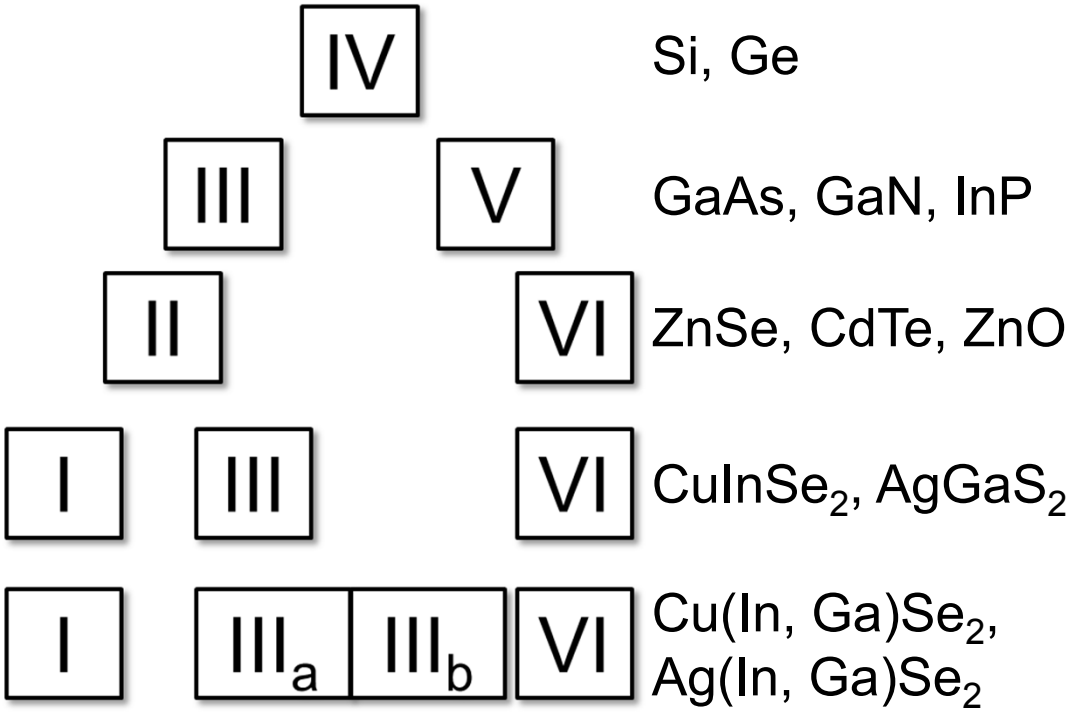
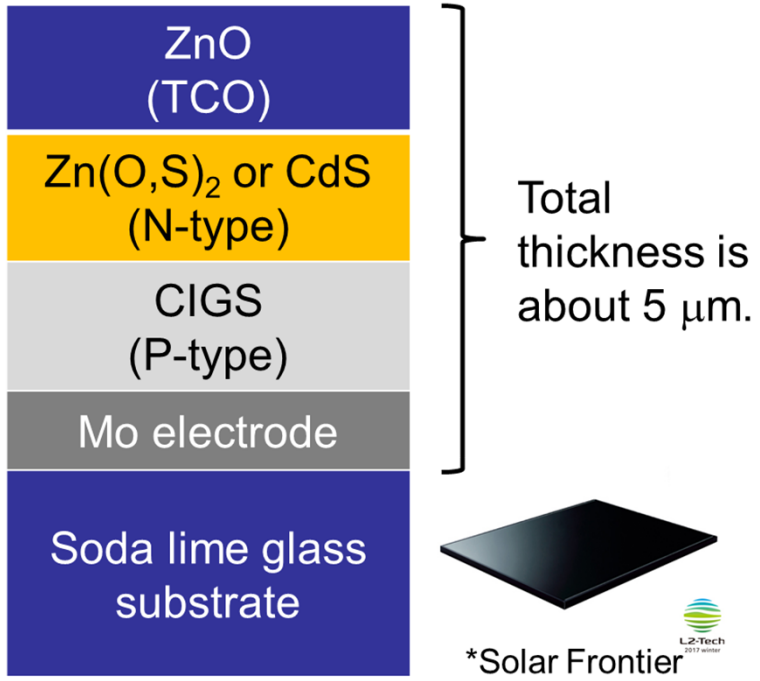
III-V族半導体基板上 Epitaxial CIGS太陽電池の開発

