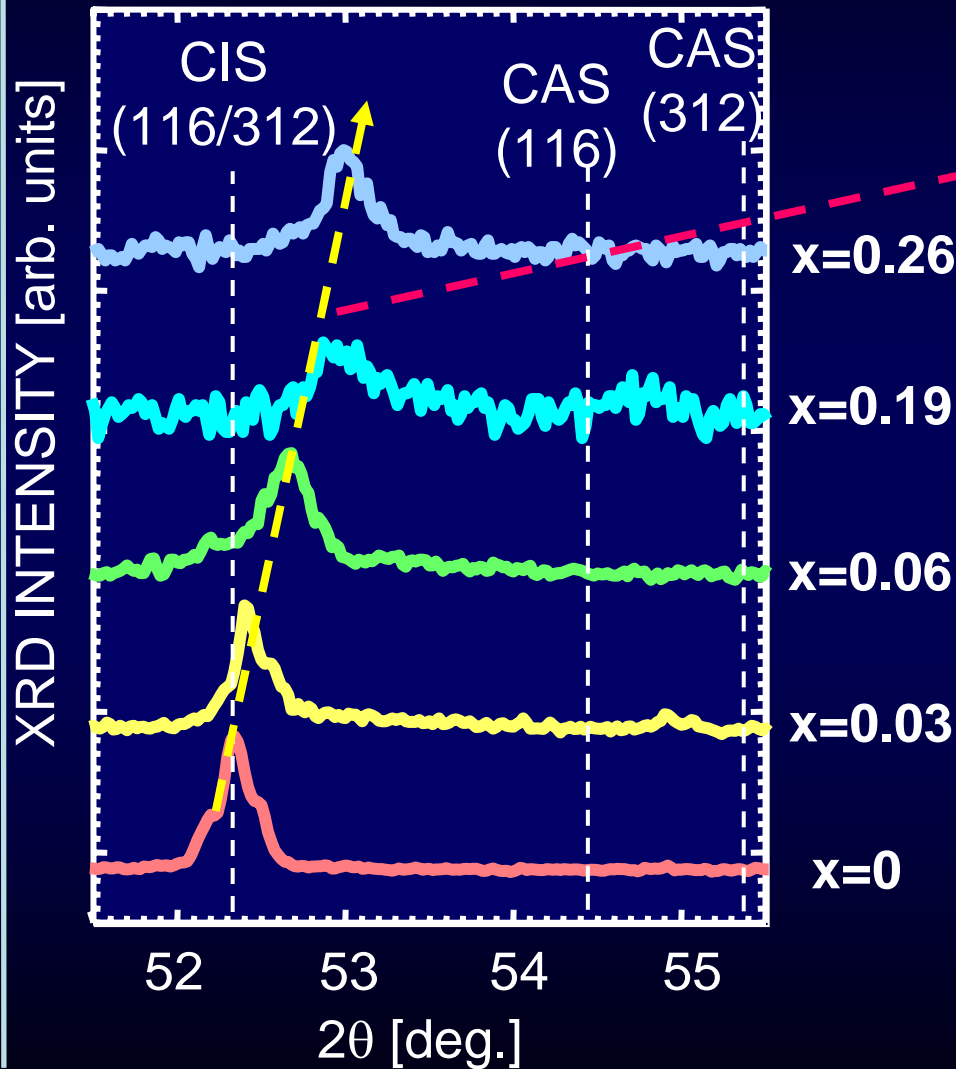
Ideal E<sub>g</sub> 1.4eV  
 $Ga/(In+Ga) > Al/(In+Al)$

Hopefully phase separation **less** likely than CIGS films





# XRD patterns of CIAS as a function of x



the decrease in lattice parameter with the **increase in x**

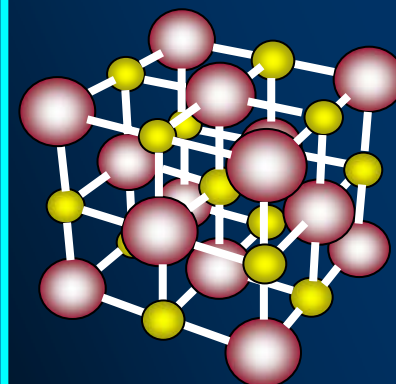
distinct peaks corresponding to **CIS CAS**  
or  
**any combination of the two phases**  
were **not observed**

