Annealing-induced Intermixing and Passivation of the Front Contact in $Cu(In,Ga)Se_2$ Devices – A Spectroscopic View on CdS and GaO_x

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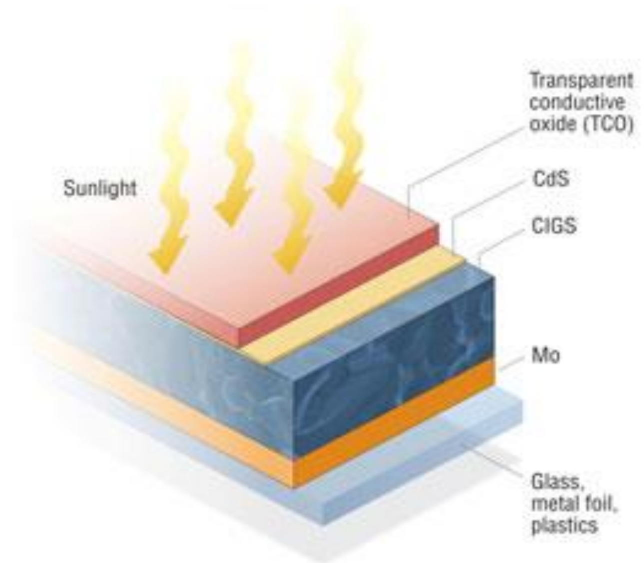
Introduction

Chalcopyrite $Cu(In,Ga)Se_2$ - CIGSe thin–film solar cells

- High efficiency thin film solar cell
- Suitable for deposition on various substrates
- Can be flexible solar cells
- Future employment in ultra-thin and tandem solar cells

$$\eta = 23.4\%$$

Press release Solar Frontier (2019-01-17)



CIGS photovoltaic cell structure. Image by Alfred Hicks/NREL

Further increase in efficiency of CIGSe solar cells:

- Depositing TCO at elevated temperatures to decrease optical losses
- For application in tandem devices, thermal stability of CIGSe stack is needed

Post-Deposition Annealing Treatment done on samples to simulate TCO deposition at elevated temperatures

Introduction

<u>Post-Deposition Annealing Treatment (PDAT)*:</u>

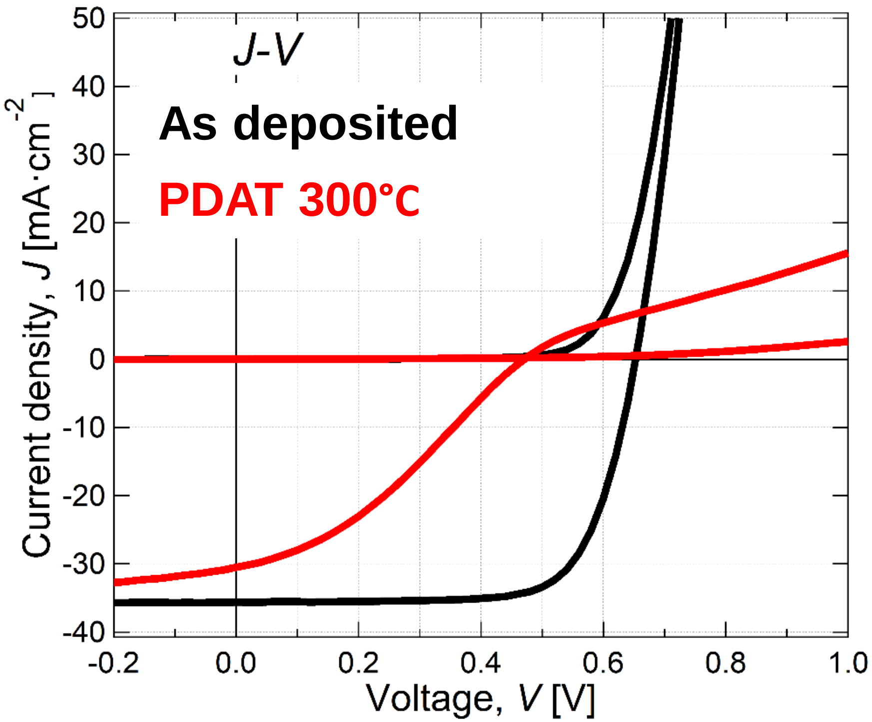
- Effectively passivates defect states in CIGSe
- Decreased recombination centers density
- Increased effective acceptor density

X. Niu et al., Applied Surface Science, No 426, 1213-1220 (2017)

Post-Deposition Annealing Treatment (PDAT)*:

- ➢ Effectively passivates defect states in CIGSe
- ➢ Decreased recombination centers density
- ➢ Increased effective acceptor density

- Critical temperature 250 - 300°C → Deterioration of CdS/CIGSe stack



- ➢ PDAT treatments at 300 °C induce severe degradation in all cell parameters
- ➢ GD-OES shows: PDAT-induced diffusion of Na into the TCO and Cd diffusion into the CIGSe which leads to stack degradation

Thermally robust buffer/absorber interface required !!!

