Present status and future prospects for super low-cost Cu_2O-based solar cells

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Outline

1. Introduction

2. Fabrication procedure of heterojunction Cu_2O solar cells

3. Photovoltaic properties for various n-type multicomponent oxide thin films/Cu_2O heterojunction solar cells

4. Conclusion

Background

Cuprous oxide (Cu_2O)

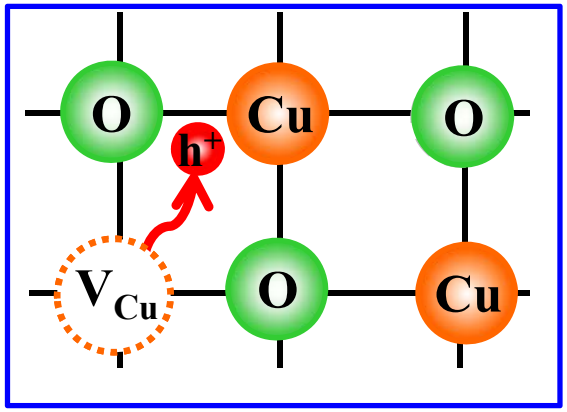
- **Bandgap energy (Eg)≒2.1eV(direct-gap)**
- **Non-toxic, low-cost**
- **Theoretical energy conversion efficiency ≒ 20%**

Long attracted much interest for application as an active layer in solar cells

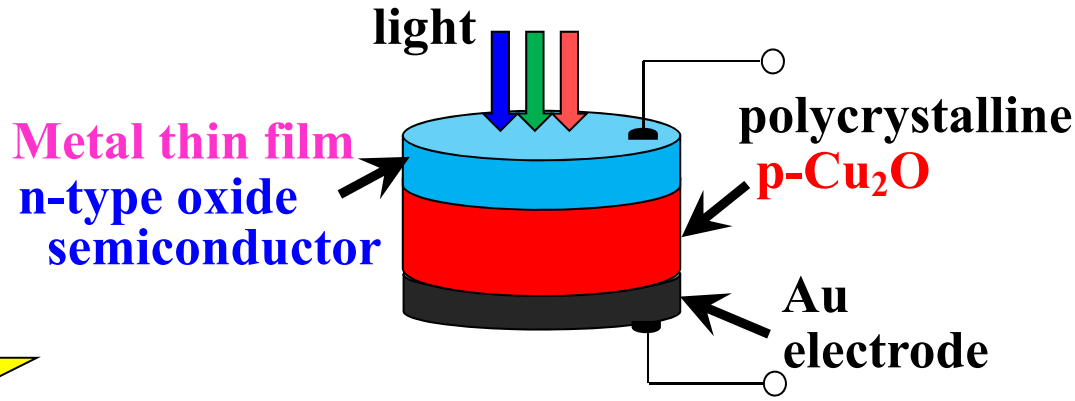


p-Cu_2O

It is very difficult to achieve a high efficiency because of the difficulty of obtaining an n-Cu_2O semiconductor. (Usually Cu2O have p-type conduction by intrinsic acceptor from Cu Vacancy.)







Metal thin film/p-Cu_2O Schottky barrier(SB) solar cells

n-type oxide semiconductor/p-Cu_2O heterojunction solar cells

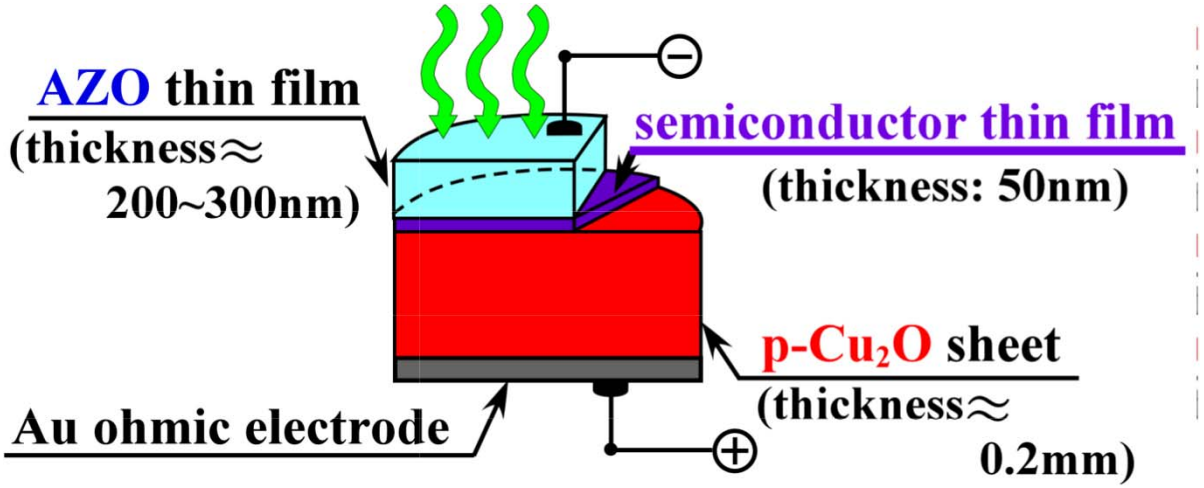
Structure and conversion efficency for Cu_2O-based solar cells

Structure	Eff.[%]	Yare	Ref.	
SiO_2/Cu/p-Cu_2O	1.76	1982	1)	Bulk
KIT Al:ZnO(AZO)/p-Cu_2O	1.20	2004	2)	Bulk
KIT Ga:ZnO(GZO)/p-Cu_2O	1.52	2006	3)	Bulk
MgF_2/ITO/ZnO/p-Cu_2O	2.01	2006	4)	Bulk
FTO/ZnO/p-Cu_2O	1.28	2007	5)	Thin film
KIT AZO/p-Cu_2O(RTA treatment)	2.18	2011	6)	Bulk
KIT AZO/Sn-Pd/p-Cu_2O	2.13	2011	6)	Bulk
KIT AZO/p-Cu_2O(RTA treatment)	2.19	2011	6)	Bulk
KIT AZO/n-ZnO/p-Cu_2O	4.12	2011	7)	Bulk
KIT AZO/n-$Zn_{0.9}Mg_{0.1}O$/p-Cu_2O	4.29	2012	8)	Bulk
KIT AZO/n-Ga_2O_3/p-Cu_2O	5.38	2012	9)	Bulk

Low damage deposition methods

1)L.C.Olsen et al. Sol. Cells 7, 240(1982).
2) T. Minami et al. Jpn.J.Phys., 43,pp-917-919 (2004).
3) T. Minami et al. Thin Solid Films 528 (2013) 72.
4) A. Mittiga, et al, J. Phys. D., 40, (2007) 3326.
5) Izaki, et al, J. Phys. D., 40, (2007) 3326.
6) Y. Nishi et al. Thin Solid Films 520 (2012) 3819.
7) Y. Nishi et al. Thin Solid Films 528 (2013) 72.
8) T. Minami et al. ECS Transactions 8 (2012), Honolulu, PRiME 2012 Photovoltaics for the 21st Century, in press.
9) T. Minami et al, Appl. Phys. Express 6 (2013) 044101.

★AZO/n-type semiconductor thin film /Cu_2O heterojunction solar cells



n-type semiconductor	V_{oc}[V]	J_{sc}[mA/cm^2]	FF	η [%]
ZnO	0.71	9.69	0.60	4.13
Ga_2O_3	0.80	9.99	0.67	5.38

An investigation of new n-type semiconductor thin film materials are very important for improvement of photo voltaic propartes of Cu_2O heterojunction solar cells

Outline

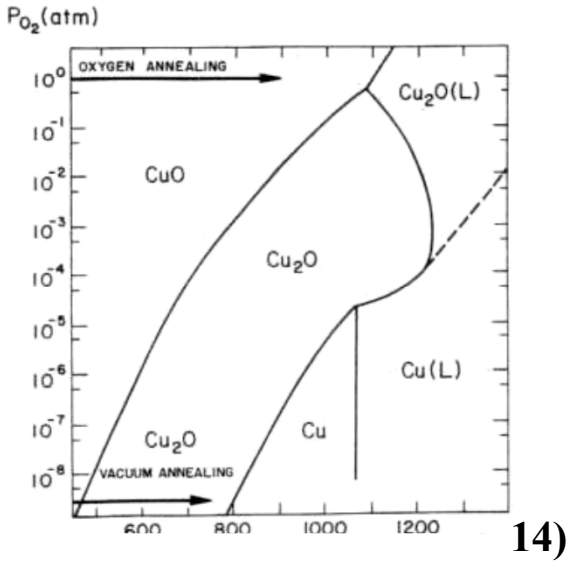
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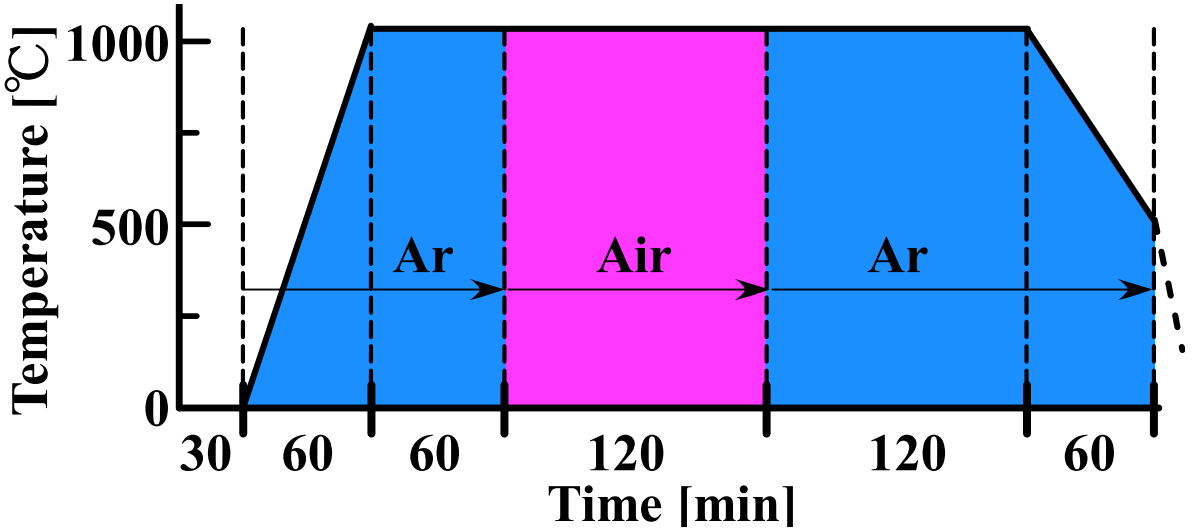
3. Photovoltaic properties for various n-type multicomponent oxide thin films/Cu_2O heterojunction solar cells

4. Conclusion

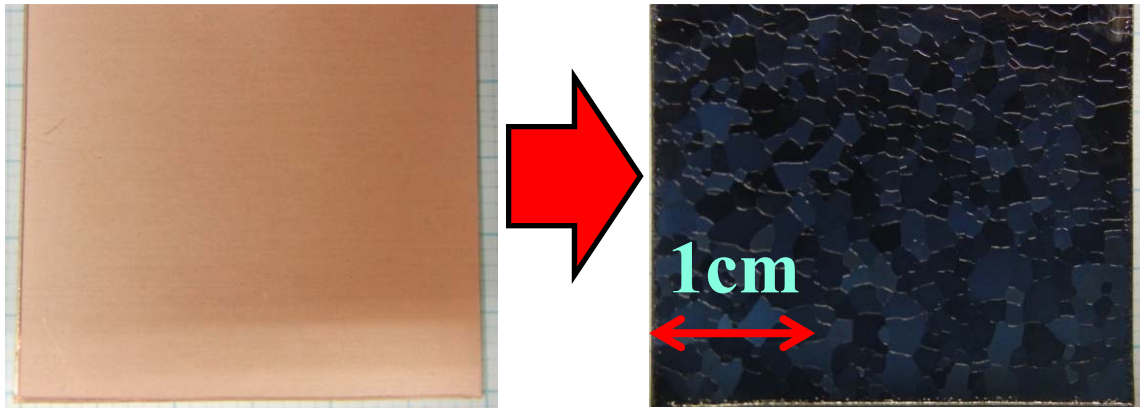
Preparation method of p-type Cu_2O sheet



14)



14) Jian Li et al., J. Appl. Phys., 1021 (1991) 69.