国立研究開発法人産業技術総合研究所
太陽光発電研究センター
化合物薄膜チーム、先進多接合デバイスチーム
西永慈郎、石塚尚吾、菅谷武芳

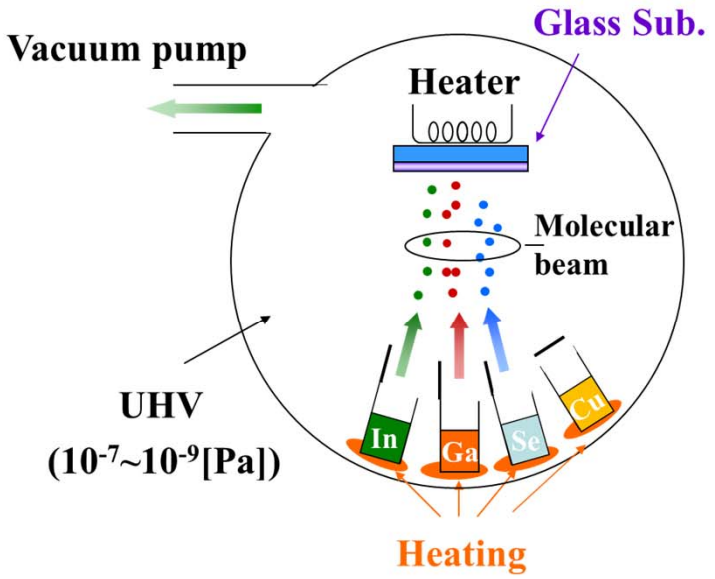
$Cu(In,Ga)Se_2$ (CIGS)太陽電池



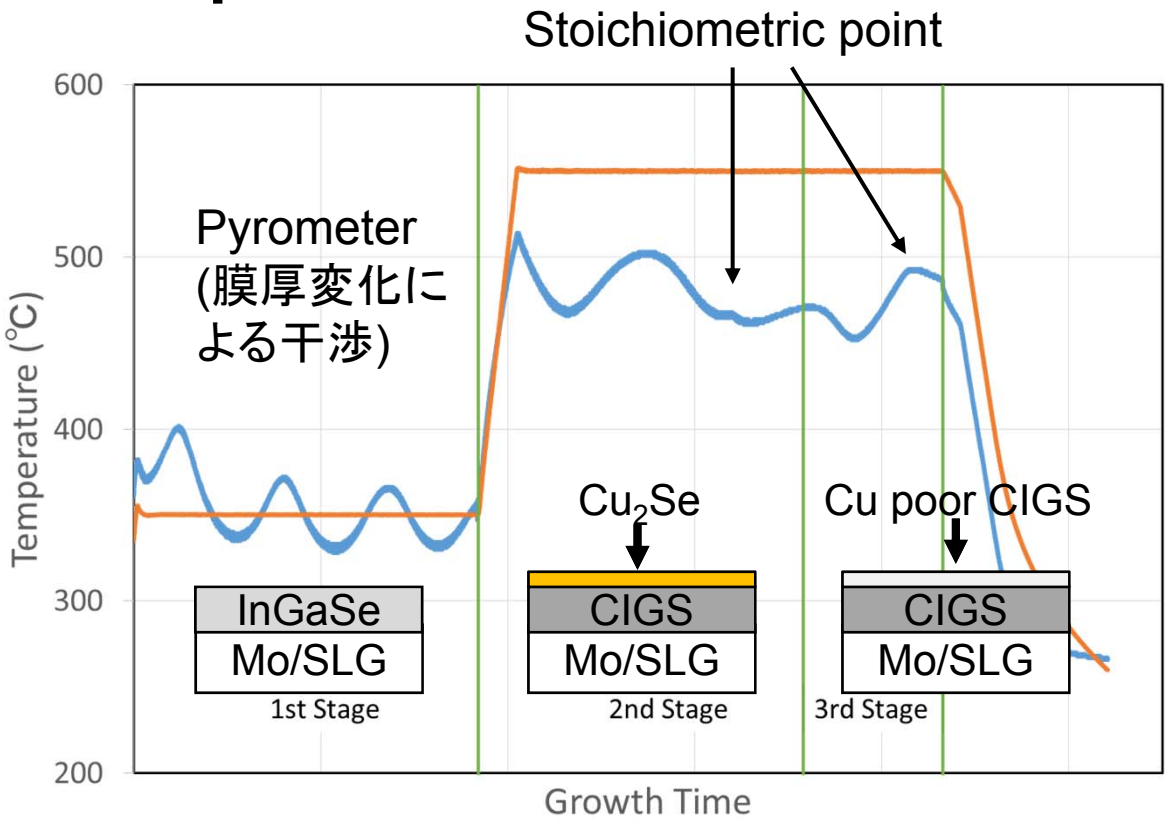


- Ⅰ-Ⅲ-Ⅵ$_2$族化合物半導体(Ⅰ-Ⅵ: イオン結合、Ⅲ-Ⅵ: 共有結合)
- 欠陥による伝導型制御(アクセプタ型欠陥($V_{Ⅰ}$)、ドナー型欠陥($V_{Ⅵ}$))
- ヘテロ構造によるデバイス応用(ドーピングが困難、ヘテロ界面急峻性制御)
- 結晶粒界の不活化、Metastability(光励起、熱励起)の存在

The 3-stage evaporation of CIGS



Molecular Beam Deposition

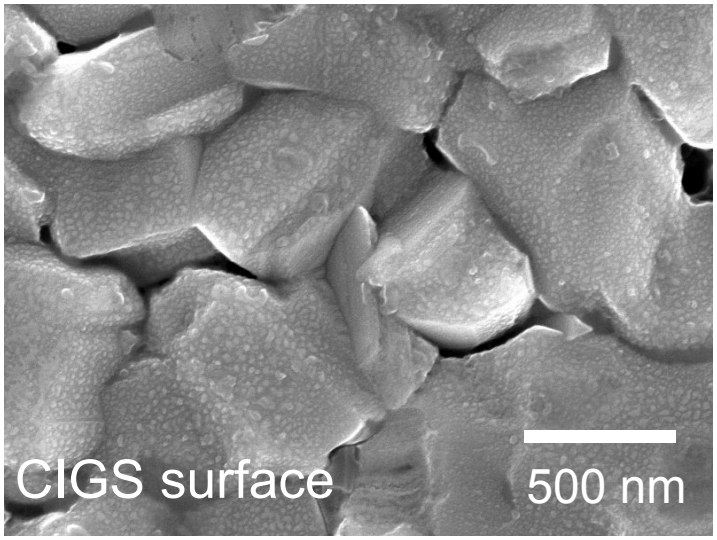


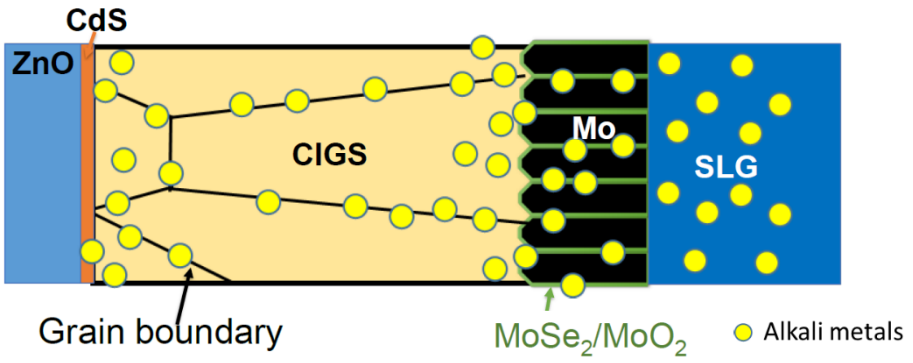
1st stage: In, Ga, Se
2nd stage: Cu, Se
3rd stage: In, Ga, Se

→

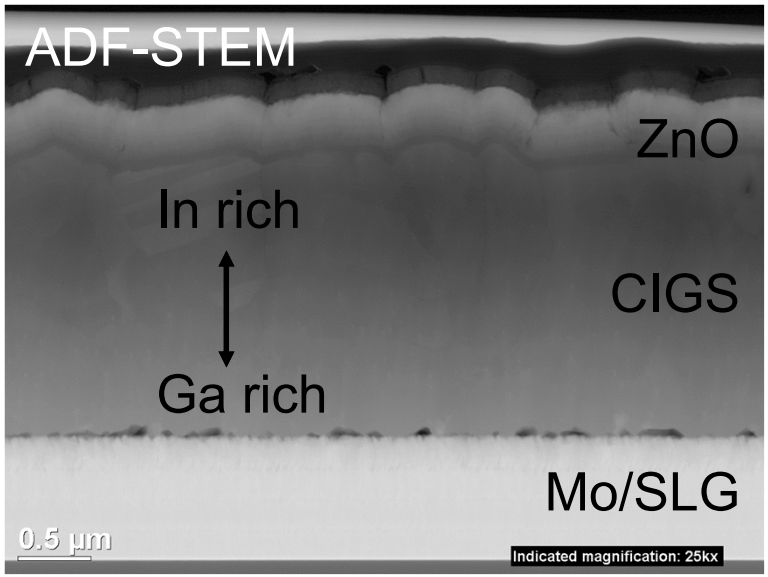
1st stage: $(In,Ga)_2Se_3$
2nd stage: $Cu(In,Ga)Se_2 + Cu_2Se$
3rd stage: $Cu(In,Ga)Se_2 + Cu(In,Ga)_3Se_5$

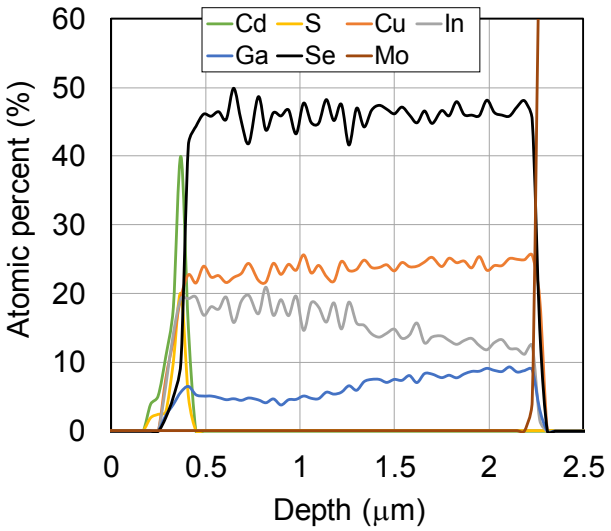
SEM, STEM images and EDX





Alkali metals passivate recombination centers.