# Material Design for 3<sup>rd</sup> generation solar cell

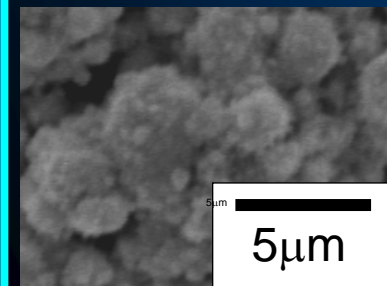
## Tin Sulfide (SnS)

- direct gap : 1.3eV indirect gap : 1.1eV  
 $\alpha \cong 10^5 \text{ cm}^{-1}$  [1]
- **SAFE** and **CHEAP** elements (Sn, S)  
Clarke numbers of the order of 31 and 15

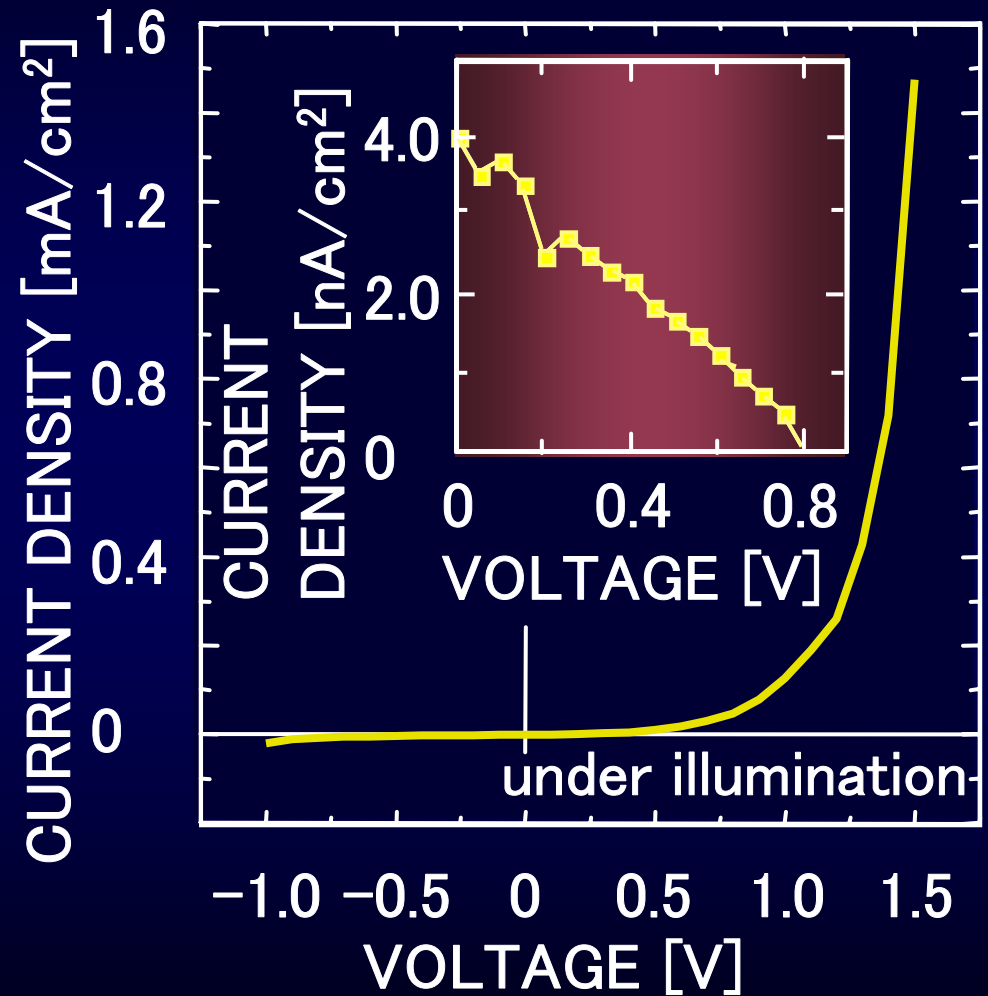
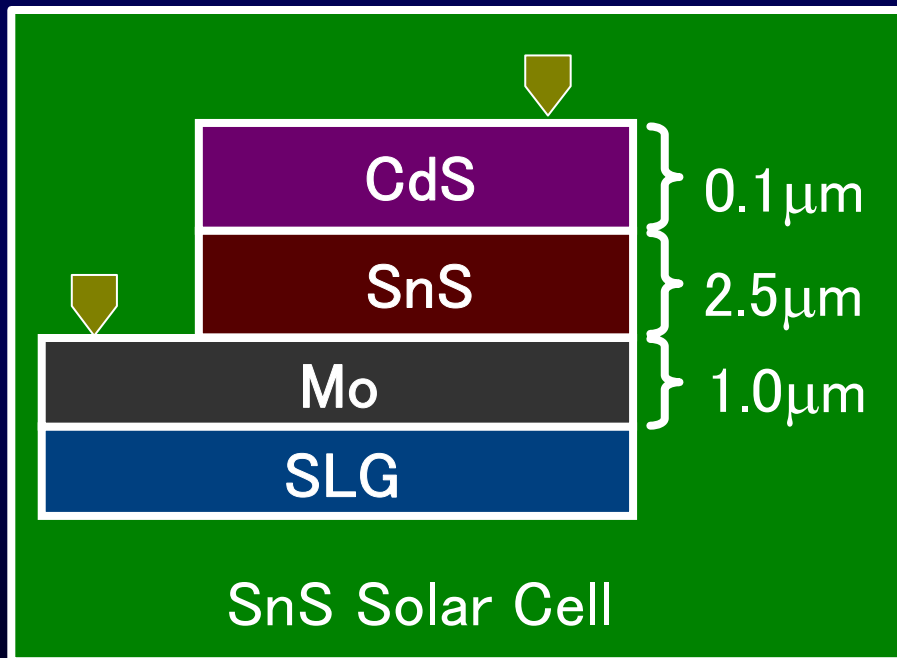
**A promising candidate as a light-absorbing medium for next generation solar cells**