Cu sheet

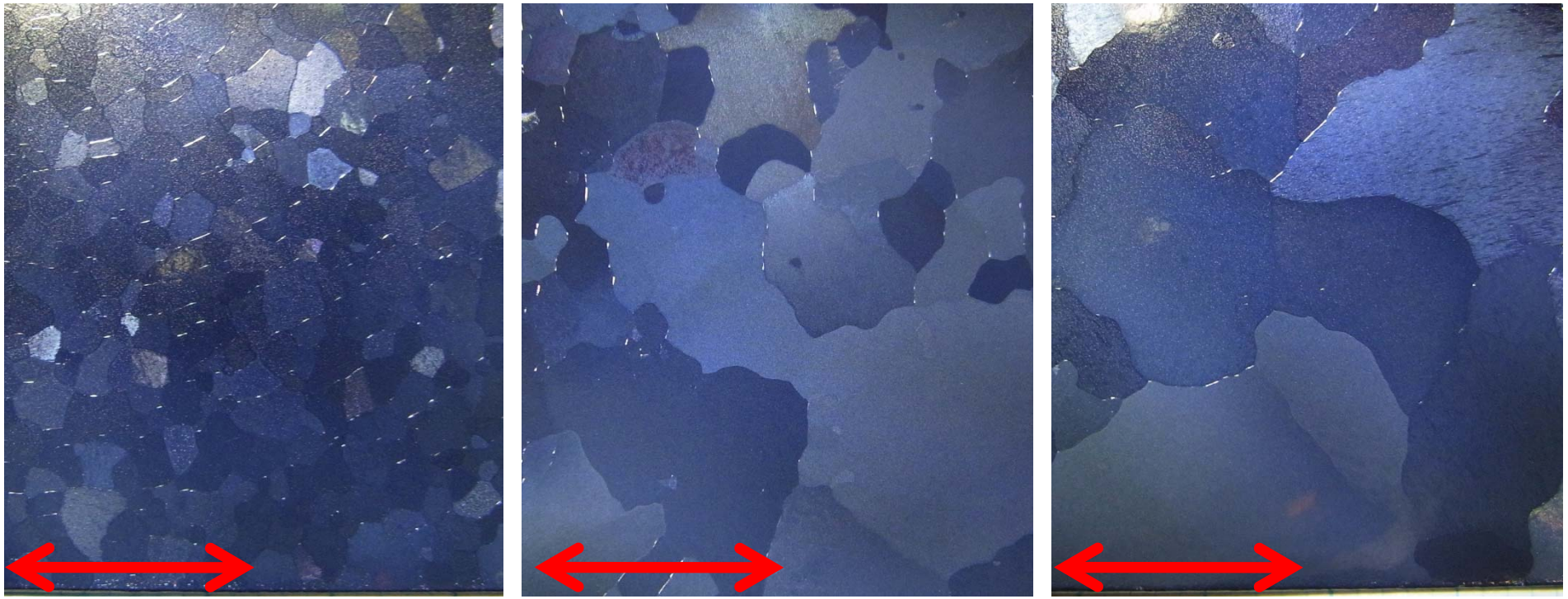
p-type Cu_2O sheet

Cu sheet (3×3[cm], thickness：0.2[mm])

Electrical properties of poly-crystal Cu_2O sheet

Resistivity ρ [Ωcm]	300-1000
Hall mobility μ [cm^2/Vs]	100-120
hole concentrations [cm^{-3}]	$3\text{-}9 \times 10^{13}$

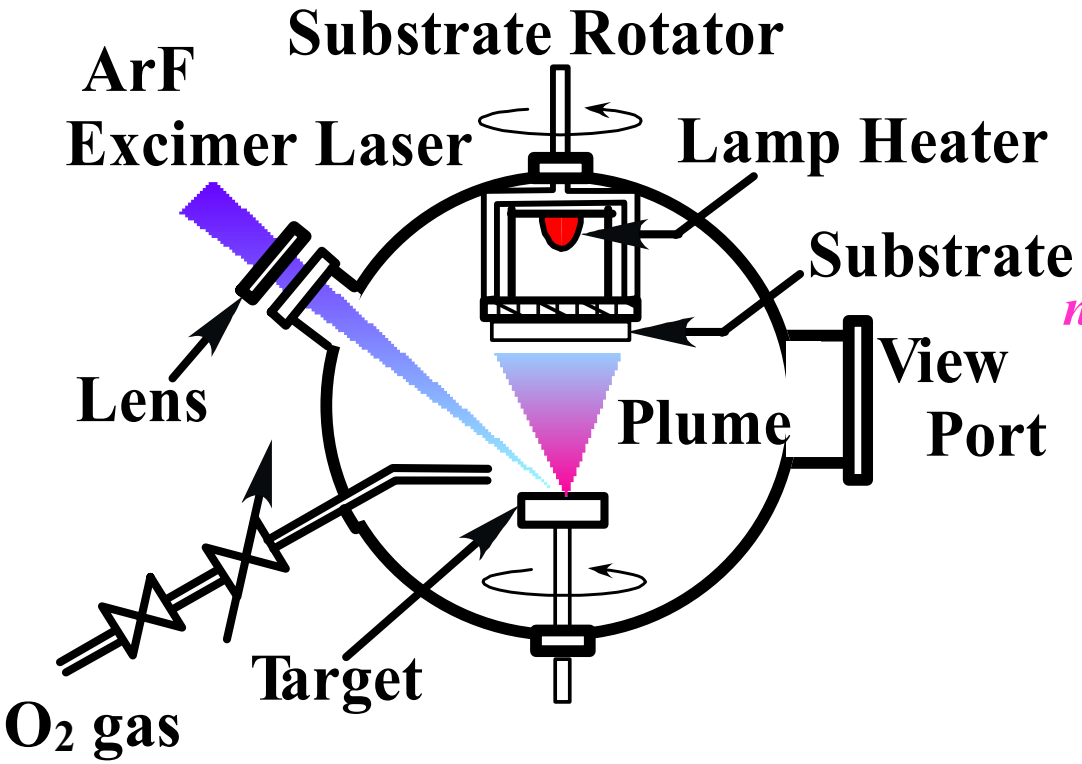
Surface image of poly-crystal Cu_2O sheet



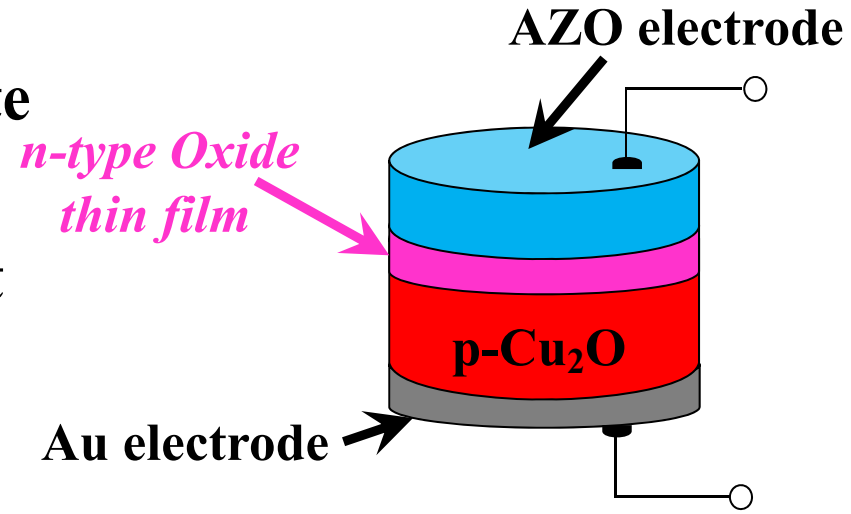
1cm 1cm 1cm

Small grain size → Large grain size

Preparation methods of n-type multicomponent oxide thin film and AZO



Pulse Laser Deposition (PLD)



Laser light source	ArF Excimer laser
Wavelength [nm]	193
Repetition rate [Hz]	20

Outline

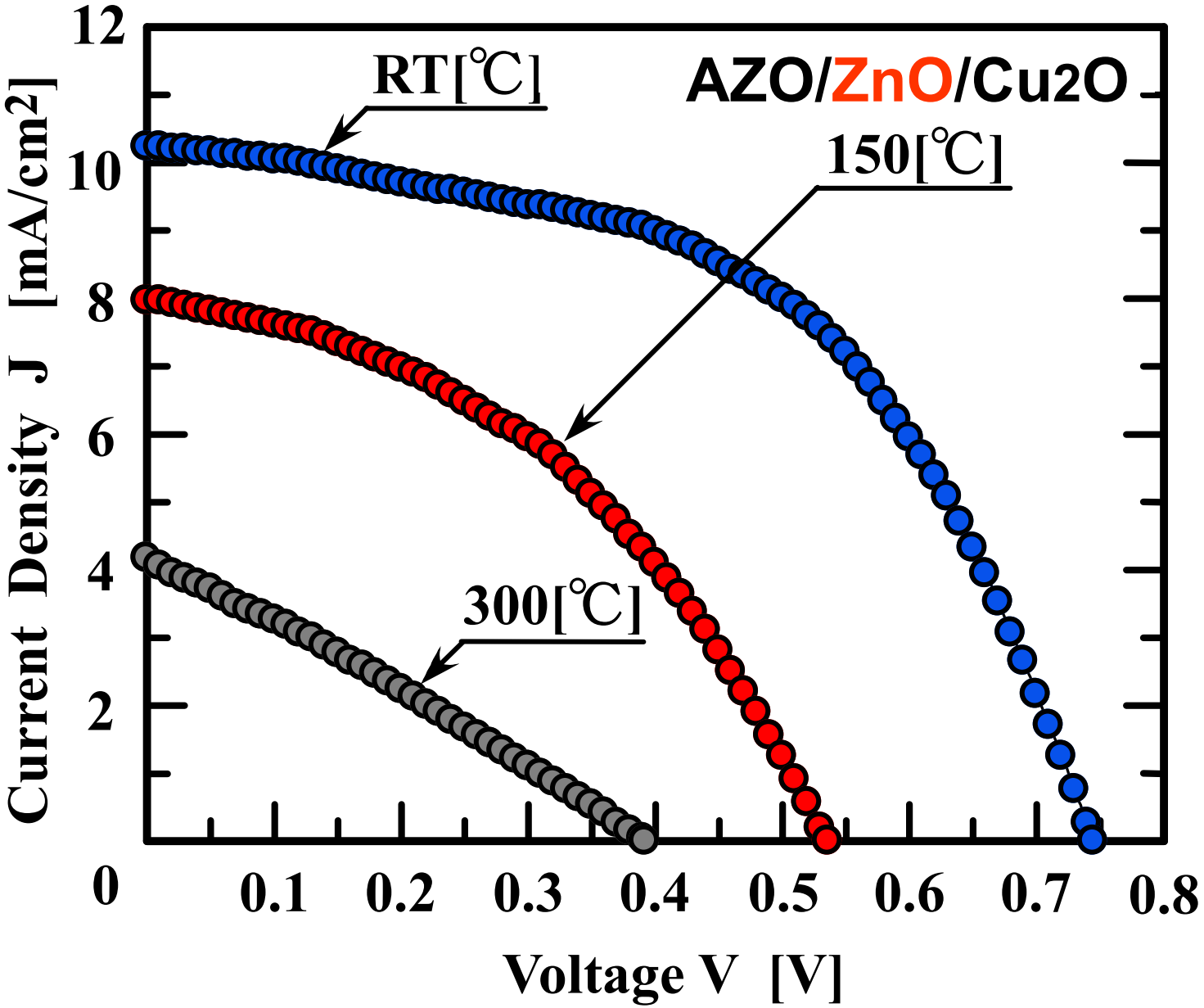
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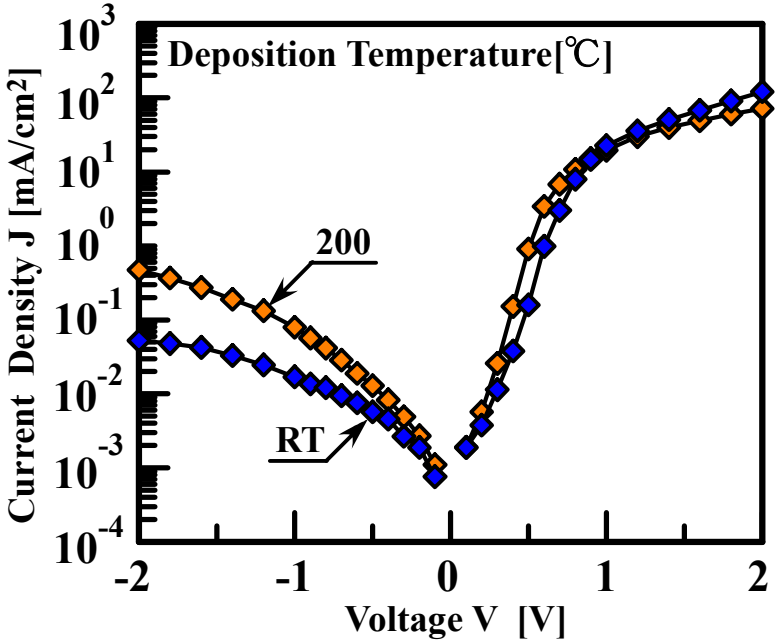
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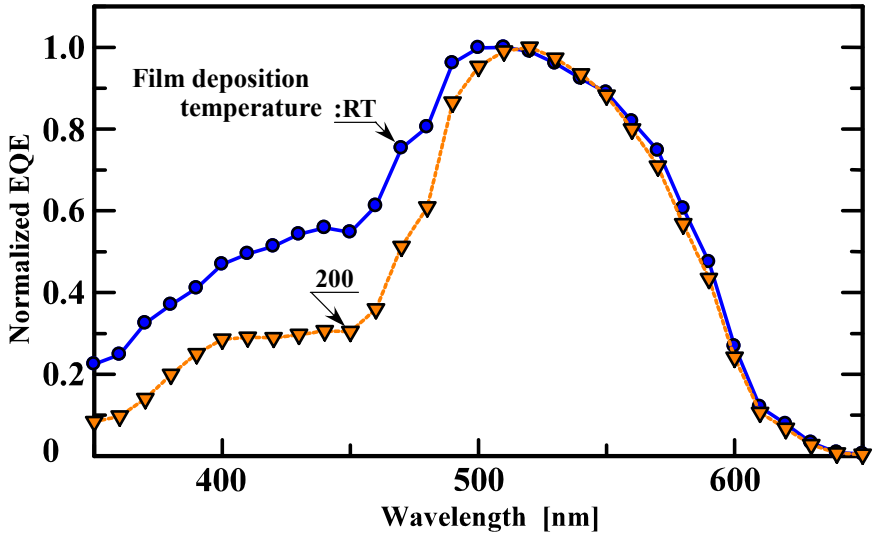
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Deposition temperature dependence of J-V characteristics for AZO/ZnO/Cu2O solar cells