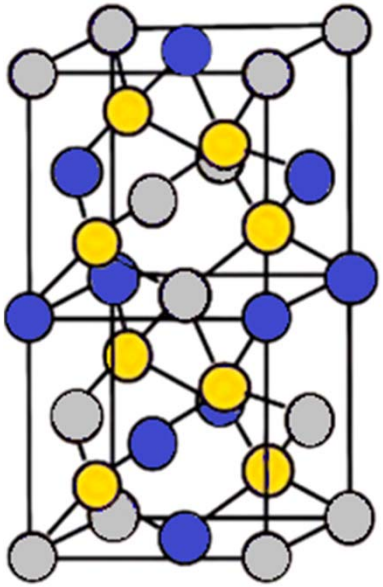


Cu_2Seへの溶解度の違いによって、In,Ga組成に勾配が発生する

変換効率23.4%（WR、ソーラーフロンティア社）を達成

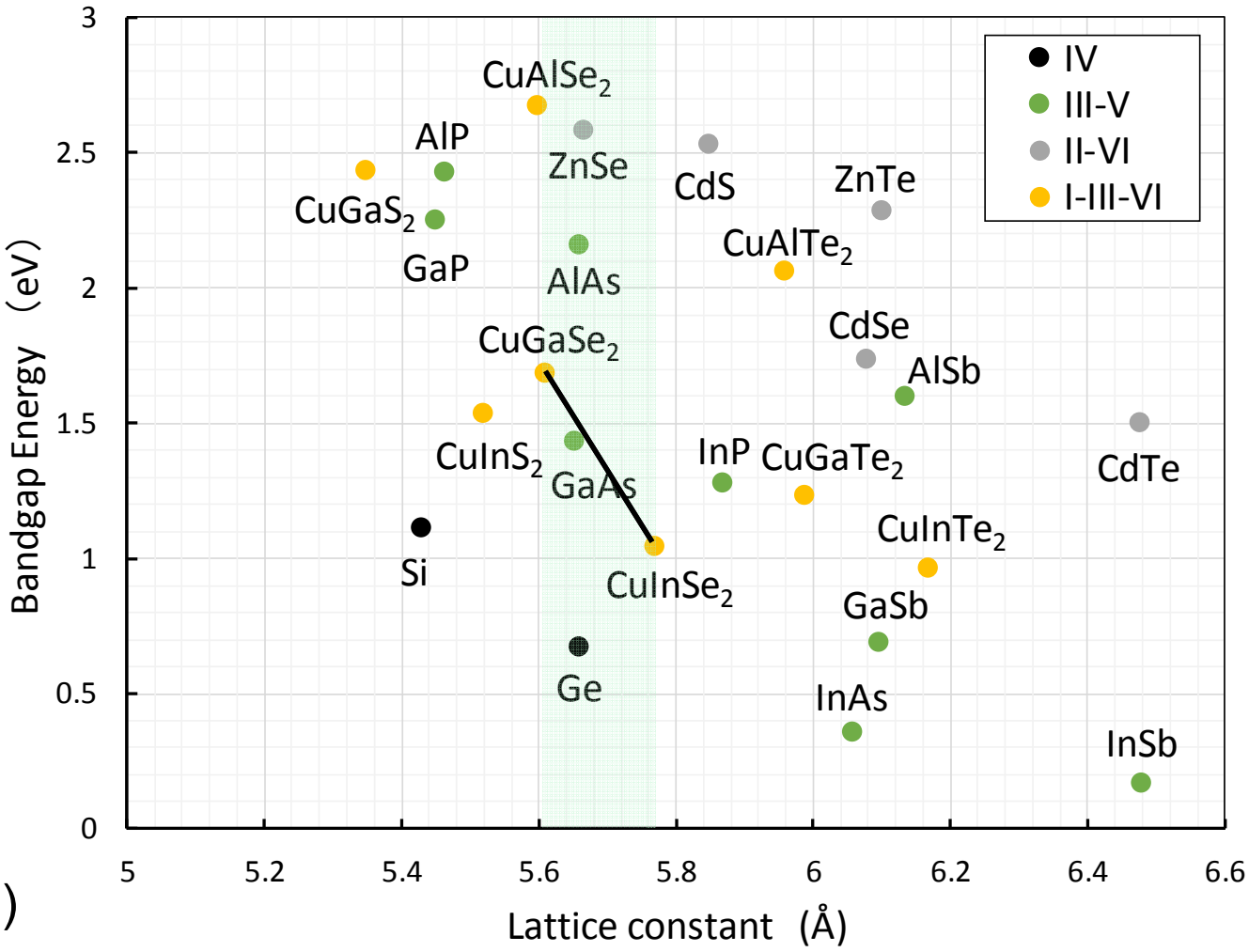
Lattice constant and Band-gap

Chalcopyrite structure

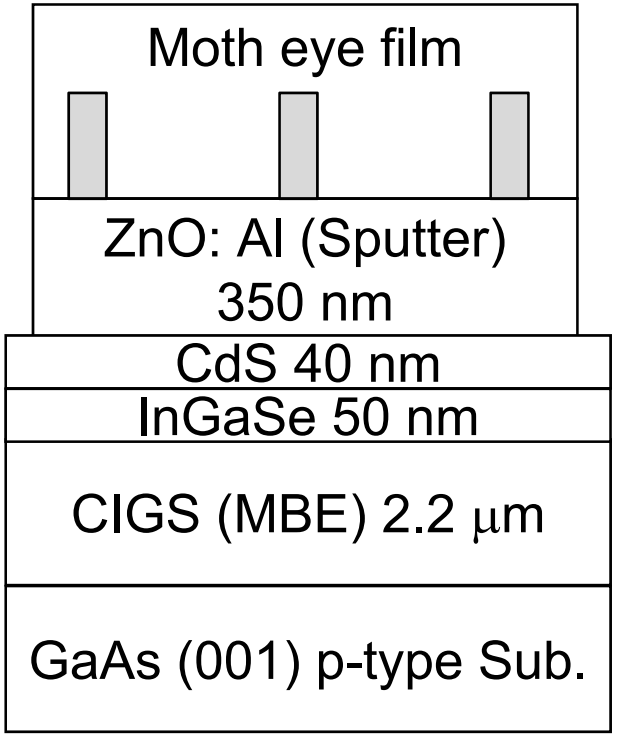


Cu
In, Ga
Se

a axis: 5.76 Å (CIS)
c axis: 11.59 Å (CIS)