*X. Niu et al., Applied Surface Science, No 426, 1213-1220 (2017)

Introduction

Criteria for more thermally robust buffer layer* :

- Diffusion barrier
- Energy band gap (E_g) > 3 eV
- Buffer layer needs to provide beneficial energy level alignment

*Heinemann at. el. Phys. Status Solidi A 214, No. 5, 160087, (2017)

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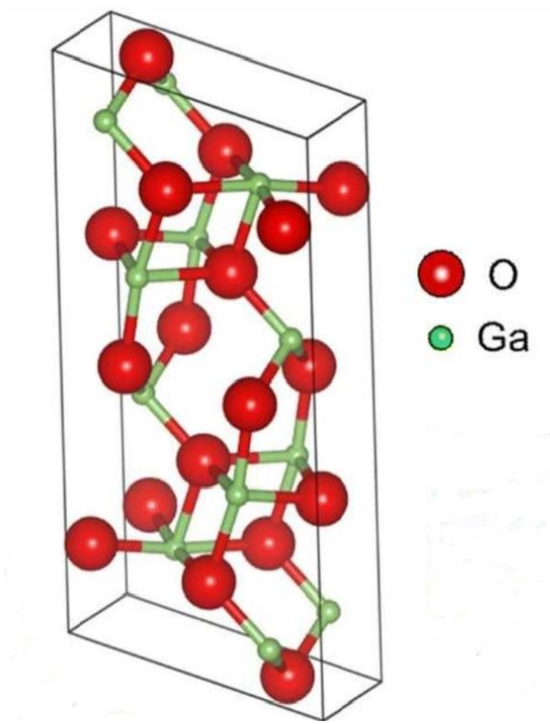
Gallium oxide – Ga_2O_3



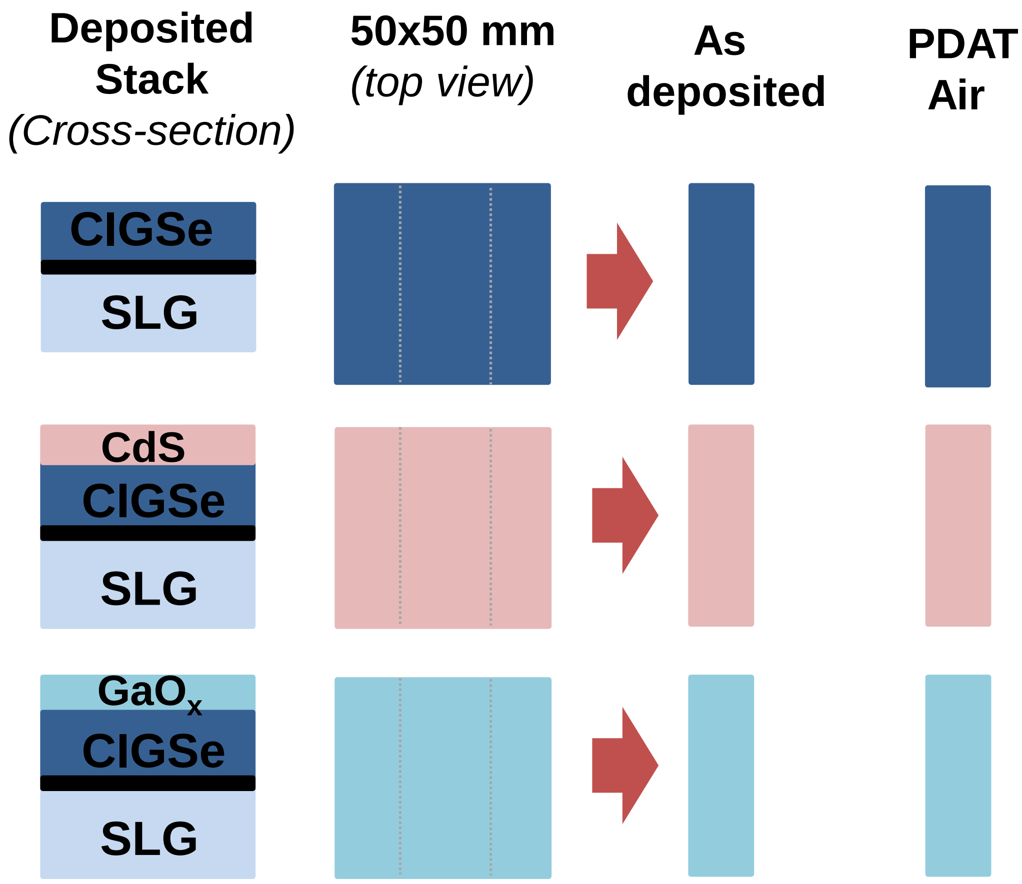
Xue et al. Nanoscale Research Letters (2018) 13:290