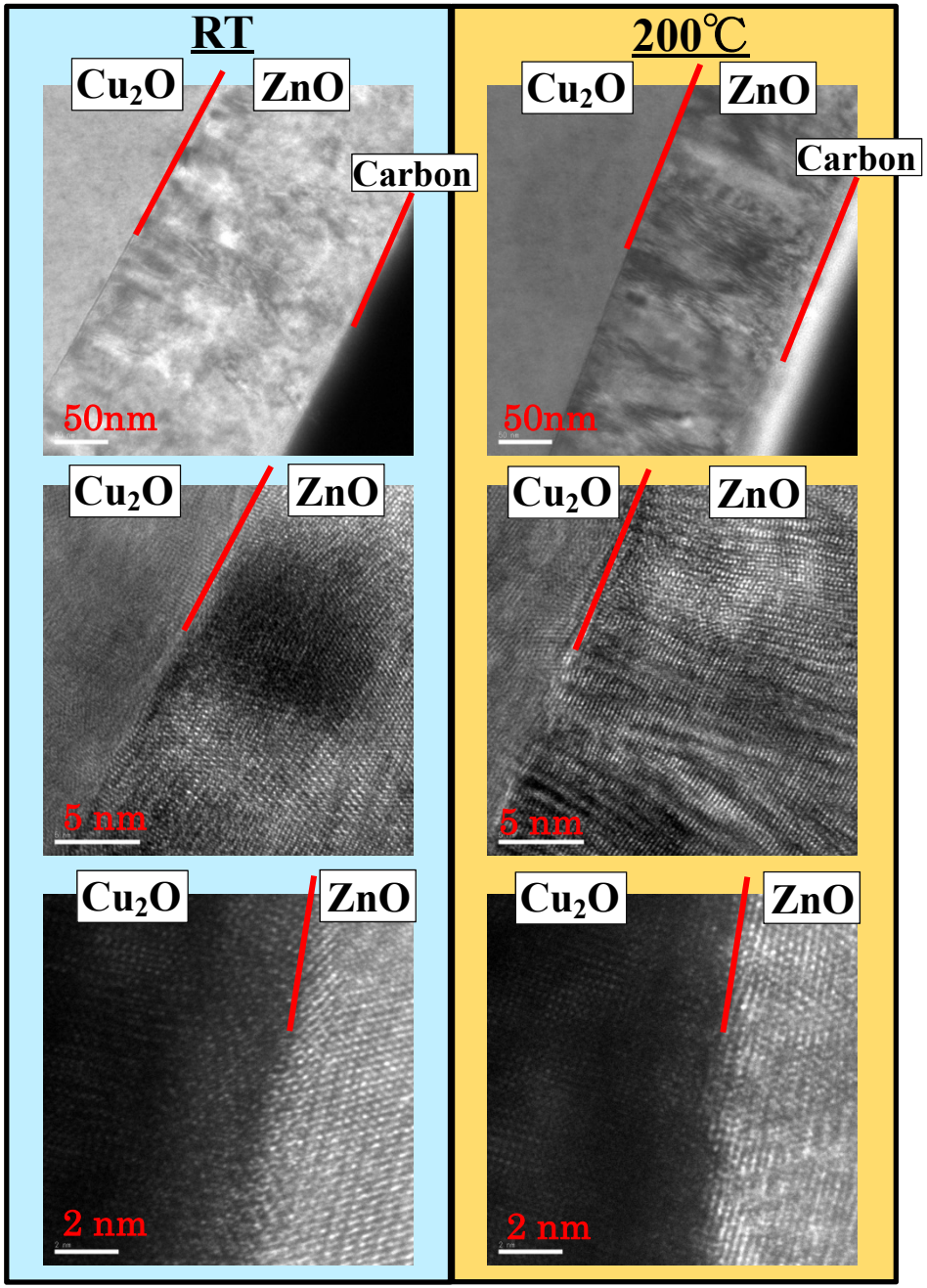


Deposition temperature dependence of the J-V characteristic obtained in AZO/ZnO/Cu_2O heterojunction solar cells measured under dark conditions.

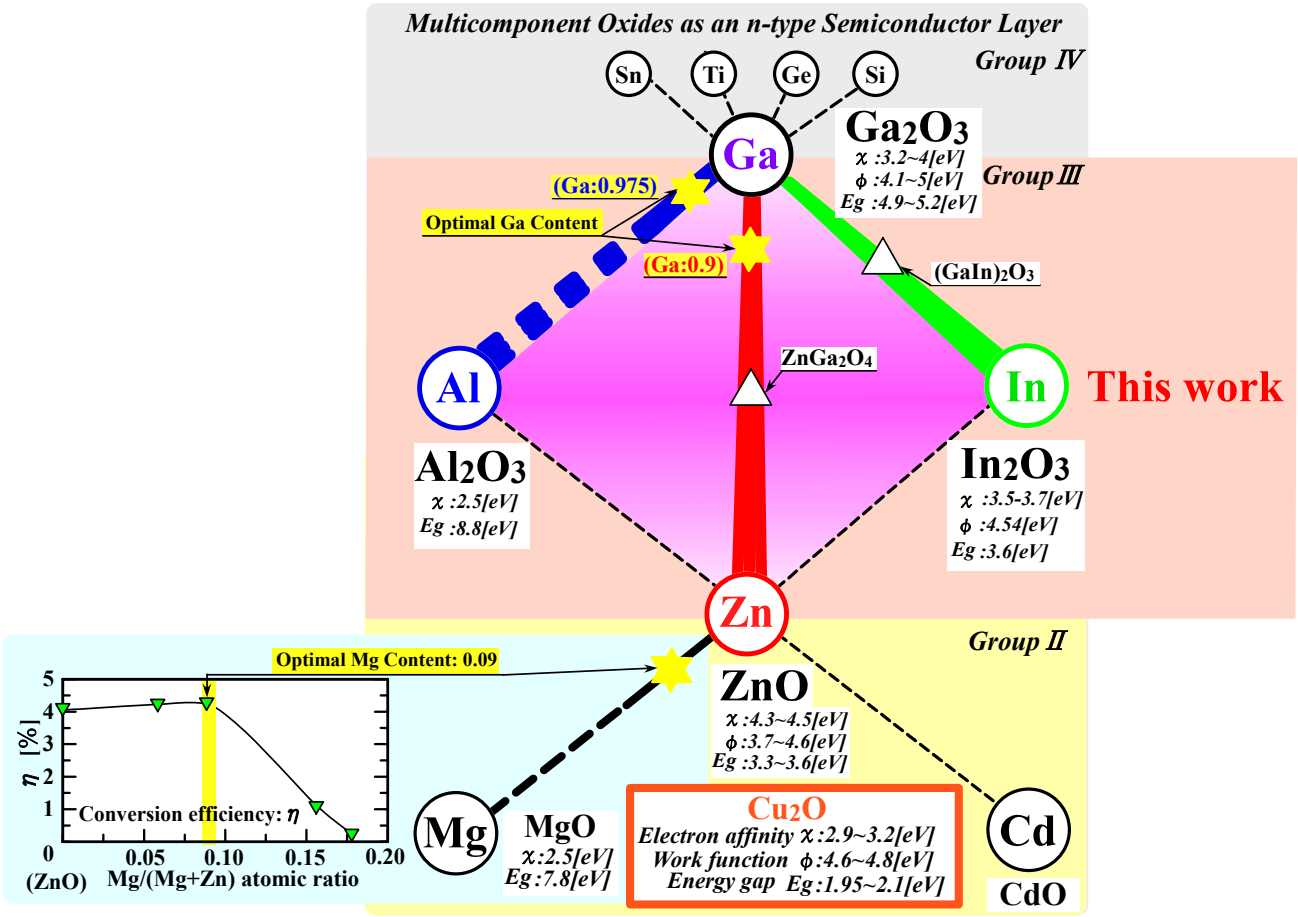


EQE observed from AZO/ZnO/Cu_2O solar cells fabricated with various deposition temperatures (R.T. And 200 [℃])

Cross TEM images of AZO/ZnO/Cu_2O heterojunction solar cells fabricated with various deposition temperatures

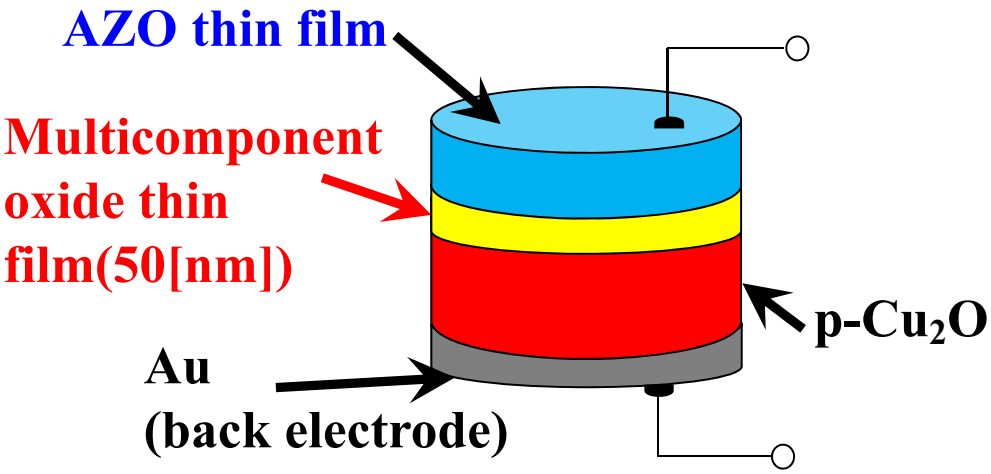


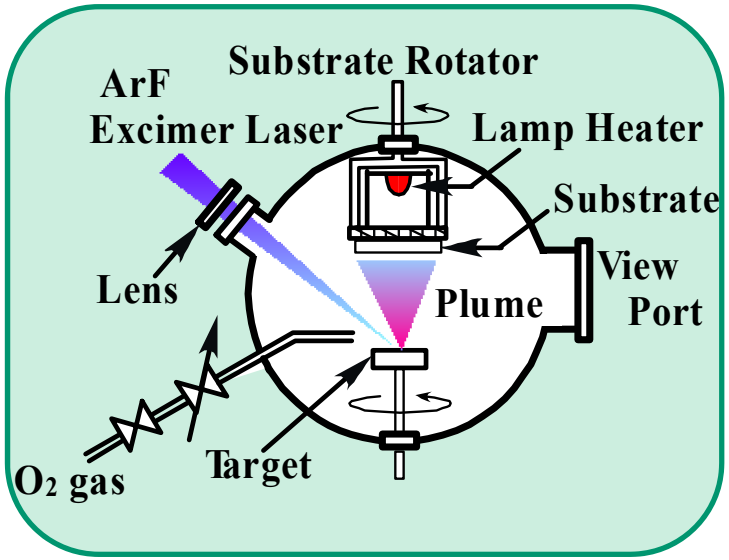
Objective



Cu_2O Heterojunction solar cells are prepared by using Ga_2O_3-based multicomponent oxide thin film as a n-type layer