Epitaxial CIGS太陽電池の開発



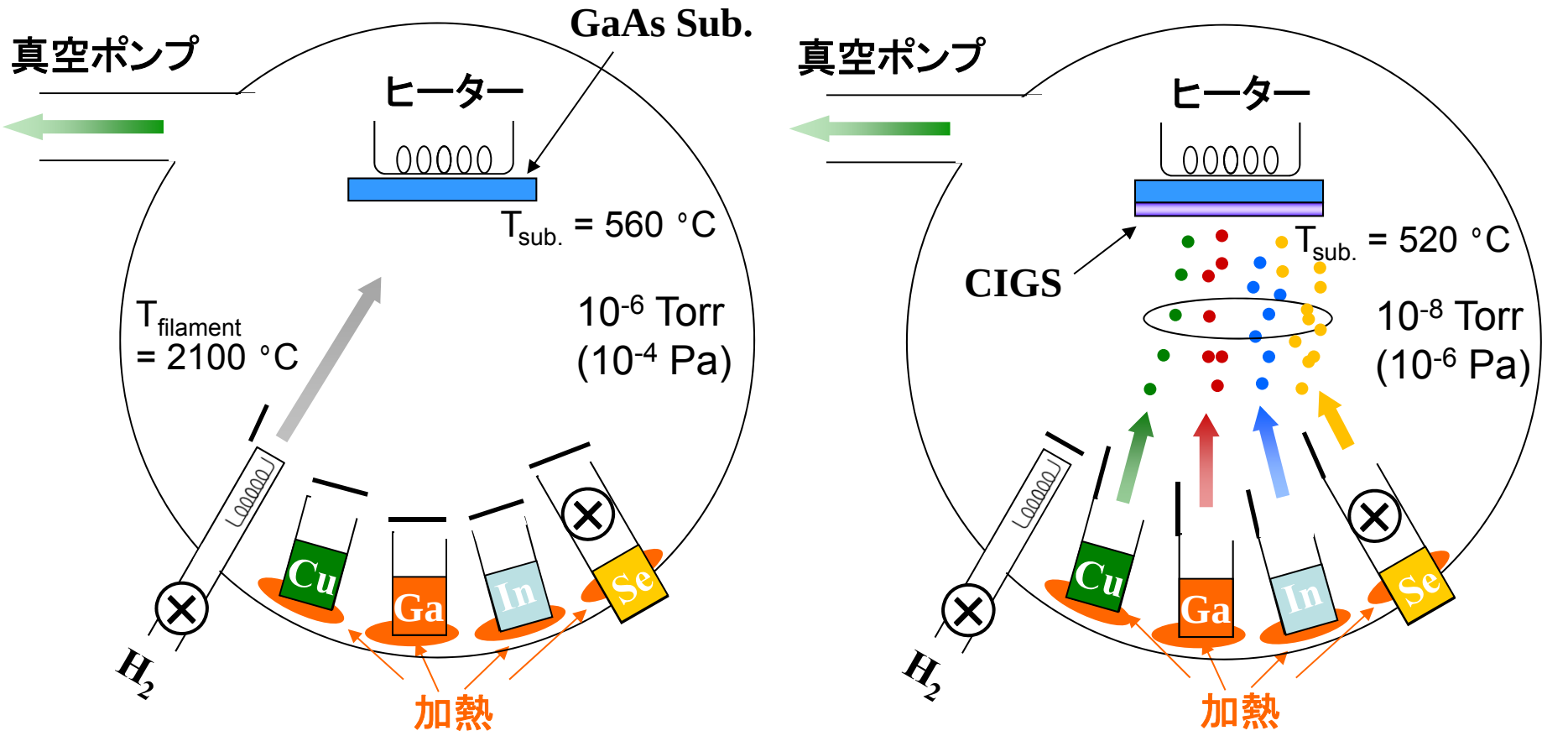
CIGS solar cells

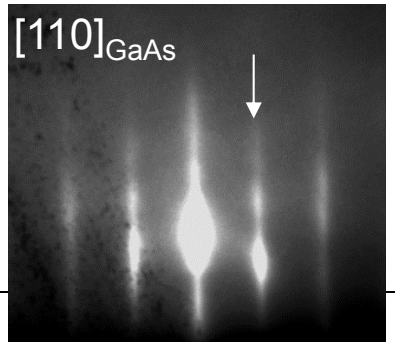
- Molecular beam epitaxy, T_{sub}=520℃
  (Same deposition: Cu, In, Ga, Se)
- E_g=1.2 eV (GGI:0.3), Cu濃度: 0.85–1.5
- アルカリ金属添加(Na doping, KF-PDT)
- CdS/AZO/Cr-Ag grid (Area: 0.2 cm^2)

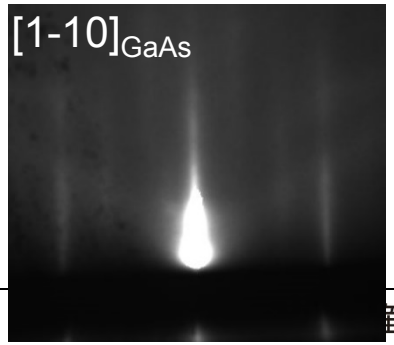
Measurements

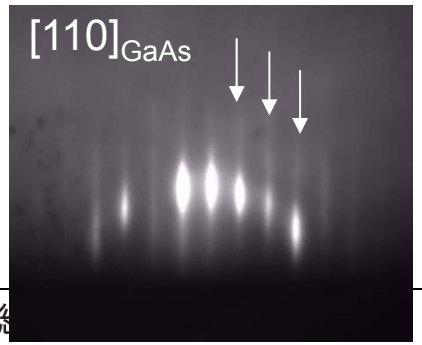
- SEM, STEM
- *I-V* curves and *C-V* measurements

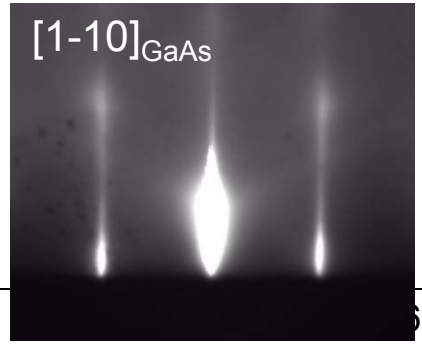
成膜法(基板表面処理、CIGS成膜)









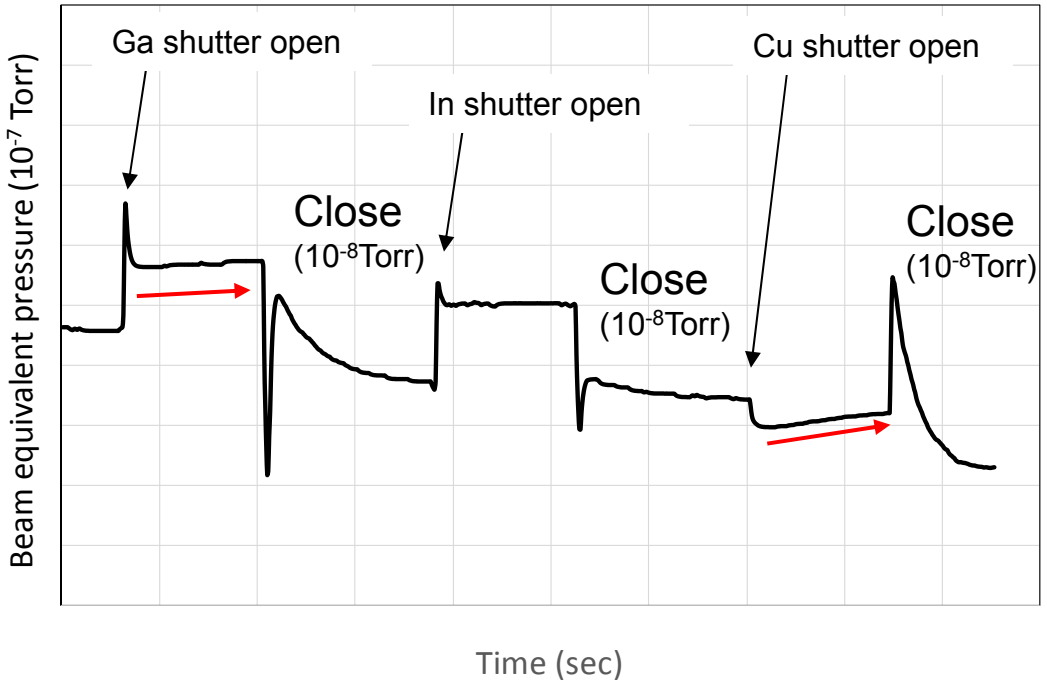


Beam Equivalent Pressure (BEP)