Ga_2O_3 as a substitute for CdS buffer layer:

- ➢ Compatible with CIGSe
- ➢ Non-toxic, non-heavy metal compound
- ➢ Wide band gap material
- ➢ Prominent material for field effect passivation
- ➢ Thermally and chemically stable

*Heinemann at. el. Phys. Status Solidi A 214, No. 5, 160087, (2017)

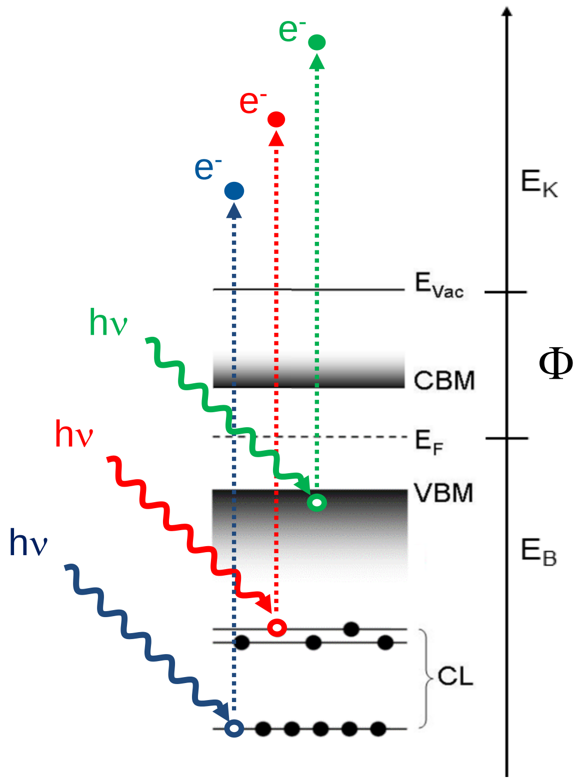
Sample Preparation



Buffer layer	Nominal thickness (nm)
CdS	10, 20, 50
GaO$_x$	5, 10, 20, 50

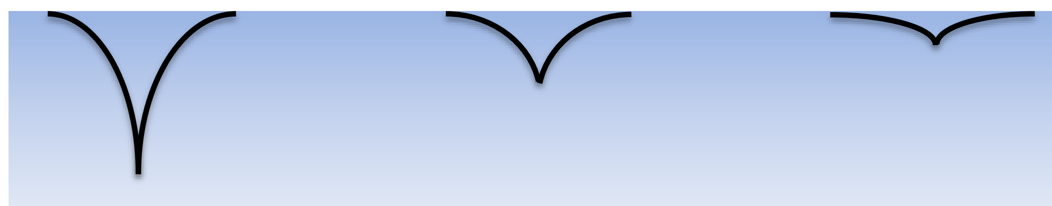
- CdS buffer layer deposited via CBD, GaO$_x$ deposition via RF- Magnetron Sputtering
- Annealed in air (PDAT – air) for 20 min at 300°C after buffer layer deposition

Photon In / Electron Out
(Direct photoemission)



Kinetic energy of released electrons:
$E_K = h\nu - E_B - \Phi$

HAXPES	XPS	UPS
hν = *5950 eV*	hν *(Mg Kα) = 1253.56 eV* hν *(Al Kα) = 1486.58 eV*	hν *(He I) = 21.2 eV* hν *(He II) = 40.8 eV*