- ◎ **Optimaization of the component**
- ◎ **Improving of band arrangement**

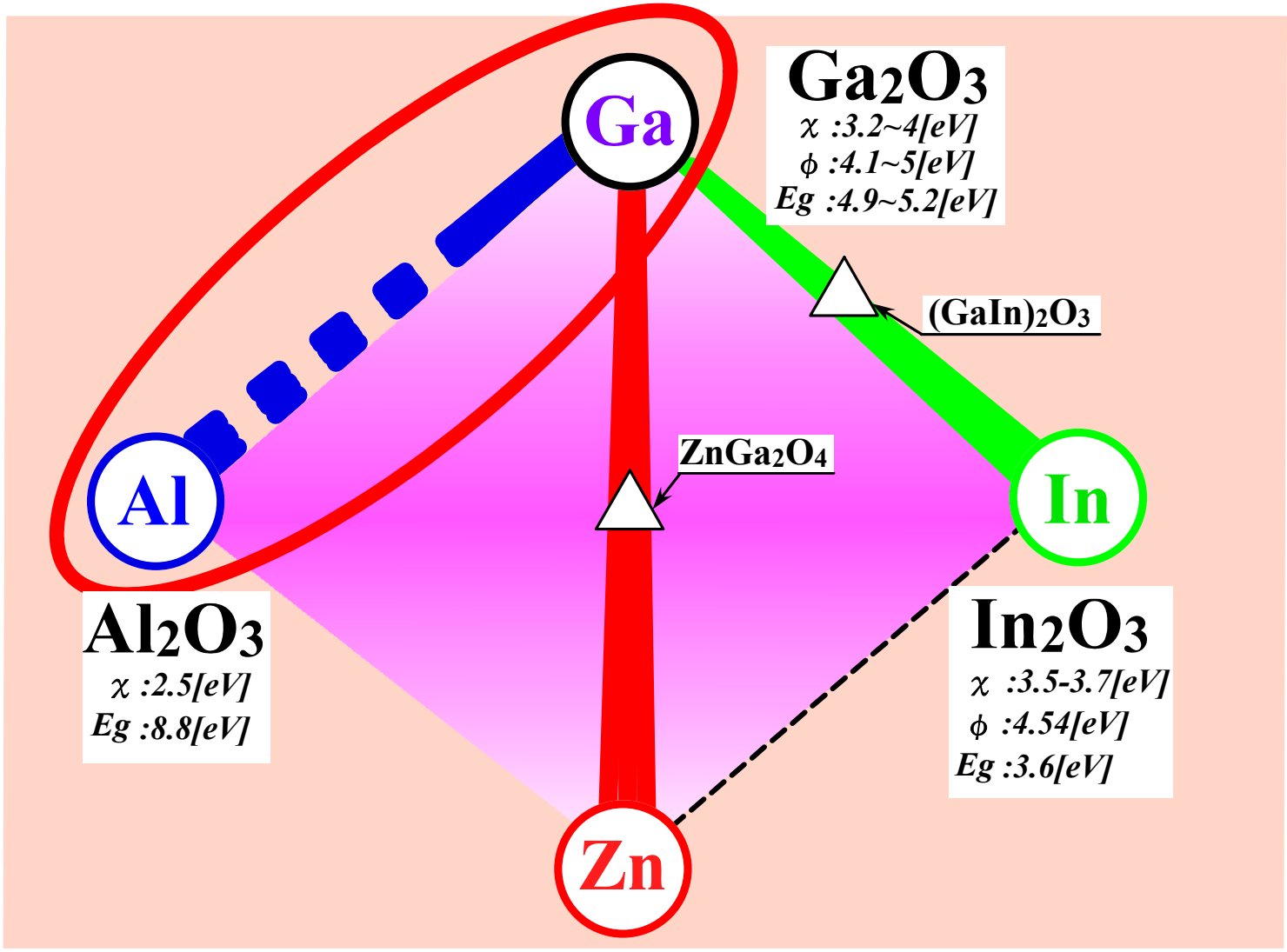




AZO and n-type Multicomponent Oxide Thin Film Deposition Conditions

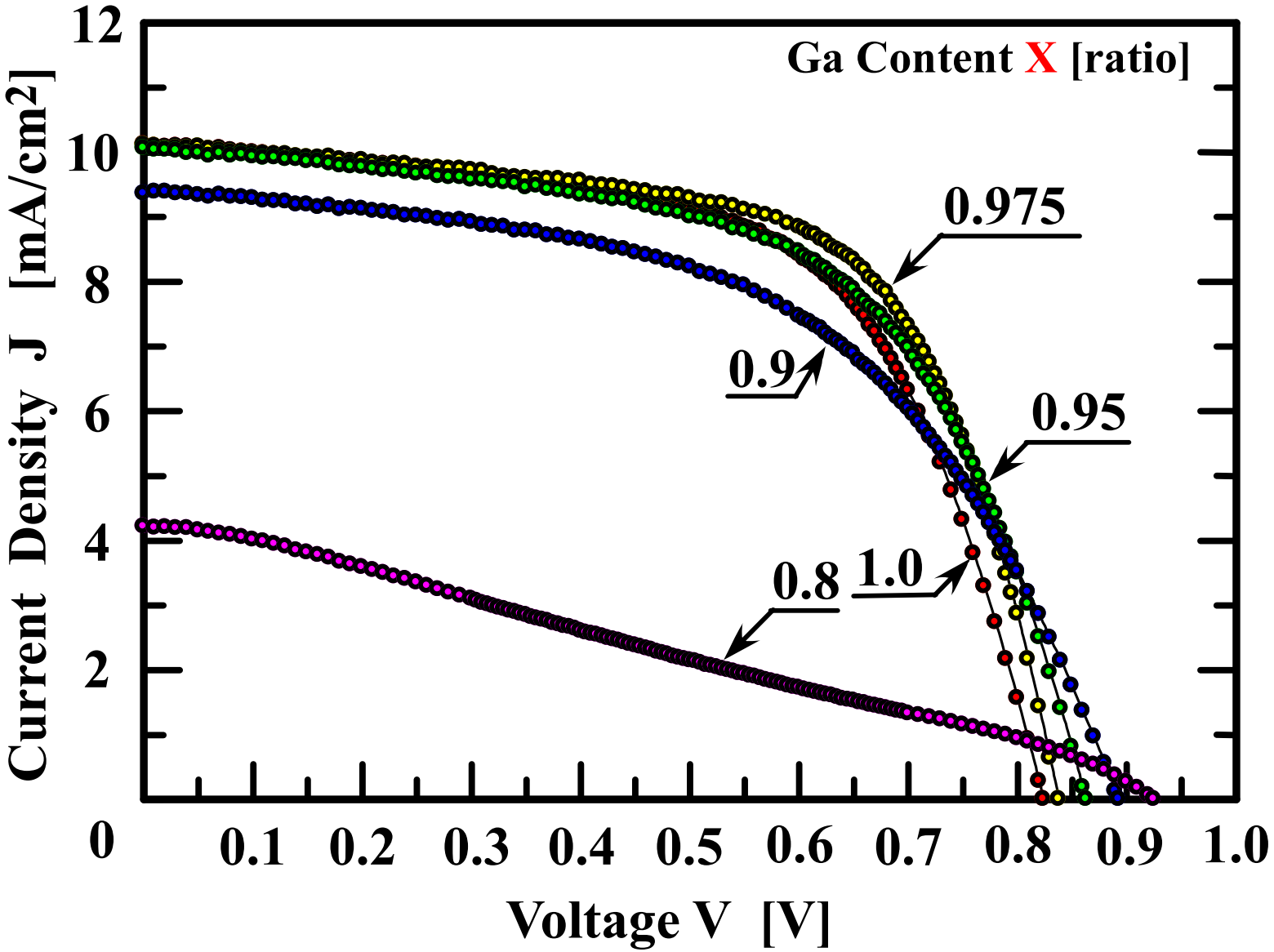
Function	n-type multicomponent oxide thin film	Transparent electrode
Target	$(Ga_2O_3)_x$-$(Al_2O_3)_{1-x}$	AZO
Atmosphere (Pressure[Pa])	O_2 gas (1.7[Pa])	O_2 gas (0.2 [Pa])
Deposition temperature [℃]	RT	RT
Film thickness [nm]	50	200

Objective



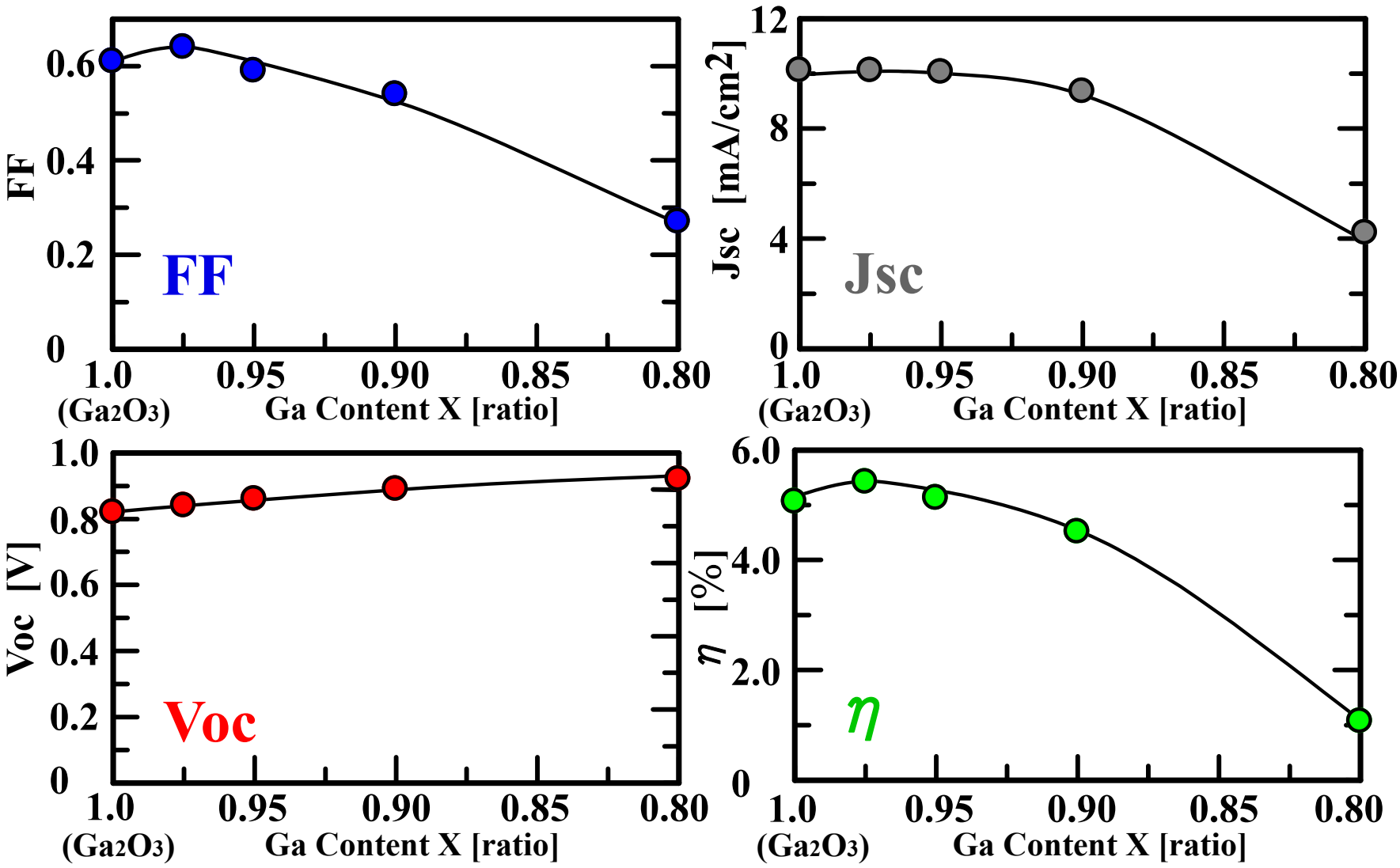
(c) $(Ga_2O_3)_X$-$(Al_2O_3)_{1-X}$

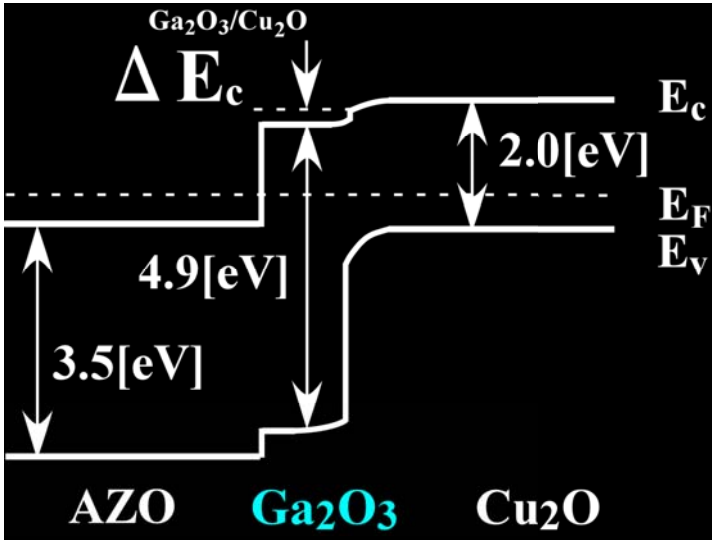
Obtained FF η Jsc and Voc as functions of Ga content (X) for AZO/$(Ga_2O_3)_X$–$(Al_2O_3)_{1-X}$/Cu_2O solar cells.



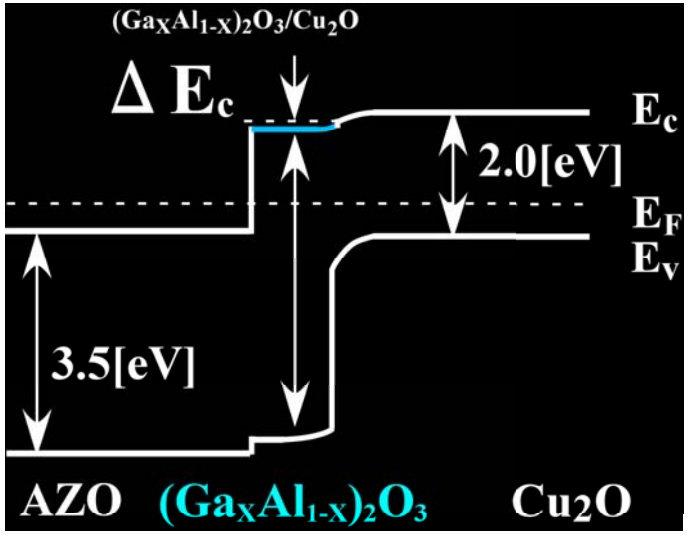
O_2=1.7[Pa]

Obtained FF η Jsc and Voc as functions of Ga content (X) for AZO/$(Ga_2O_3)_X$-$(Al_2O_3)_{1-X}$/Cu_2O solar cells.