$$\frac{J_i}{J_{Ga}} = \frac{P_i \eta_{Ga}}{P_{Ga} \eta_i} \sqrt{\frac{T_i M_{Ga}}{T_{Ga} M_i}}$$

$$\frac{\eta_i}{\eta_{N_2}} = \left(\frac{0.6 Z_i}{14} + 0.4 \right)$$

P_i: Beam equivalent pressure
M_i: Relative molecular mass
T_i: Absolute cell temperature
η_i: ionization efficiency
Z_i: number of electrons



$$BEP = BEP_{open} - BEP_{close} - BEP_{extra}$$

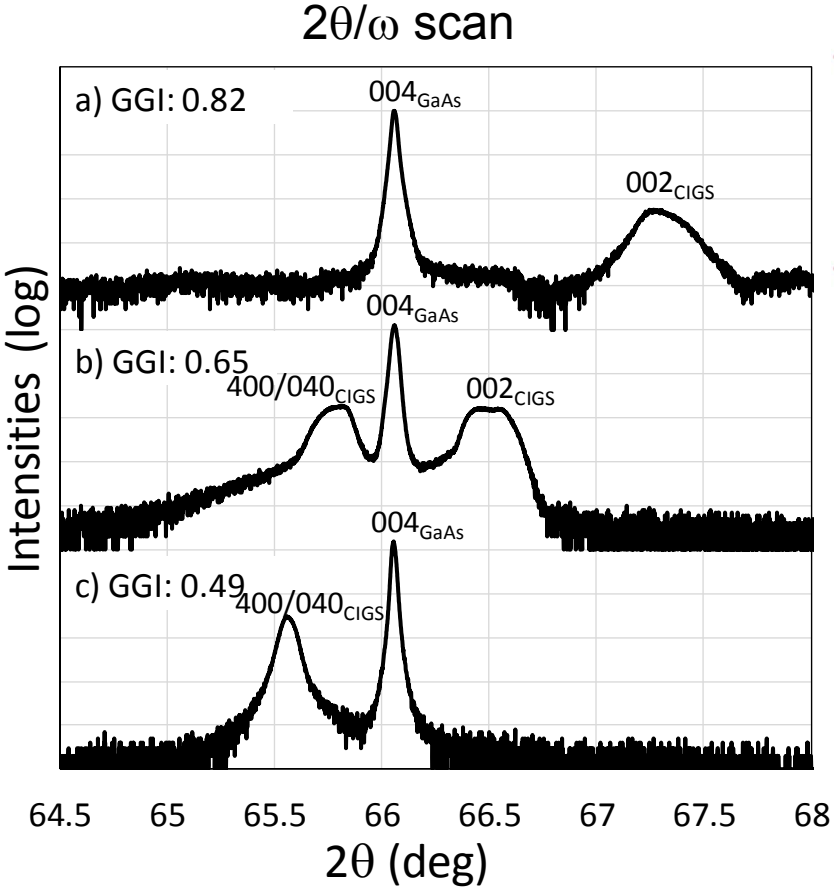
- T_{Ga} = 945°C, P_{Ga} = 3.22 x 10^{-7} Torr
- T_{In} = 745°C, P_{In} = 2.82 x 10^{-7} Torr

} GGI_{flux} = 0.7

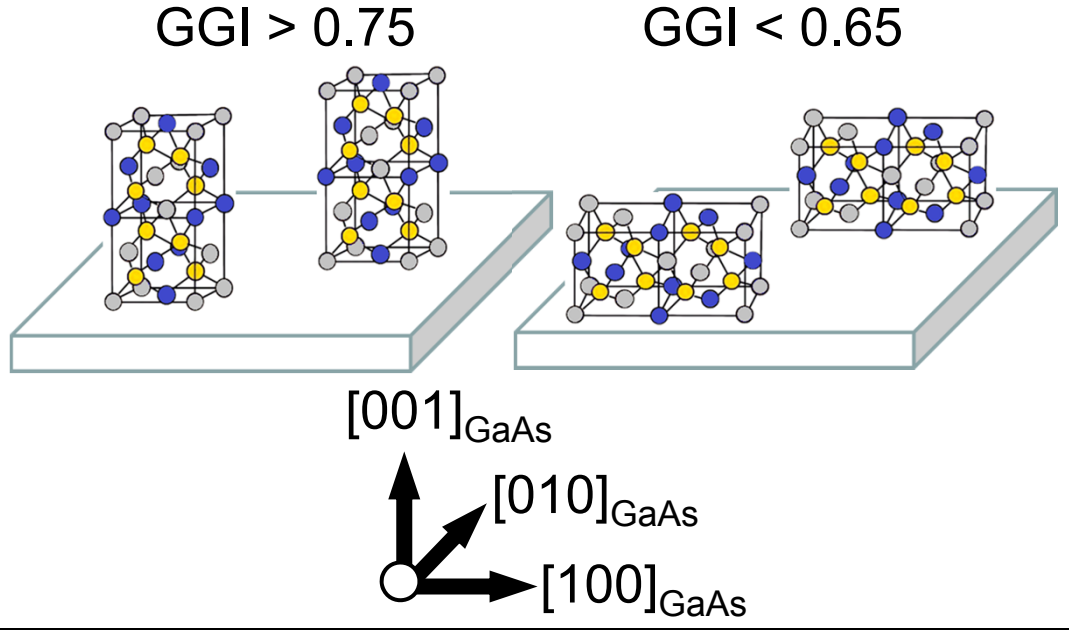
- T_{Cu} = 1180°C, P_{Cu} = 1.33 x 10^{-7} Torr (CGI was measured by EPMA)