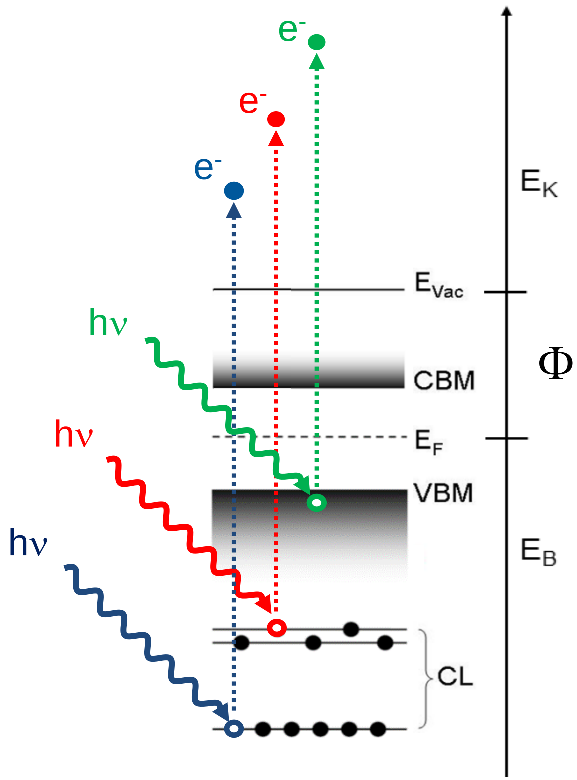
IMFP ~ 8.5 nm	IMFP ~ 2 nm	IMFP < 1 nm

- Inelastic Mean Free Path – IMFP calculated with Quases software*

*http://www.quases.com/products/quases-imfp-tpp2m/

Photoelectron Spectroscopy (PES)

Photon In / Electron Out *(Direct photoemission)*	Electron In / Photon Out *(Inverse photoemission)*



Kinetic energy of released electrons:

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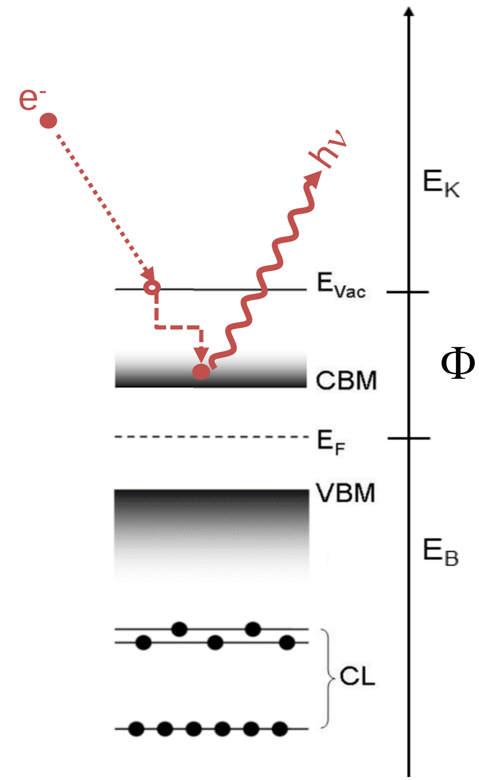
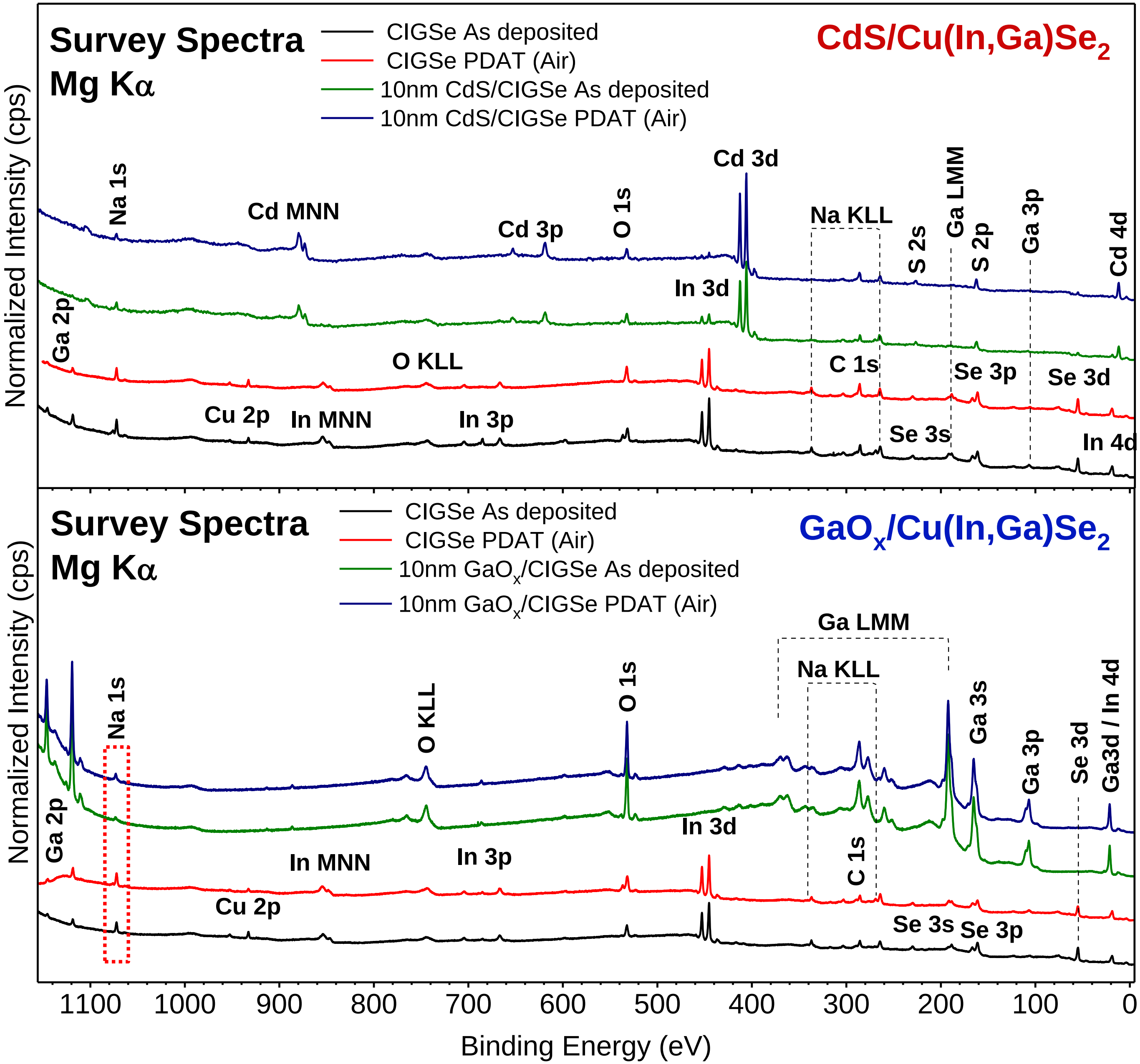