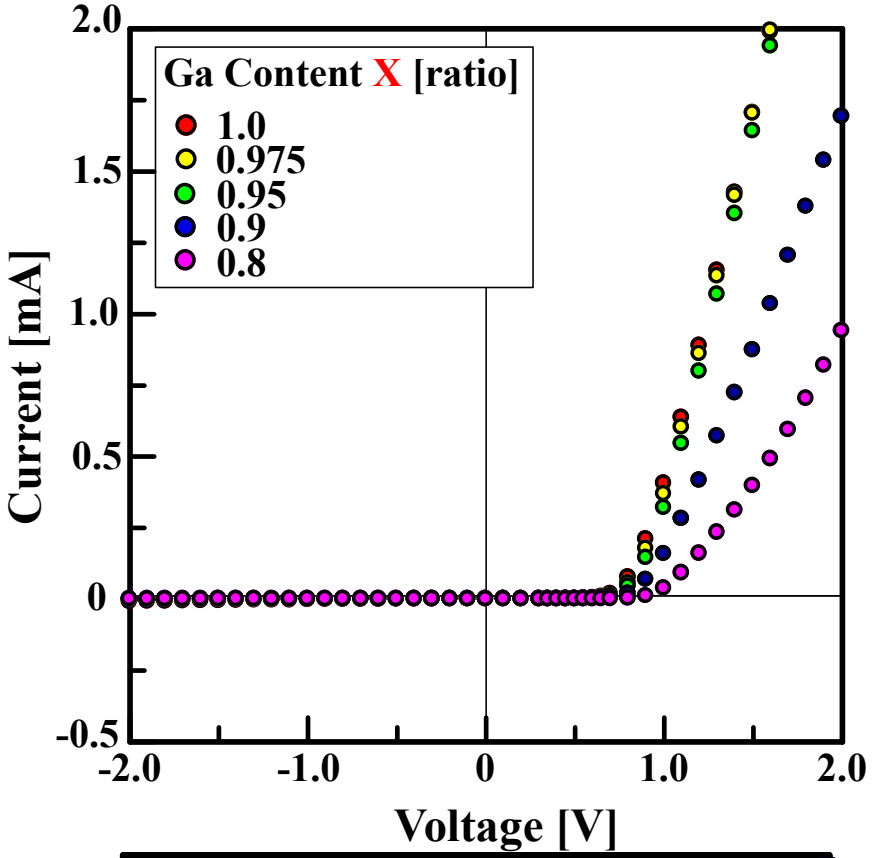


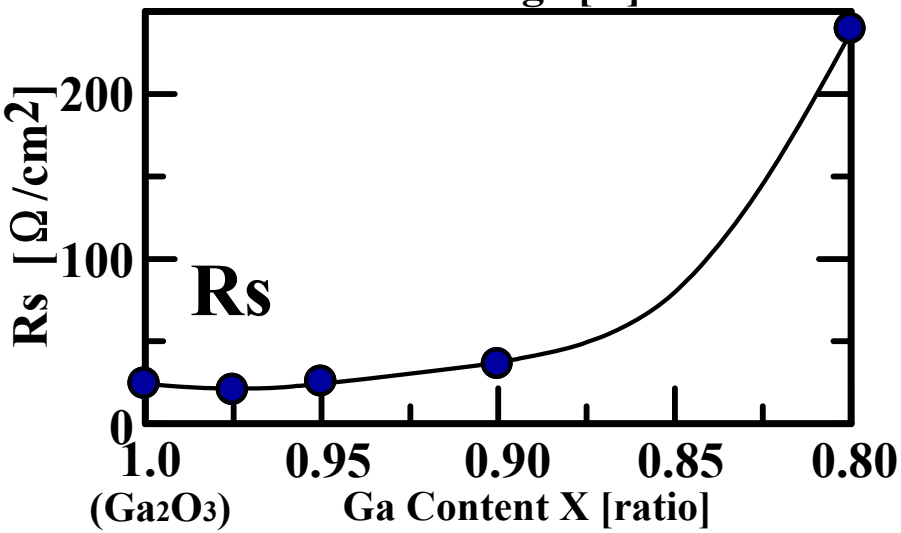


AZO/Ga_2O_3/Cu_2O

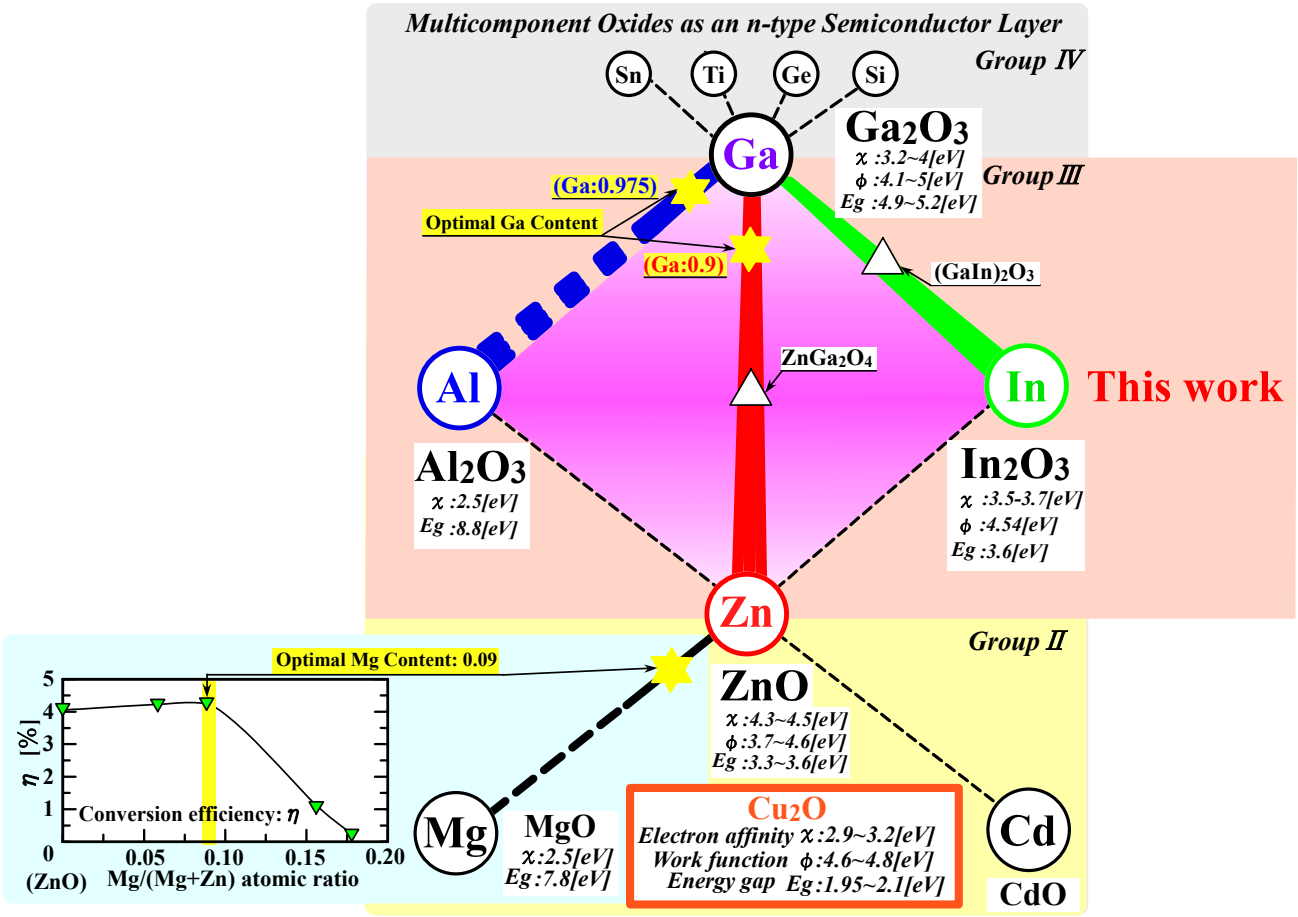


AZO/$(Ga_XAl_{1-X})_2O_3$/Cu_2O





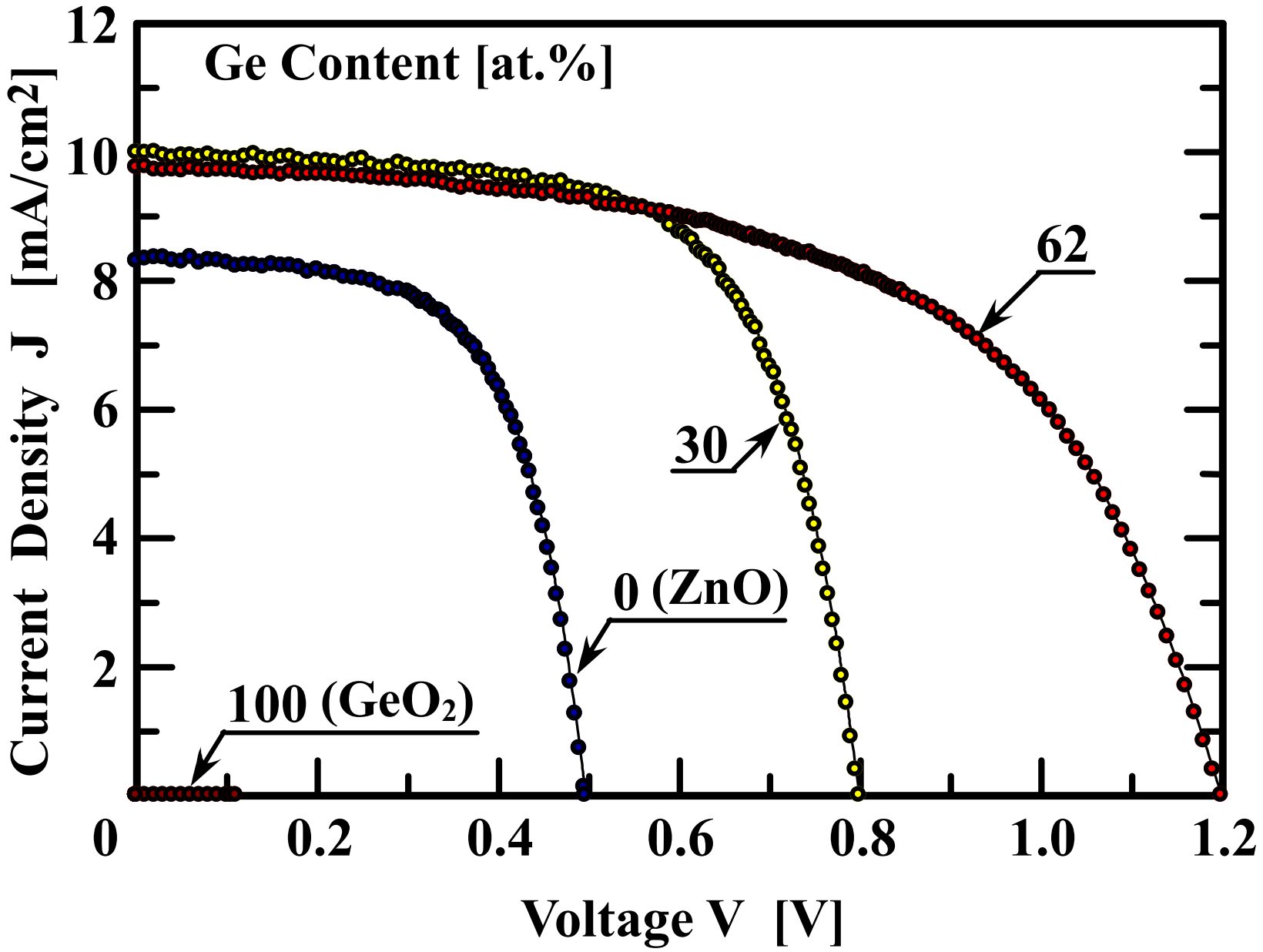
Objective



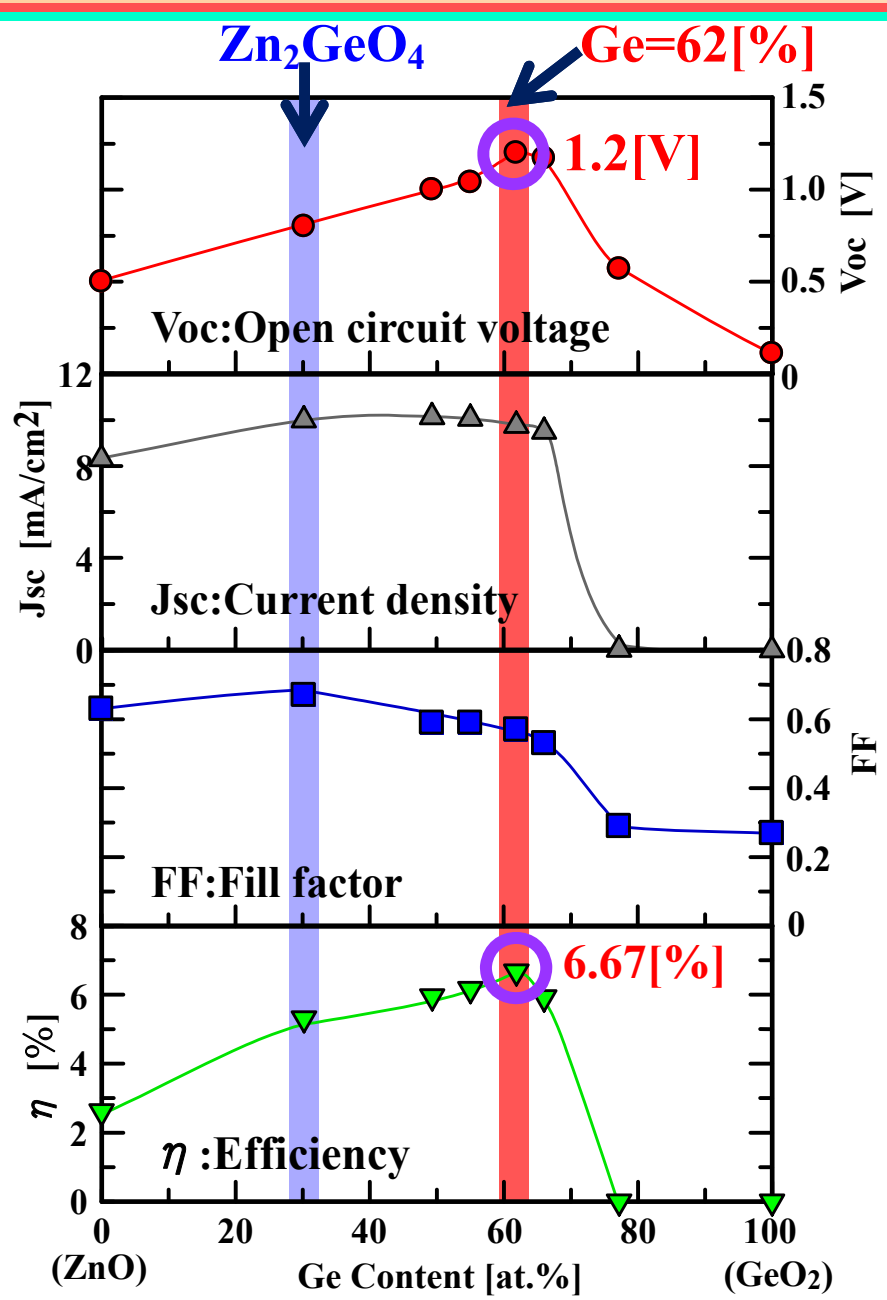
Cu_2O Heterojunction solar cells are prepared by using ZnO-based multicomponent oxide thin film (Zn-Ge-O) as a n-type layer