} CGI = 0.80

Epitaxial Orientation of CIGS

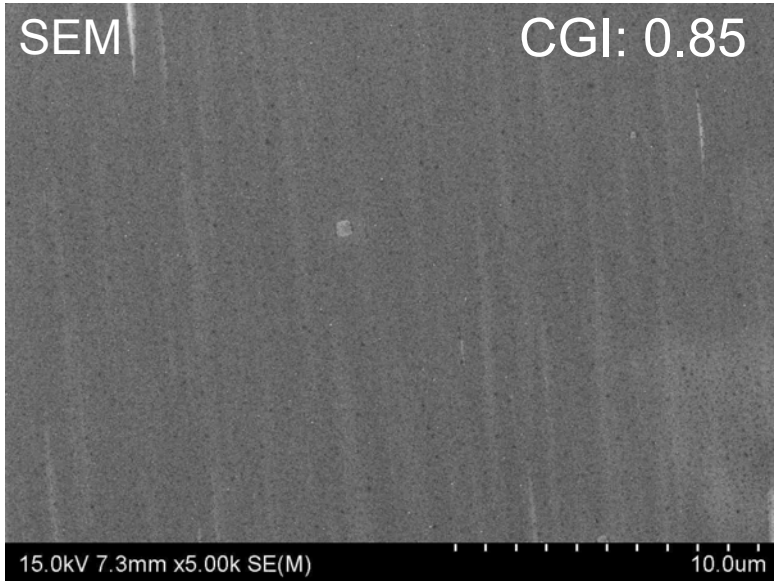


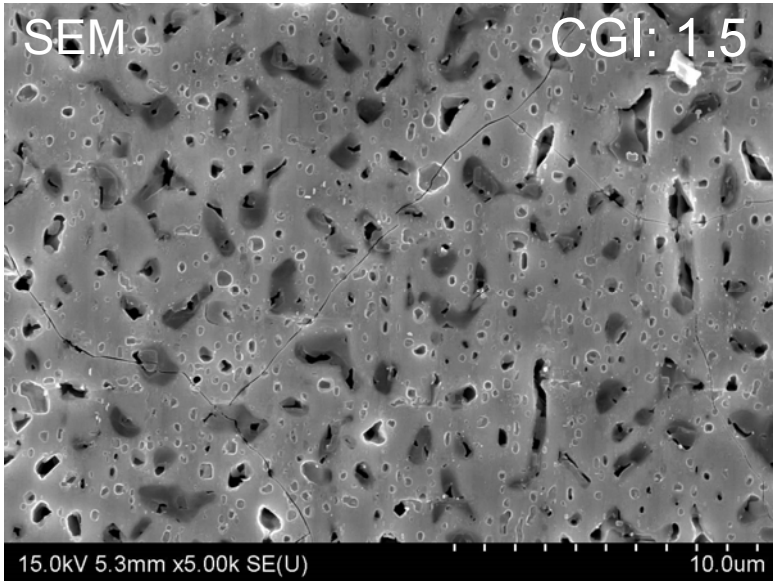
- GGI > 0.75 $[002]_{CIGS}$ // $[001]_{GaAs}$
  GGI = 0.8: a = b = 5.65 Å, c/2 = 5.57 Å
- GGI < 0.65 $[100]_{CIGS}$ // $[001]_{GaAs}$
  $[010]_{CIGS}$ // $[001]_{GaAs}$
  GGI = 0.5: a = b = 5.69 Å, c/2 = 5.65 Å