Detected photon energy:

$h\nu = E_B + E_K + \Phi$

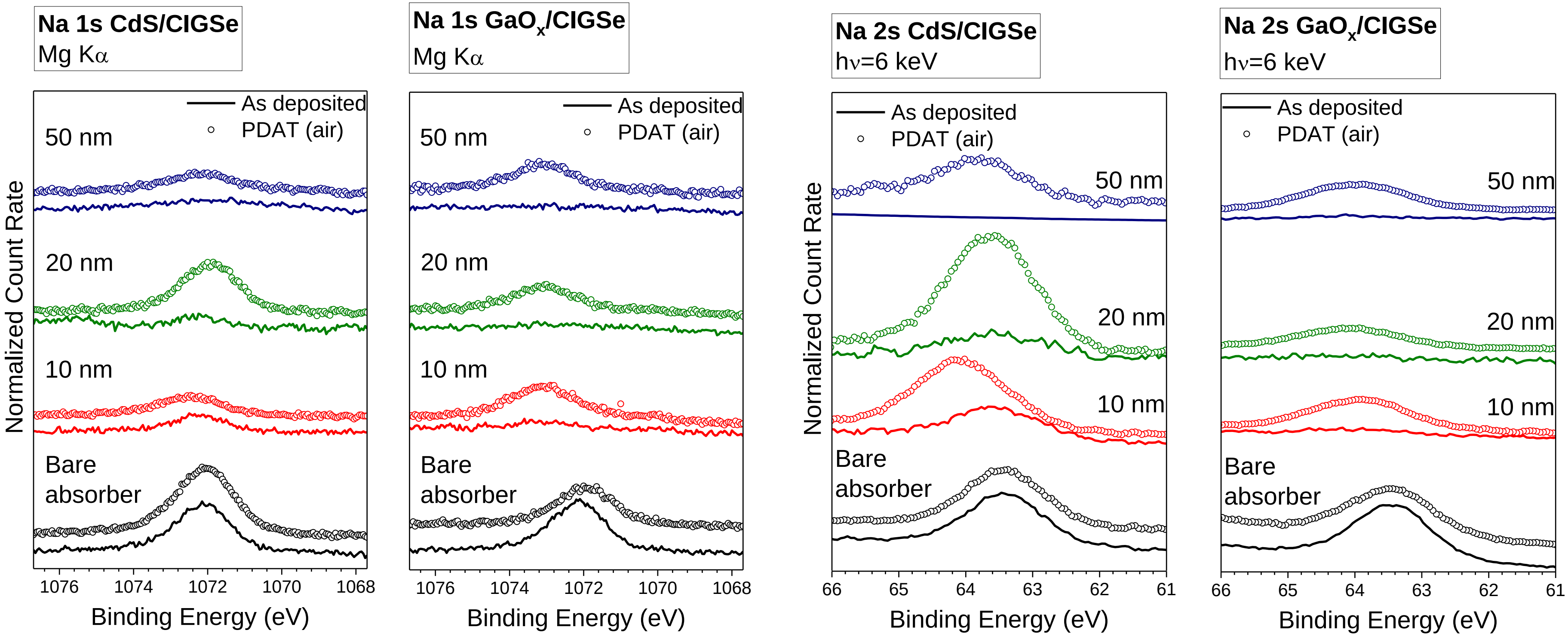
CdS & GaO_x/CIGSe Survey Spectra



- From survey spectra visible attenuation of CIGSe peaks with buffer layer deposition
- GaO_x related samples have better coverage, but Na peak still visible in spectra

Na Diffusion Into Buffer Layer

Na 1s | Na 2s

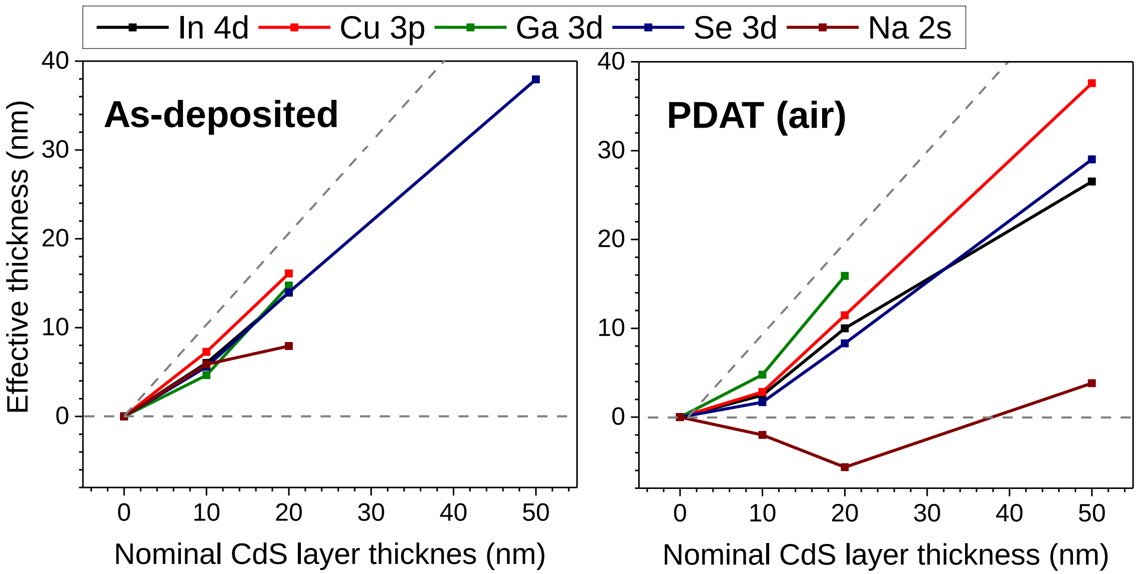


- PDAT induced Na diffusion present in all samples
- Na diffuses from SLG through whole stack
- GaO_x acts as a Na barrier