Orthorhombic structure

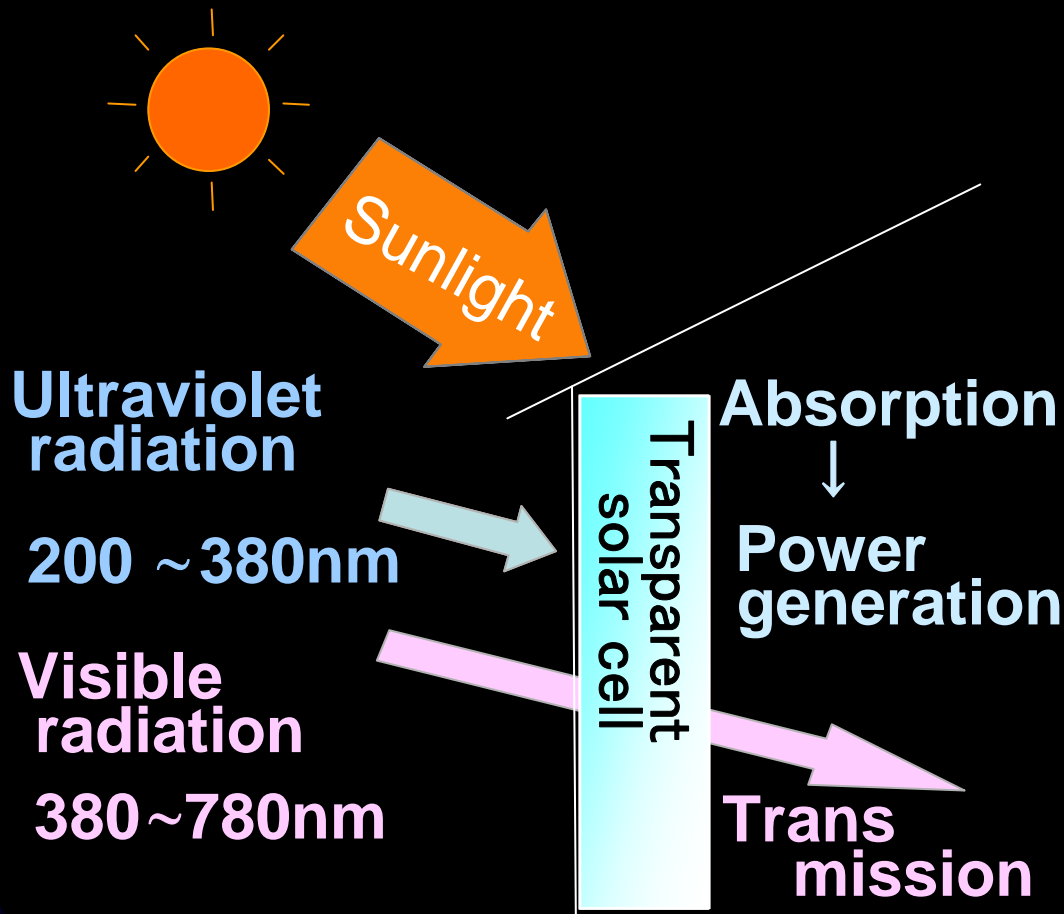


# Fabrication of SnS Solar Cell

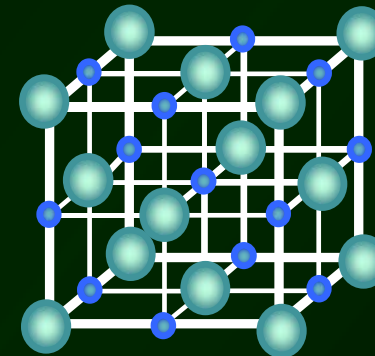
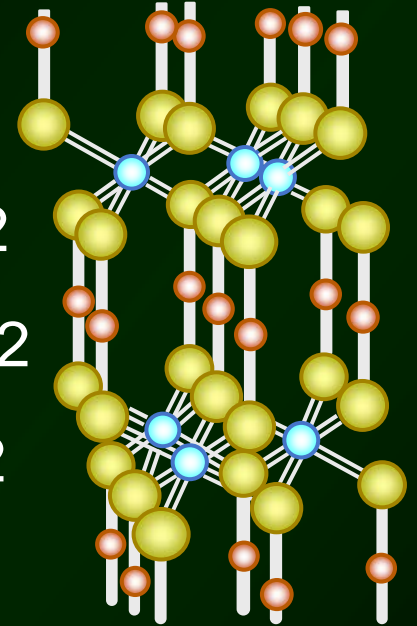
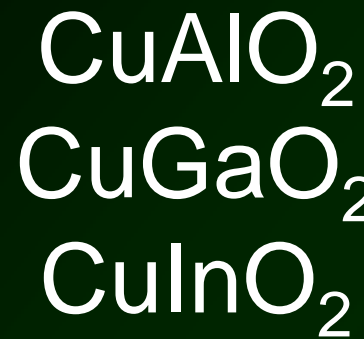