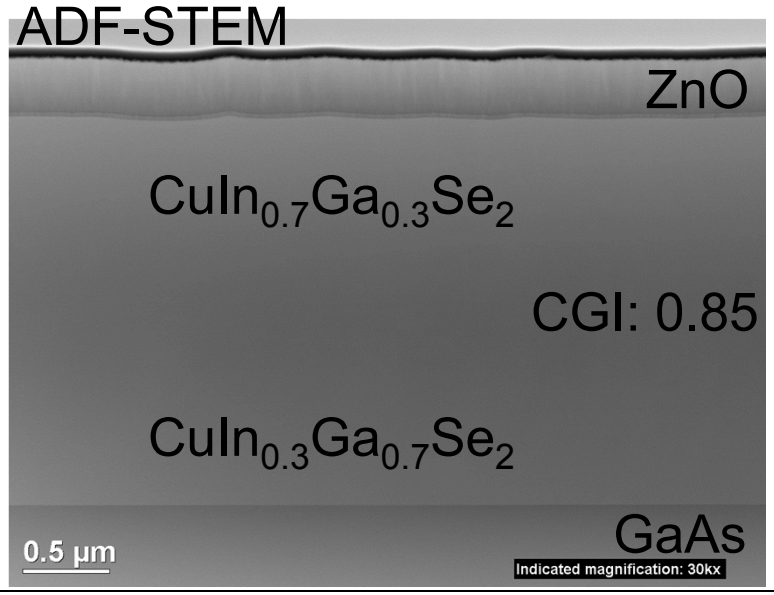


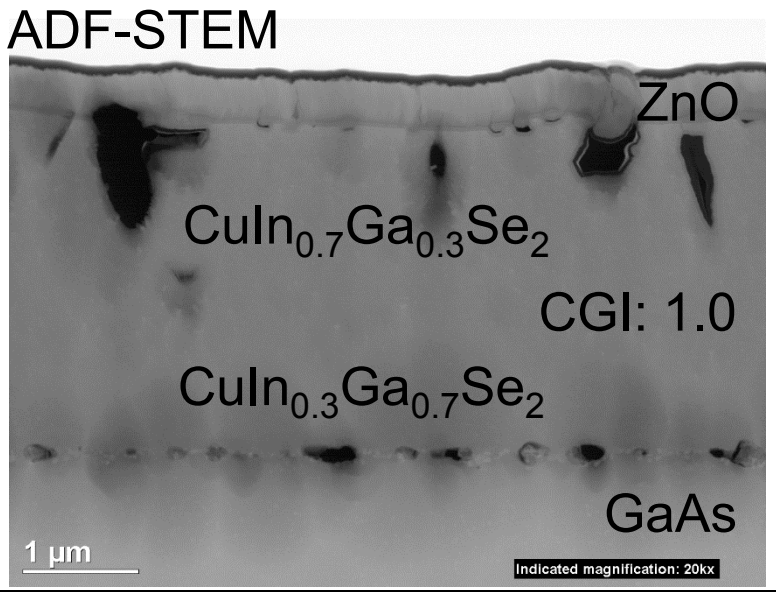
GaAs (zinc blende)
a = b = c = 5.65 Å

Cu poor CIGS or Cu rich CIGS

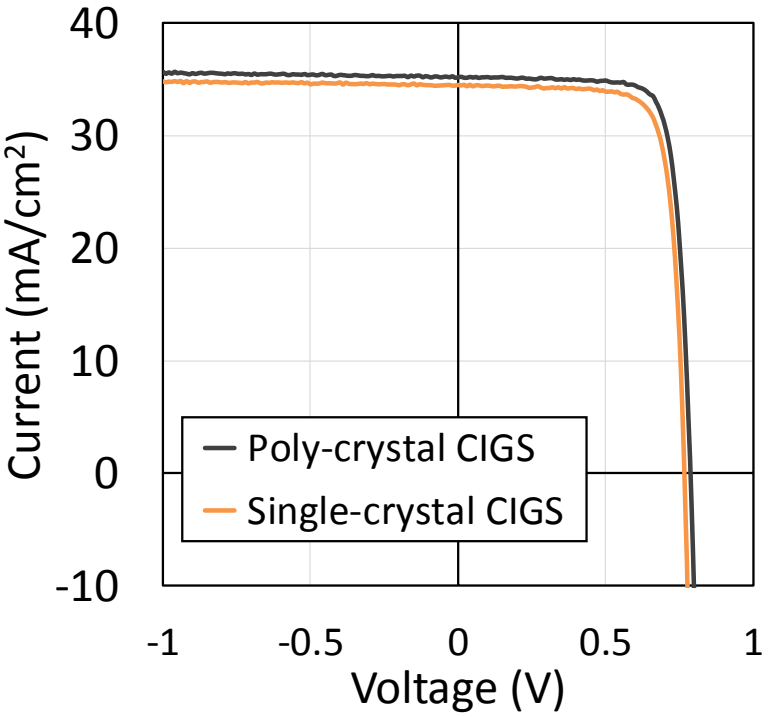


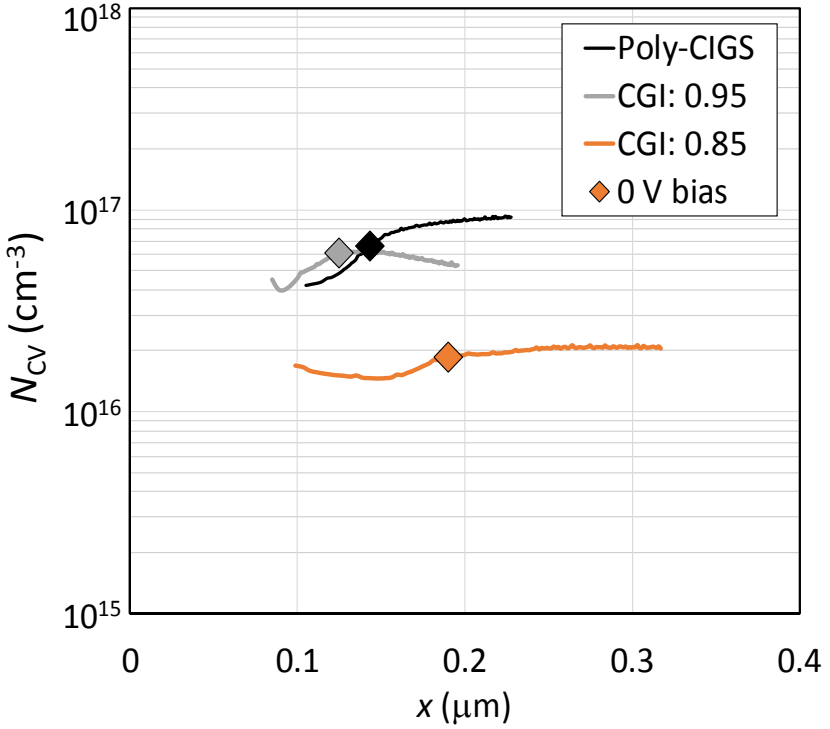






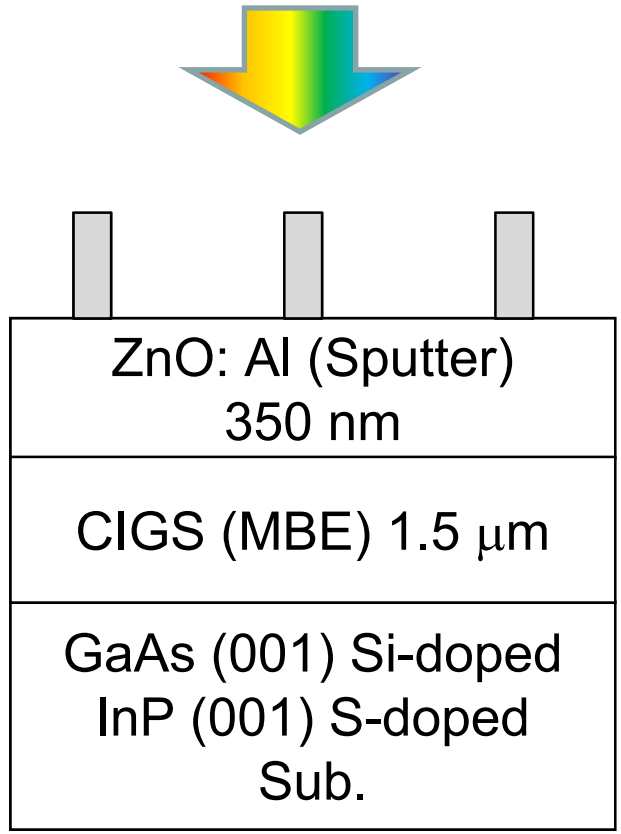
J-V curves and N_{CV} profiles





	Eff. (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	$R_{sh,\ dark}$ (Ωcm^2)	$R_{ser,\ dark}$ (Ωcm^2)	$N_{cv,0V}$ (cm^{-3})	$J_{0,dark}$ (mA/cm^2)	n_{dark}
CGI: 0.85	20.9	0.767	34.5	0.789	1×10^5	0.08	2×10^{16}	4×10^{-9}	1.3
CGI: 0.95	16.7	0.737	33.2	0.683	26000	0.5	6×10^{16}	1×10^{-6}	1.7
Poly-CIGS	22.1	0.786	35.1	0.800	5700	0.34	7×10^{16}	3×10^{-9}	1.3

CIGS / n-type Ⅲ-Ⅴ族化合物半導体



CIGS solar cells

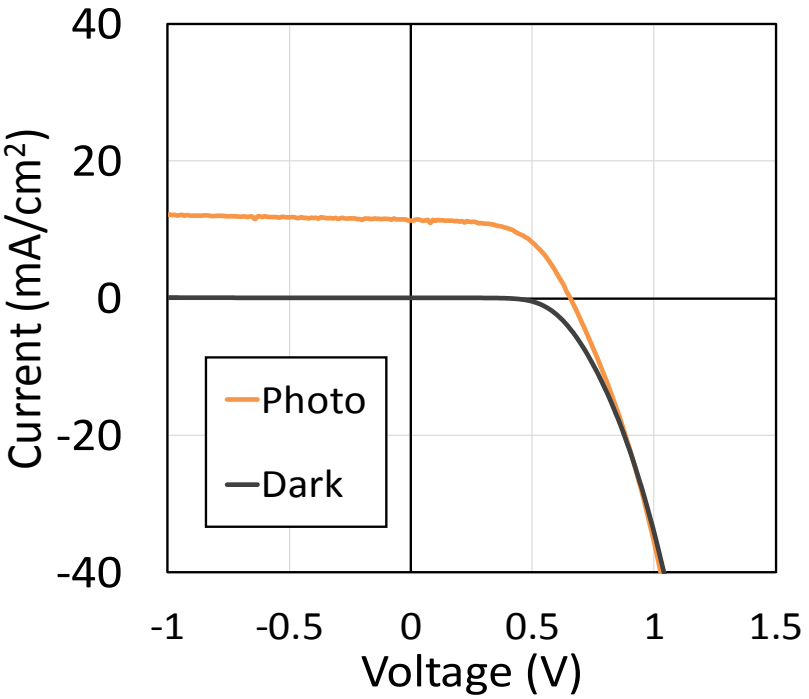
- Molecular beam epitaxy
  (Same deposition: Cu, In, Ga, Se)
- E_g=1.1, 1.5 eV, Cu濃度: 0.85
- T_{Sub}=480 - 520℃
- NaF doping
- AZO/Cr-Ag grid (Area: 0.25 cm^2)