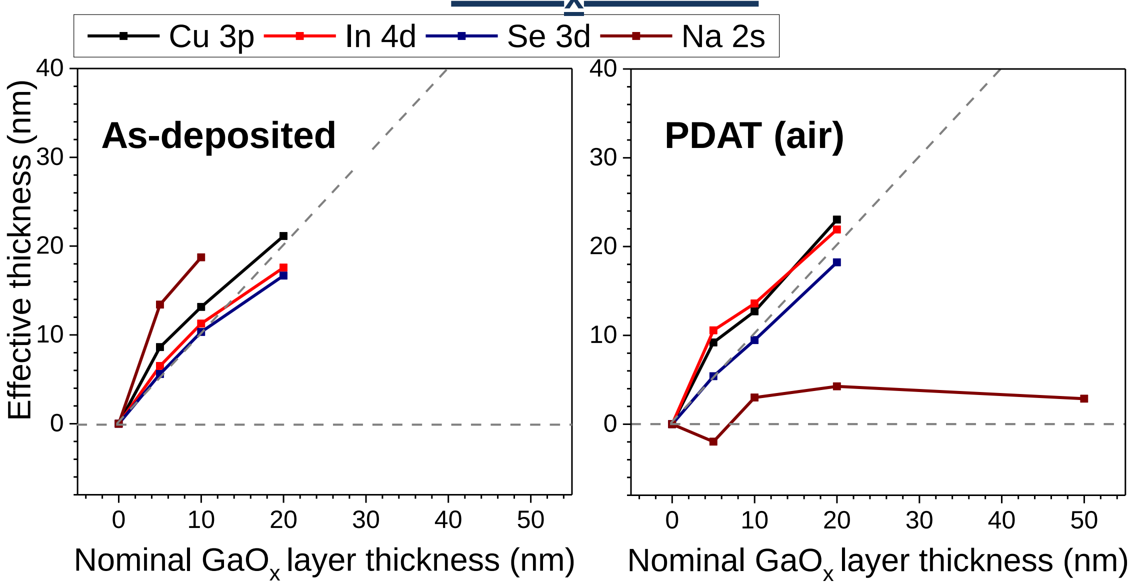
Core level	Excitation energy (eV)	IMFP (nm)	Cross-section
Na 1s	1253.56	< 2	~ 100
Na 2s	5950	< 8.5	~ 0.39