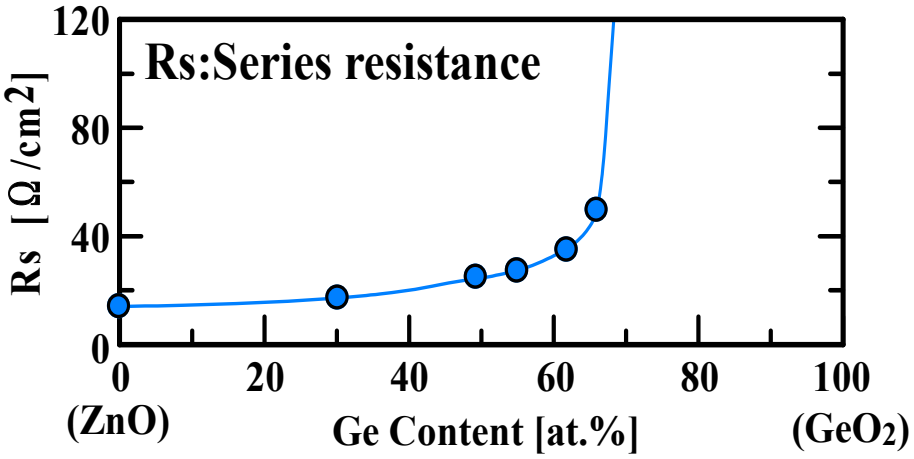
- ◎ **Optimaization of the component**
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J-V characteristics for AZO/ $Zn_{1-X}Ge_X$-O /Cu_2O:Na solar cells using various Ge content

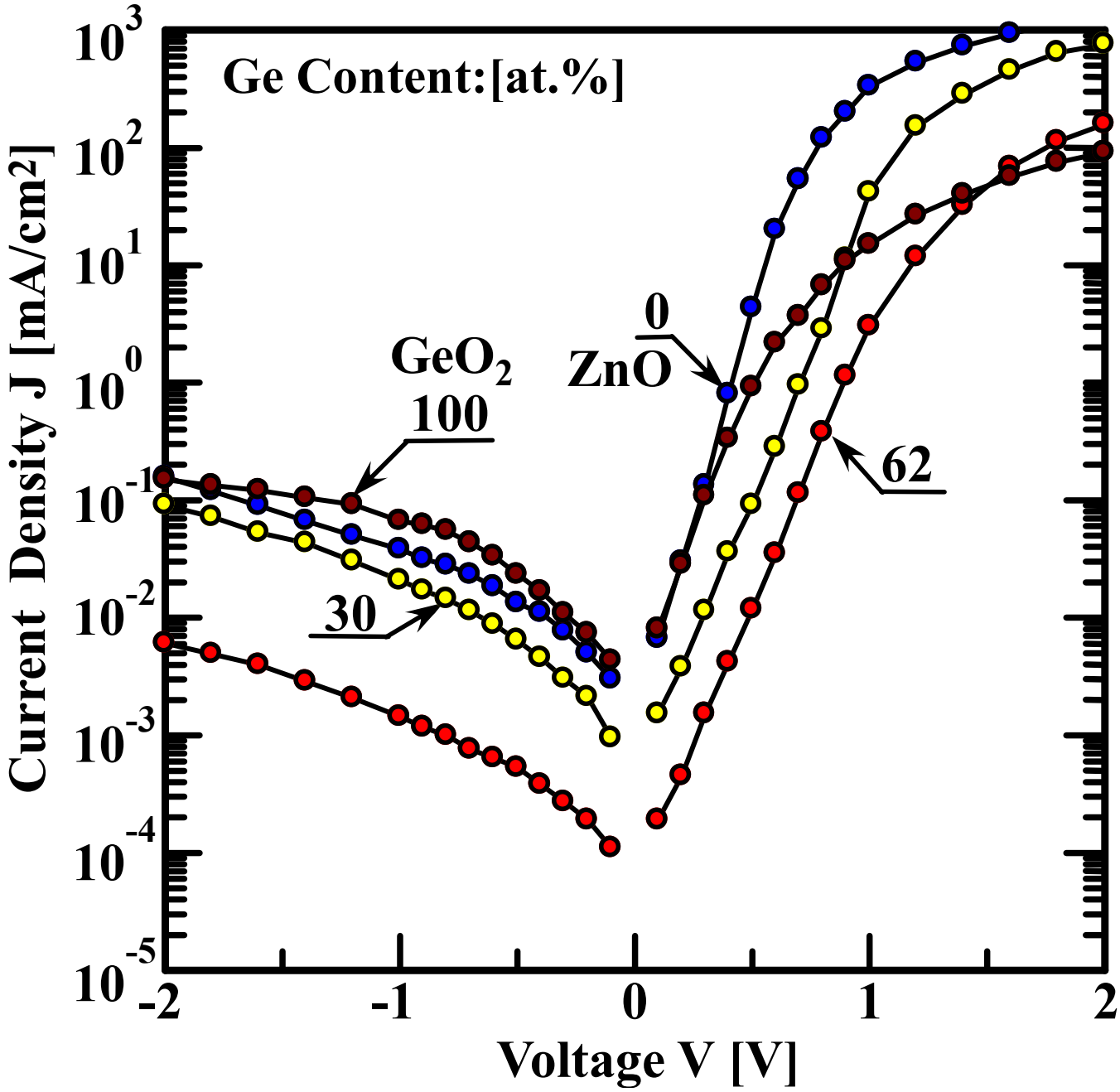


Ge content dependence of photovoltaice properties for AZO/ $Zn_{1-X}Ge_X$-O /Cu_2O:Na solar cells

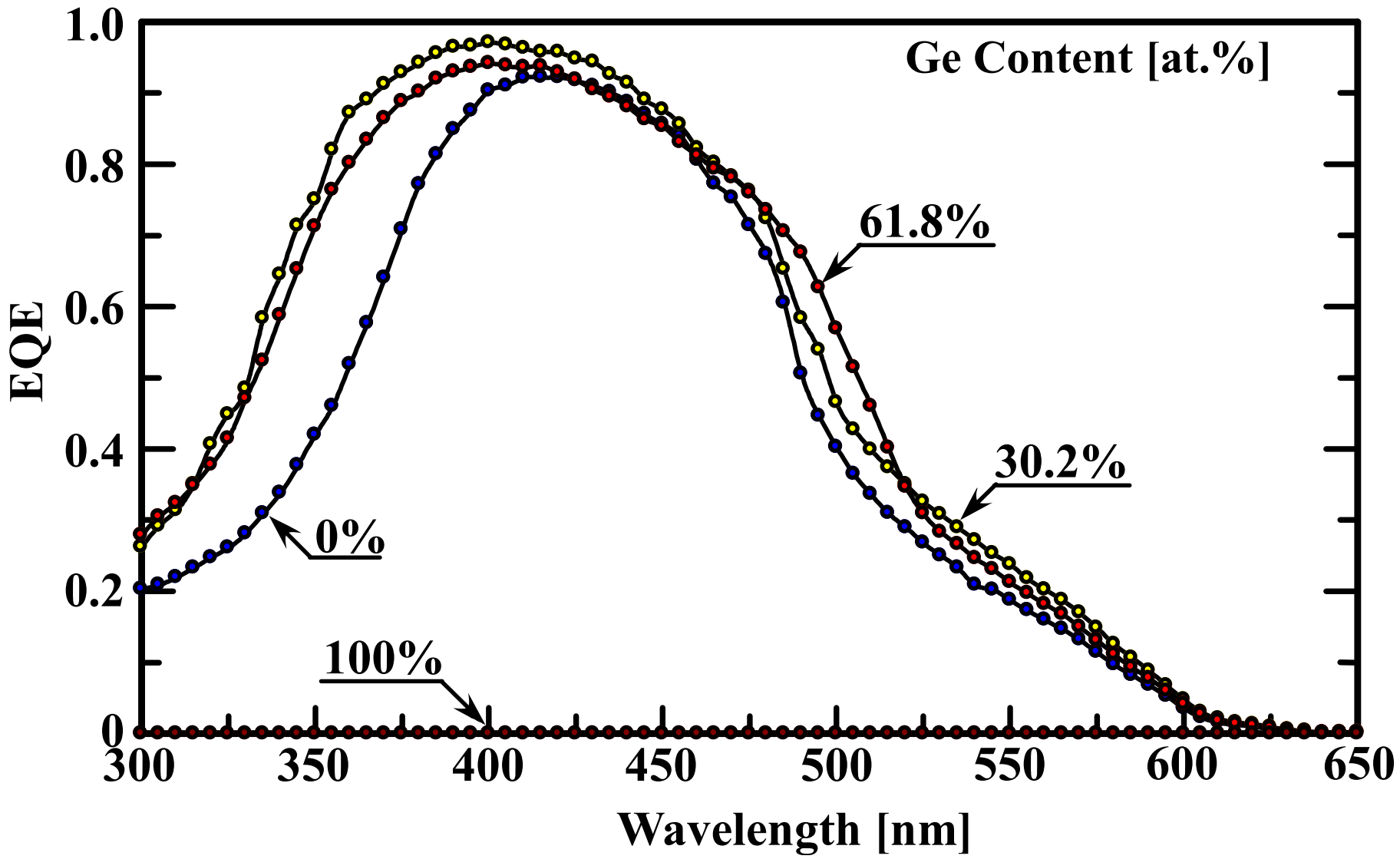


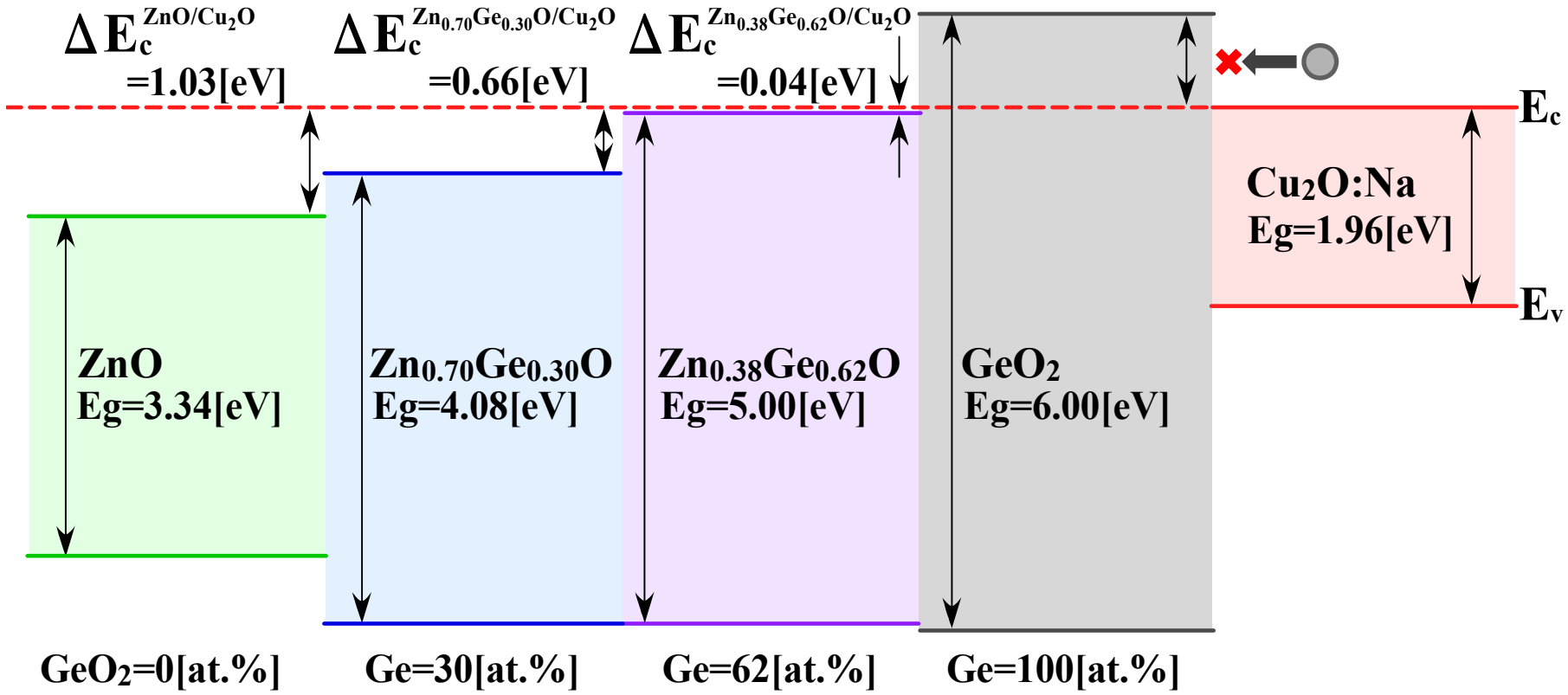


Dark J-V characteristics for AZO/ $Zn_{1-X}Ge_X$-O /Cu_2O:Na solar cells using various Ge content