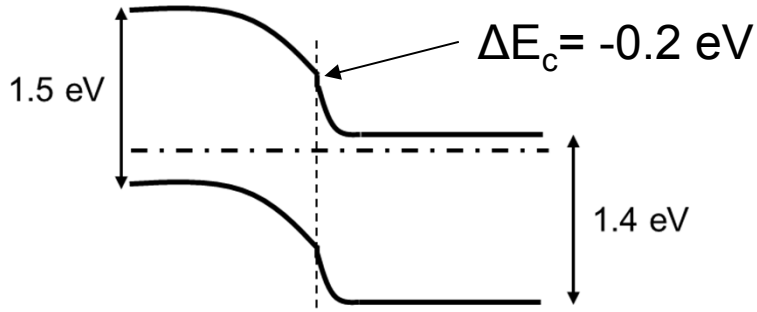
Measurements

- *I-V* curves and *EQE*

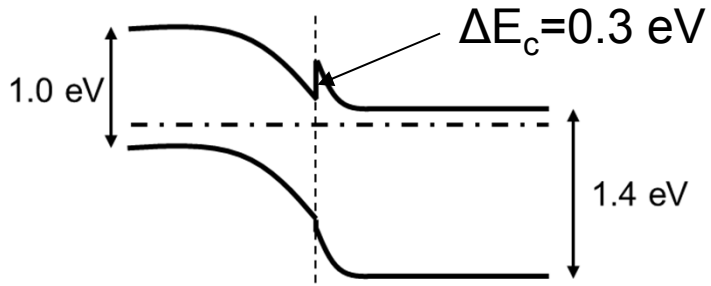
CIGS / GaAs n-type

CIGS(E_g=1.5 eV) / GaAs n-type





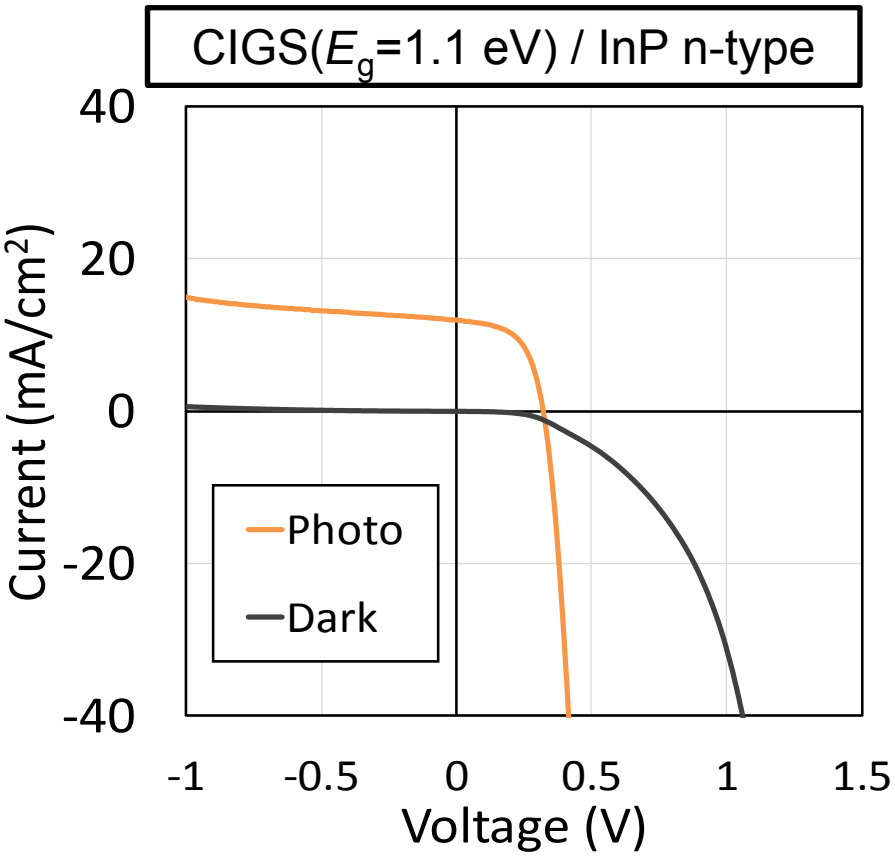
p-$CuIn_{0.3}Ga_{0.7}Se_2$ / n-GaAs

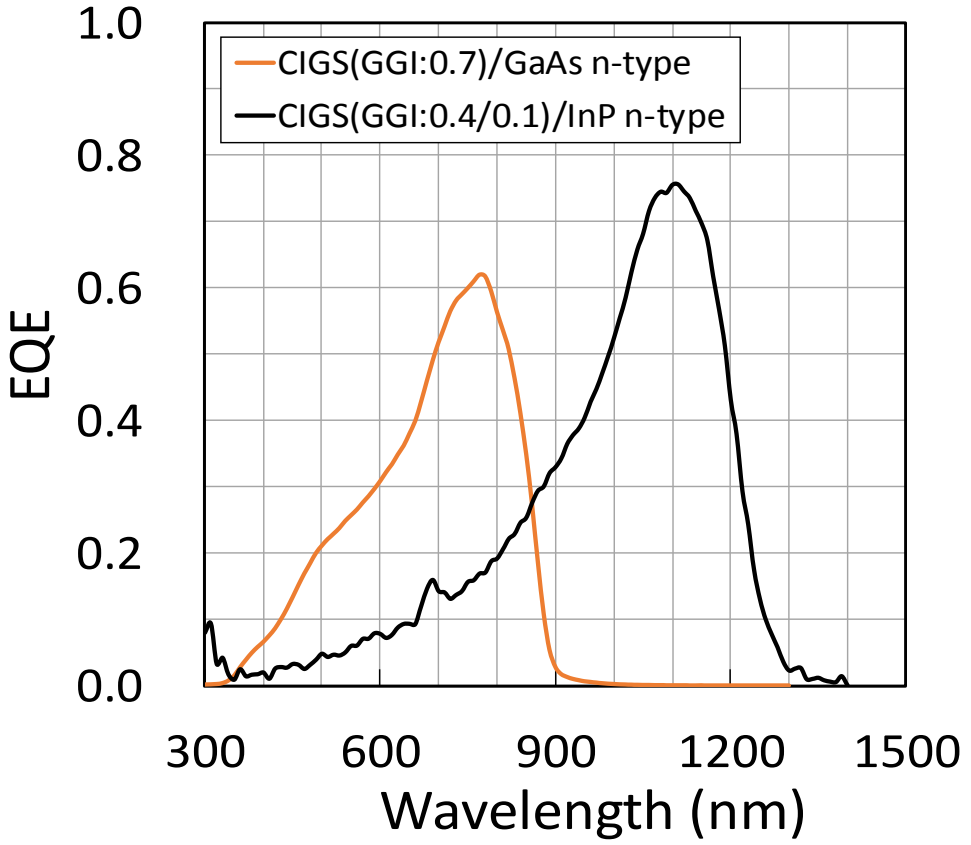


p-$CuInSe_2$ / n-GaAs

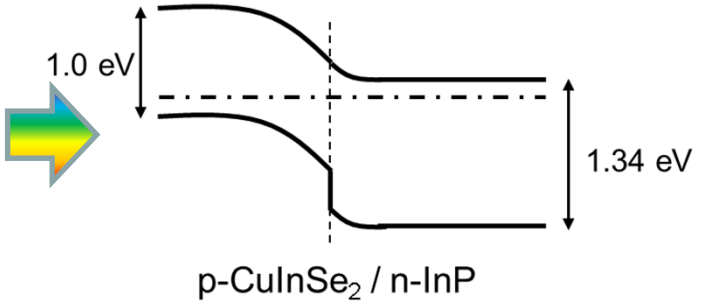
	Eff. (%)	V_{oc} (V)	J_{sc} (mA/cm²)	FF
GGI: 0.7	4.2	0.655	11.3	0.57
GGI: 0.4/0.1	0.0	0.0	0.0	-

低Ga濃度CIGS / InP n-type





	Eff. (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF
CIGS(GGI:0.4/0.1) / InP n-type	2.2	0.322	12.0	0.56



まとめ

- Ⅰ－Ⅲ－$Ⅵ_2$族化合物半導体の組成制御

  - 相分離を利用した気相・固相成長、組成制御
  - CIGS系の特徴は、薄膜太陽電池応用に最適

- Ⅲ－Ⅴ族化合物半導体/CIGSヘテロ構造

  - 格子定数、組成、界面反応の制御が重要
  - 電子親和力でバンド構造を説明可能

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