Effective Thickness Calculation

CdS/CIGSe



GaO_x/CIGSe



Beer-Lambert law

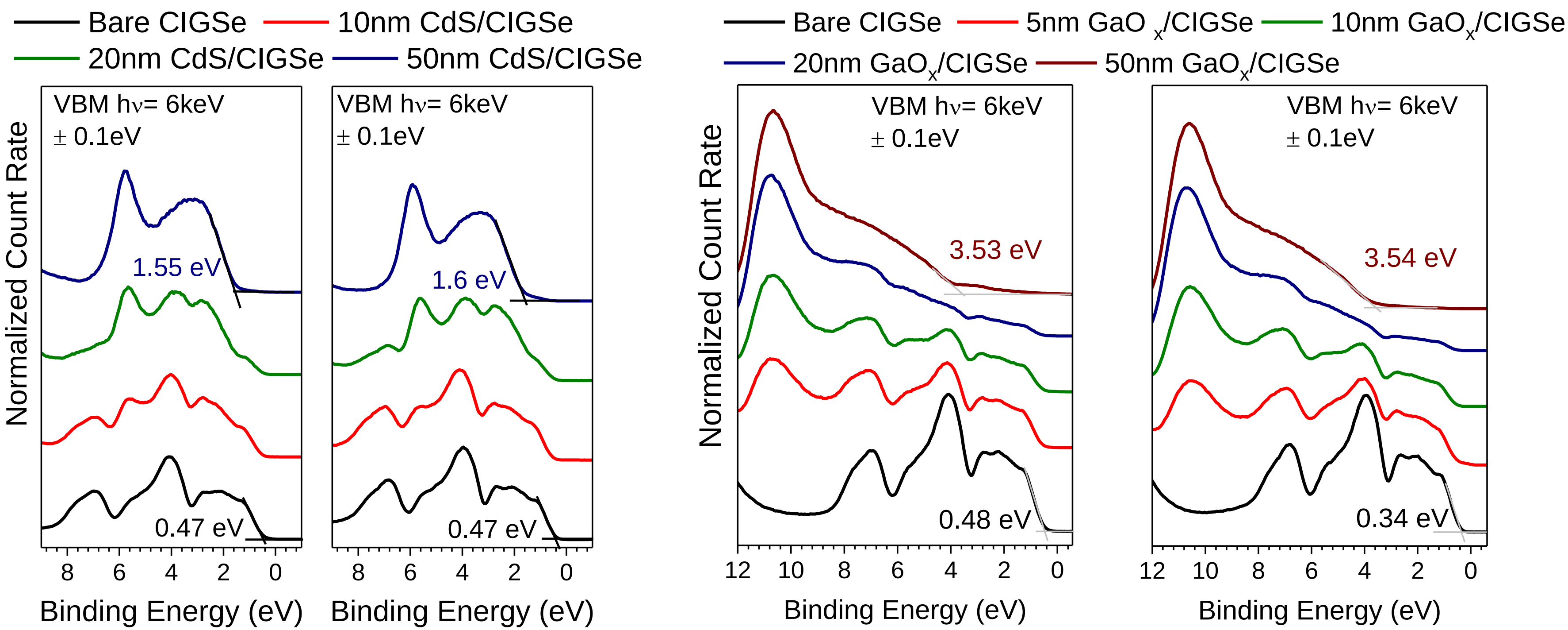
$$\frac{I}{I_0} = e^{-x/IMFP}$$

- Effective thickness calculated from shallow core levels signals via Beer-Lambert law
- Excitation energy hν = *6 eV*, IMFP ~ 8.5 nm