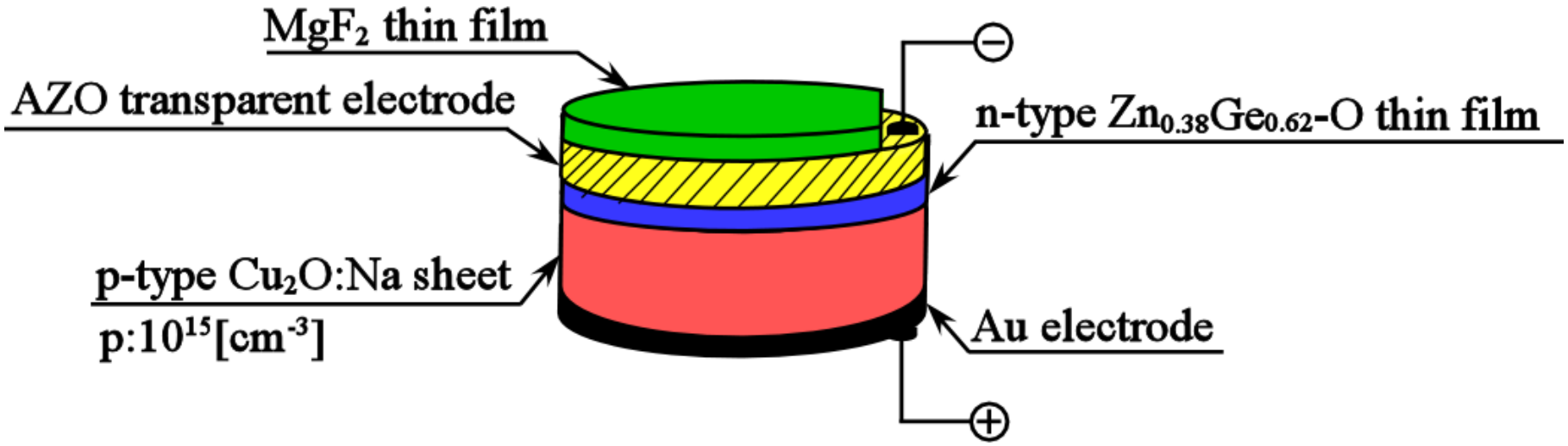
EQE spectra for AZO/ $Zn_{1-X}Ge_X$-O /Cu_2O:Na solar cells using various Ge content





- As the Ge composition increased, ΔEc decreased and ΔEc reached a minimum (about 0.04 [eV]) at a Ge composition of 62% at which the highest conversion efficiency was obtained
- Reduction of ΔEc suppressed recombination at the interface
- The decrease of Jsc and FF over the Ge composition of 70 [%] or more is due to the formation of TYPE I junction

Deposition conditions for MgF_2 thin film (anti reflection film)

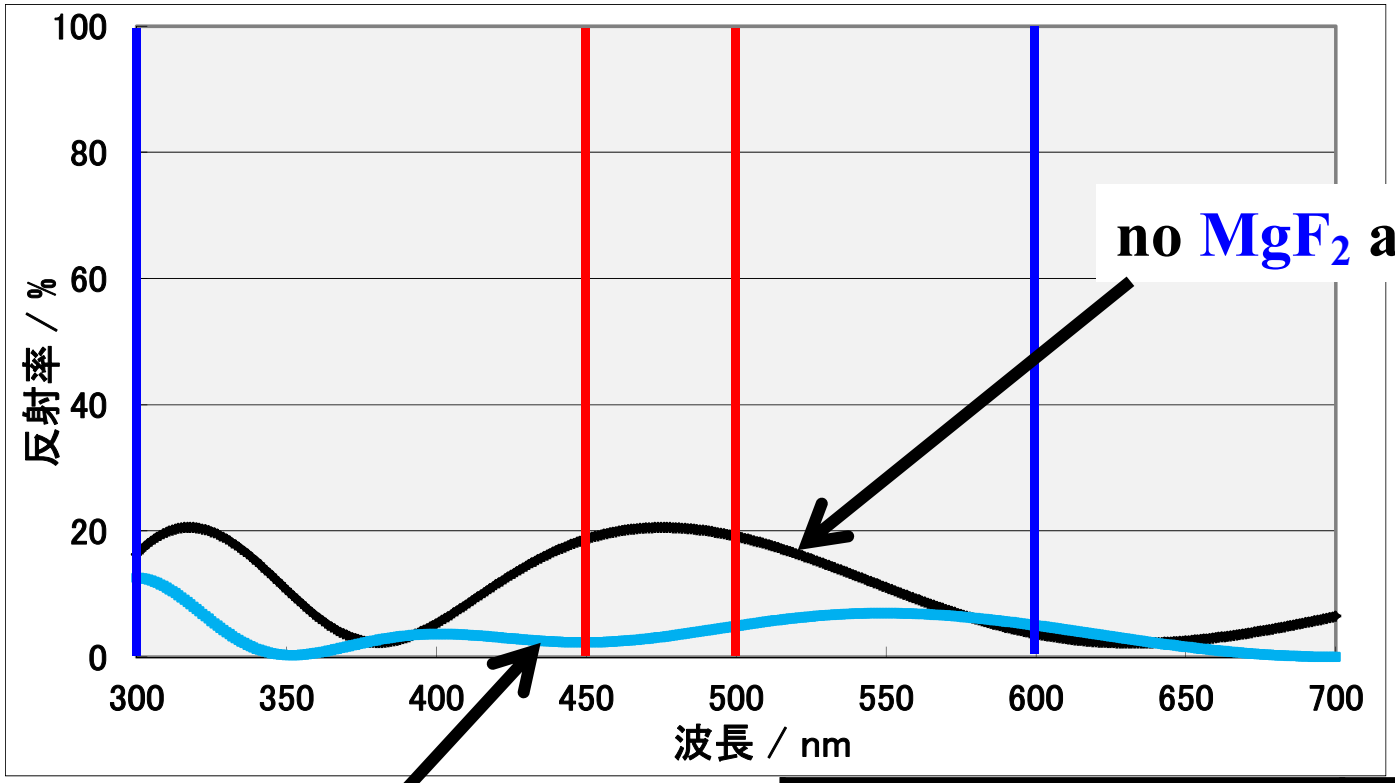


Deposition technology and deposition conditions for MgF_2

Deposition technology	Vacuum deposition method
Deposition material	MgF_2
Deposition temperature [℃]	RT
Film thickness[nm]	75(Determined by simulation)
Atmosphere(pressure[Pa])	Vacuum(10^{-4})

Reflectance properties of MgF_2 film

MgF_2/AZO/n-$(Ga_{0.975}Al_{0.025})_2O_3$/p-$Cu_2O$:Na soler cells



wavelength 300-600[nm]

Average reflectance reduction: about 8.4[%]

material	Film thickness[nm]
MgF_2	78
AZO	200
n-$(Ga_{0.975}Al_{0.025})_2O_3$	50
p-Cu_2O	∞

Ge content dependence of photovoltaic properties of MgF_2/AZO/ $Zn_{1-X}Ge_X$-O /Cu_2O:Na solar cells

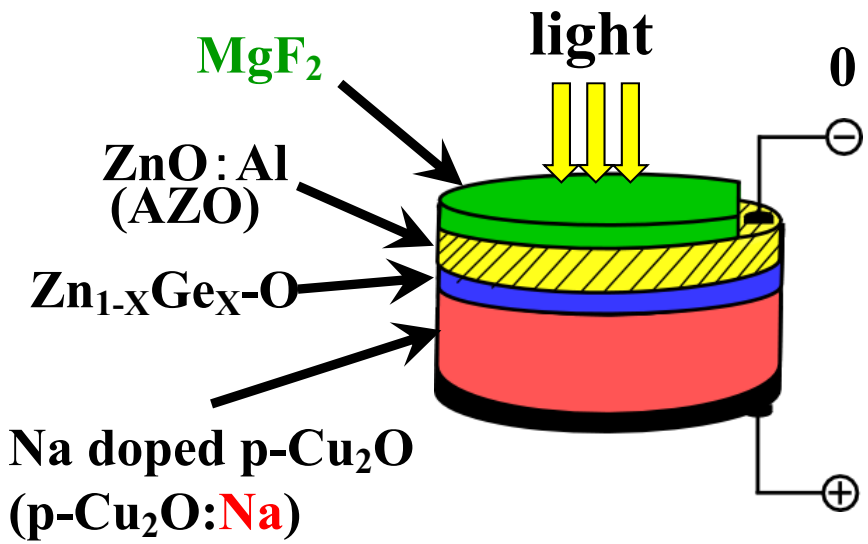
Ge content :(Ge/(Ge+Zn)×100)[%]

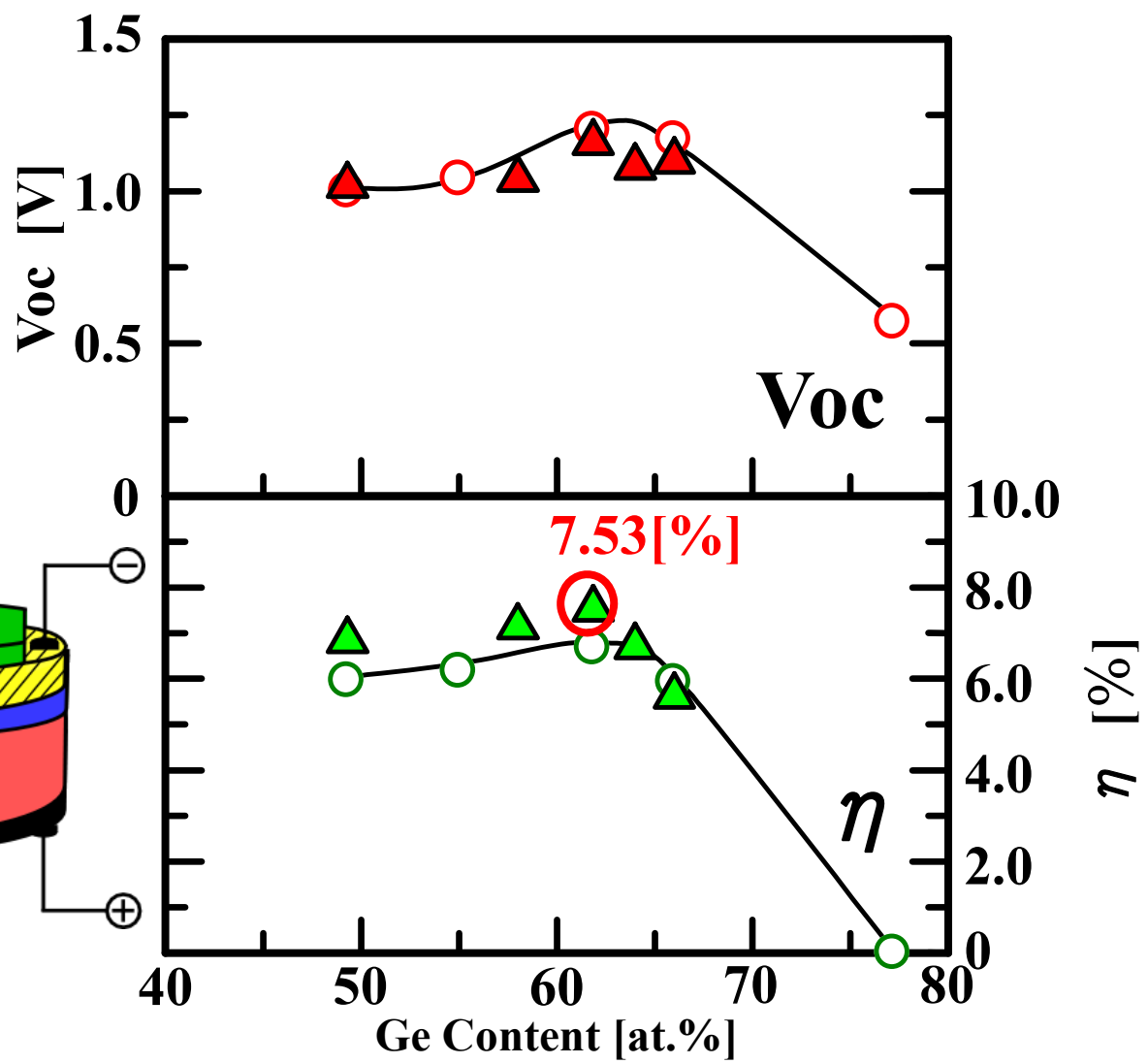
Oxygen pressure:4.0[Pa]

Film thickness :50[nm]

Simulated sunlight (AM1.5G):100[mW/cm^2]

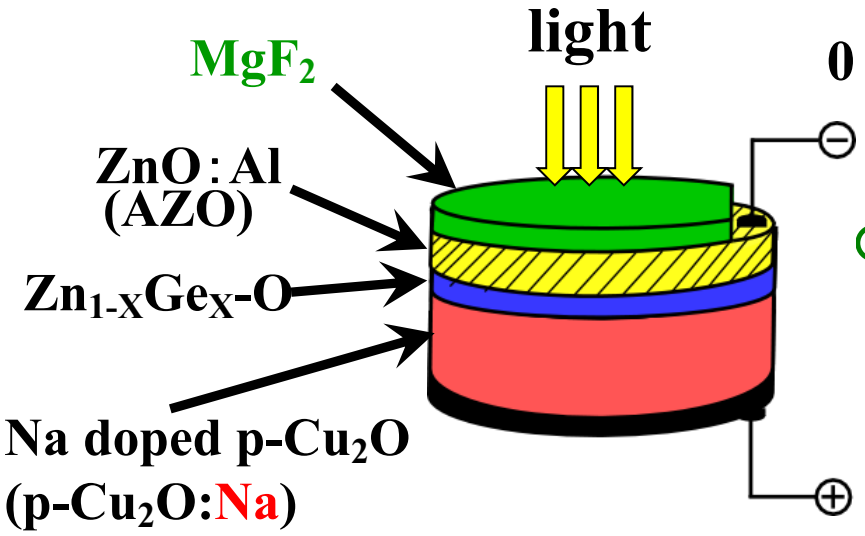
Element temperature is constant at 25[℃]