# Material design for transparent solar cells

Ex: Transparent solar cell

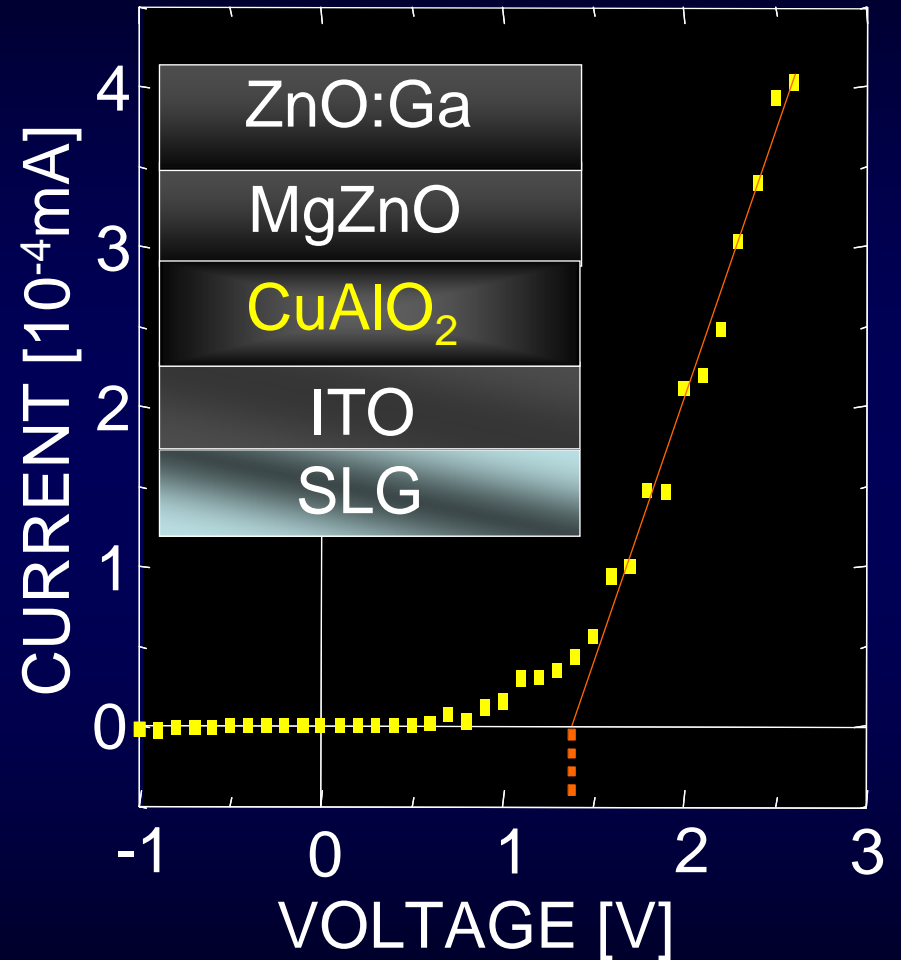
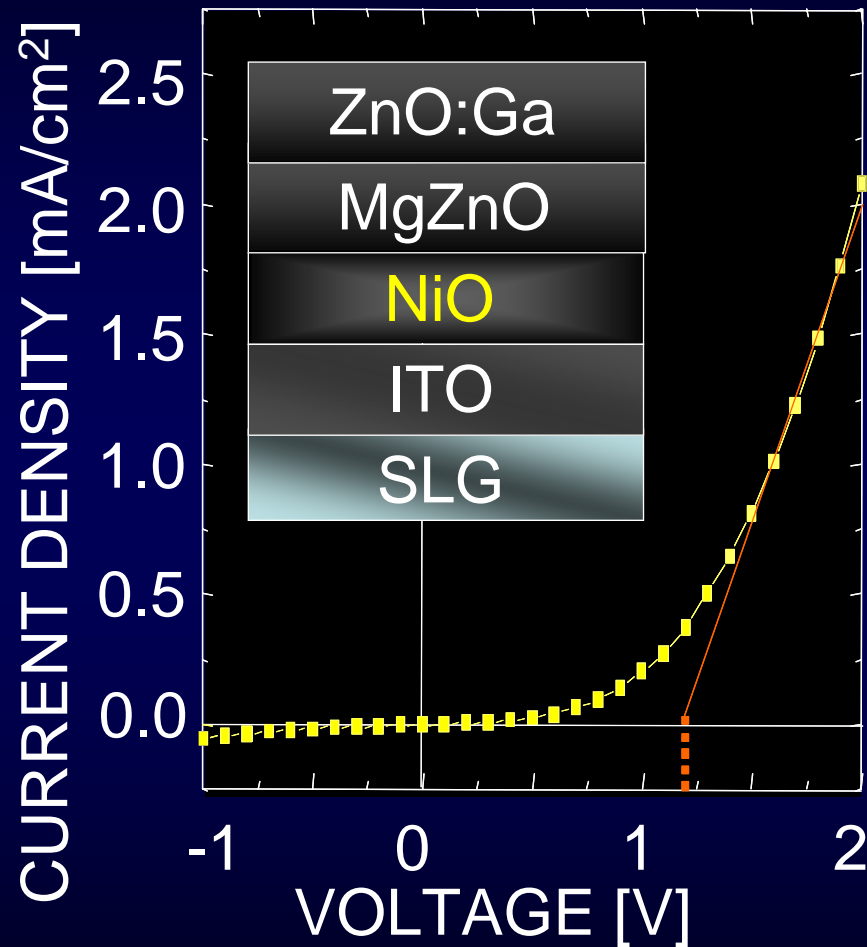


Main *p*-type TCO



$\text{NiO}$

# Transparent pn Diodes for Solar Cell



# Summary

## Progress and Prospects of Next-Generation Solar Cells

- Simple and high efficiency solar cells
- Variety of fabrication technique
- Variety of Material

**Rapid!, Cheap!, Good! Fabrication**