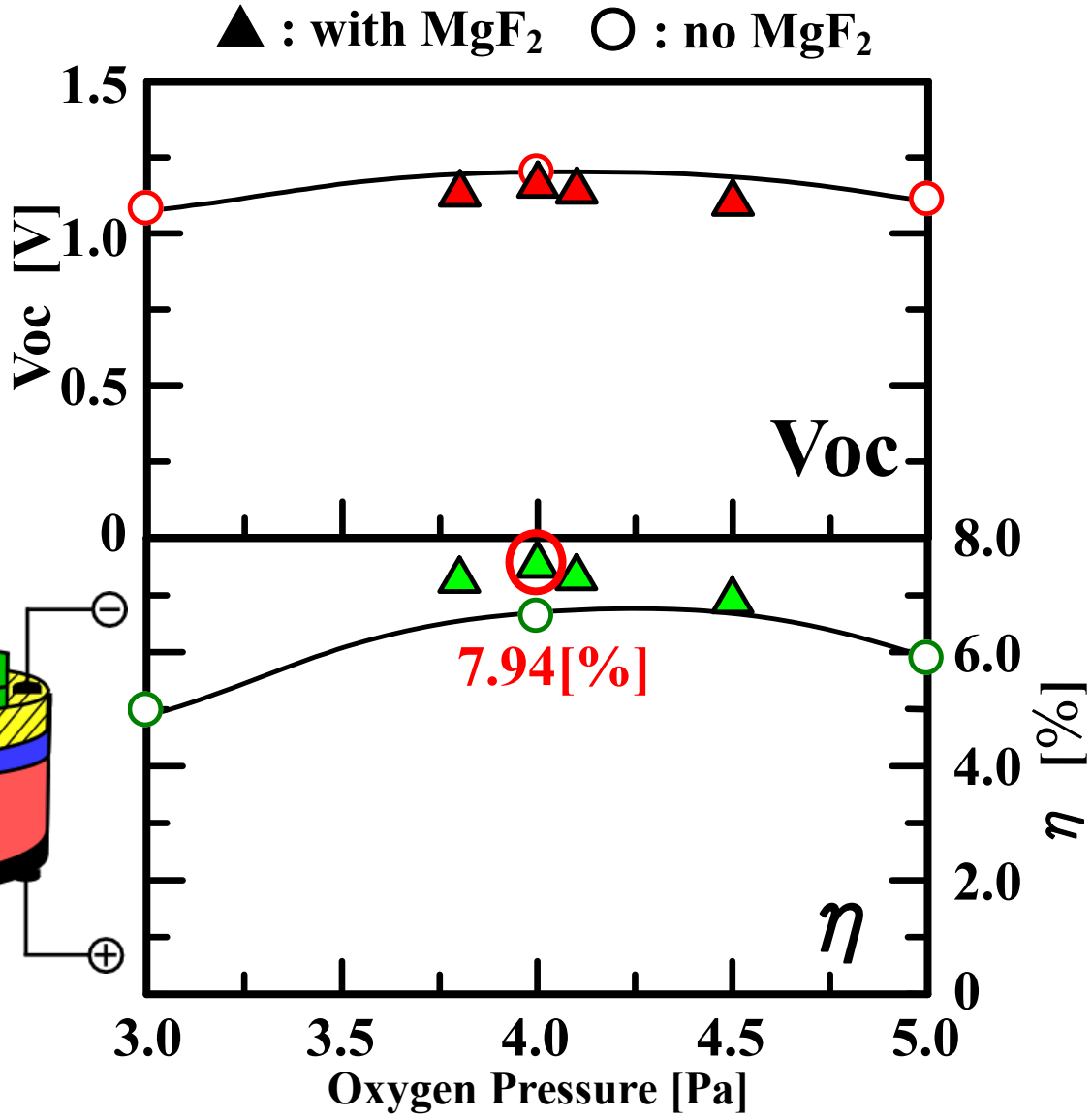




Oxygen pressure dependence of photovoltaic properties of MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na solar cells

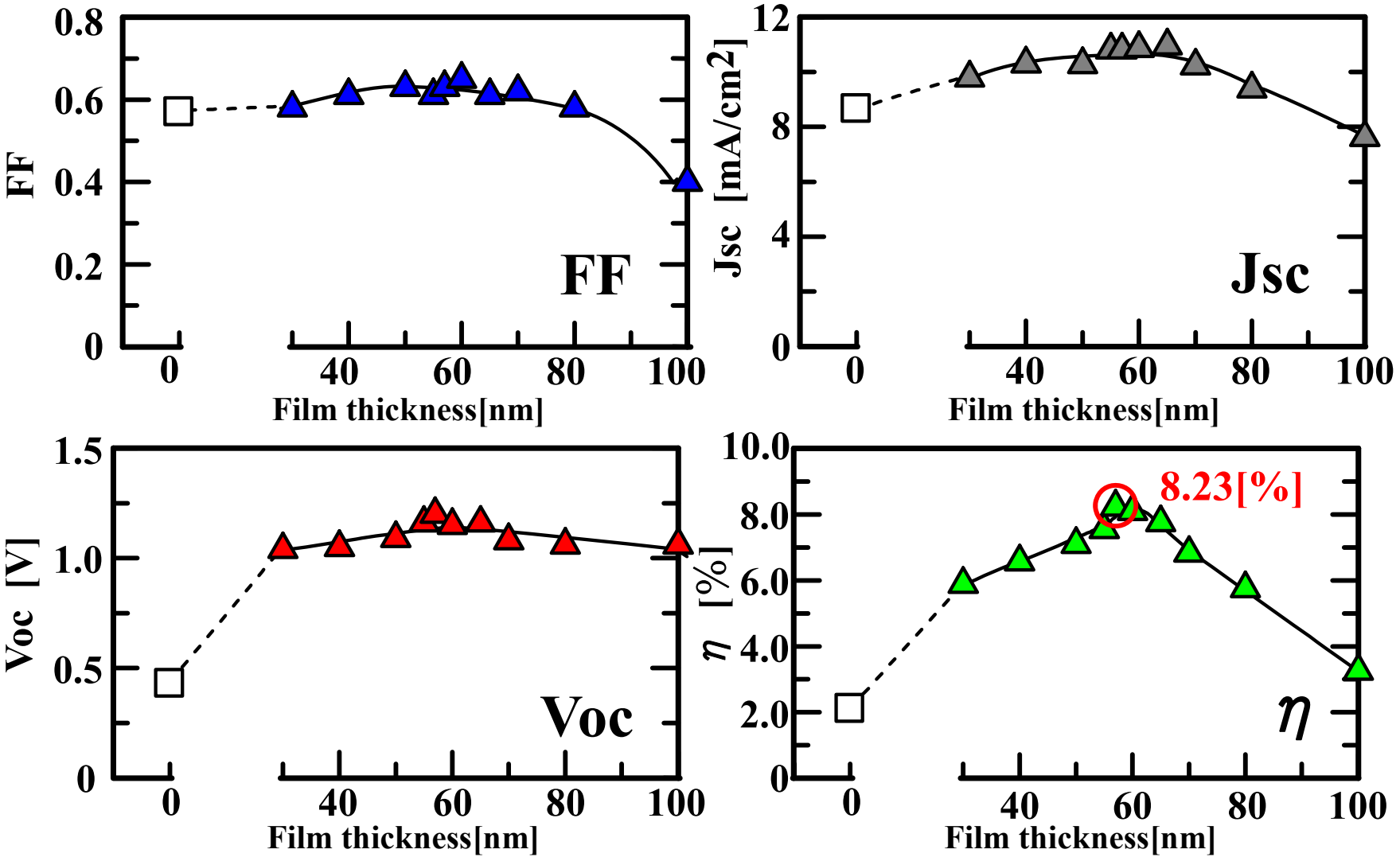
Ge content :62[%]
Film thickness :50[nm]
Simulated sunlight (AM1.5G):100[mW/cm^2]
Element temperature is constant at 25[℃]





Film thickness dependence of photovoltaic properties of MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na solar cells

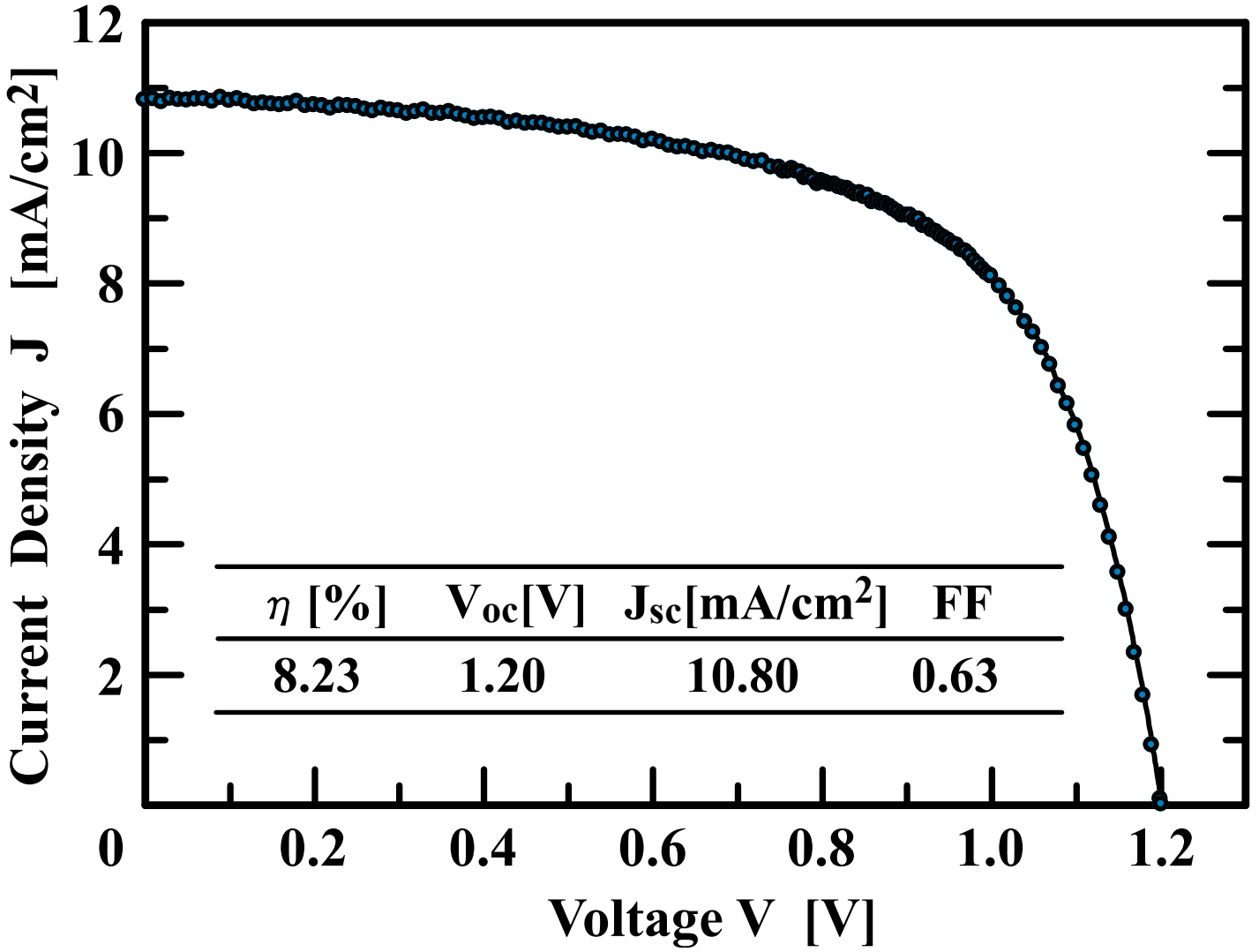
Ge content :62[%]
Oxygen pressure:4.0[Pa]
Simulated sunlight (AM1.5G):100[mW/cm^2]
Element temperature is constant at 25[℃]



Film thickness dependence of photovoltaic properties of MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na solar cells

Ge content :62[%]
Oxygen pressure:4.0[Pa]
Film thickness :57[nm]

Simulated sunlight (AM1.5G):100[mW/cm^2]
Element temperature is constant at 25[℃]



η [%]	V_{oc}[V]	J_{sc}[mA/cm^2]	FF
8.23	1.20	10.80	0.63

Conclusion

◎AZO/n-type multicomponent oxide thin film/p-Cu_2O solar cells

1) **Photo voltaic properties are not only dependent on the component of metal element but also preparation conditions.**

2) **The efficiency was improved by using multicomponent oxide thin film as a n-type layer, such as Ga-Al-O and Zn-Ge-O.**

3) **The highest conversion efficiency of 8.23% could be achieved in a MgF_2/AZO/ $Zn_{0.38}$-$Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cell fabricated using a 75-nm-thick $Zn_{0.38}$-$Ge_{0.62}$-O thin film and a Cu_2O:Na sheet with a P of approximately 4×10^{15} cm^{-3}.**