- Deposited CdS buffer layers thinner than nominal thickness

CdS & GaO_x: Valence Band Maximum

CdS/CIGSe

GaO_x/CIGSe



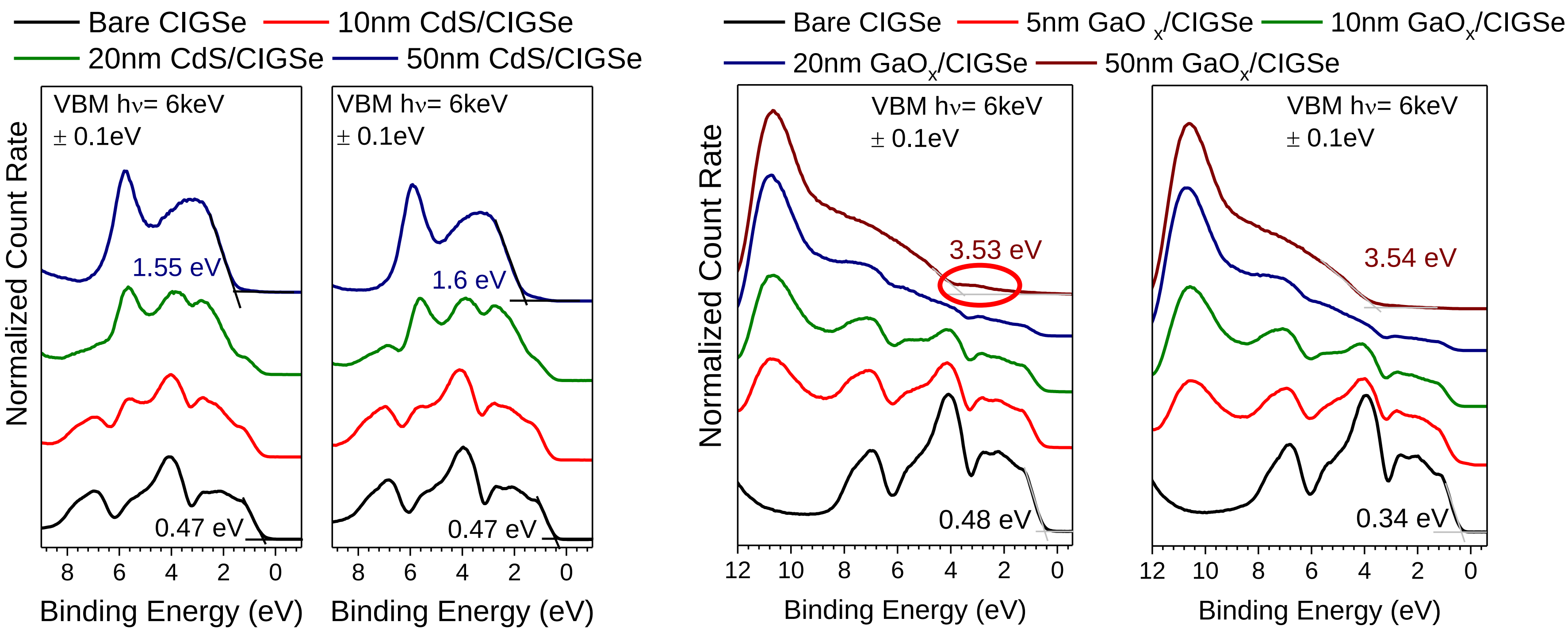
- VBM shape changes with increasing buffer layer thickness
- PDAT shows no major effect on VBM position

CdS & GaO_x: Valence Band Maximum

CdS/CIGSe

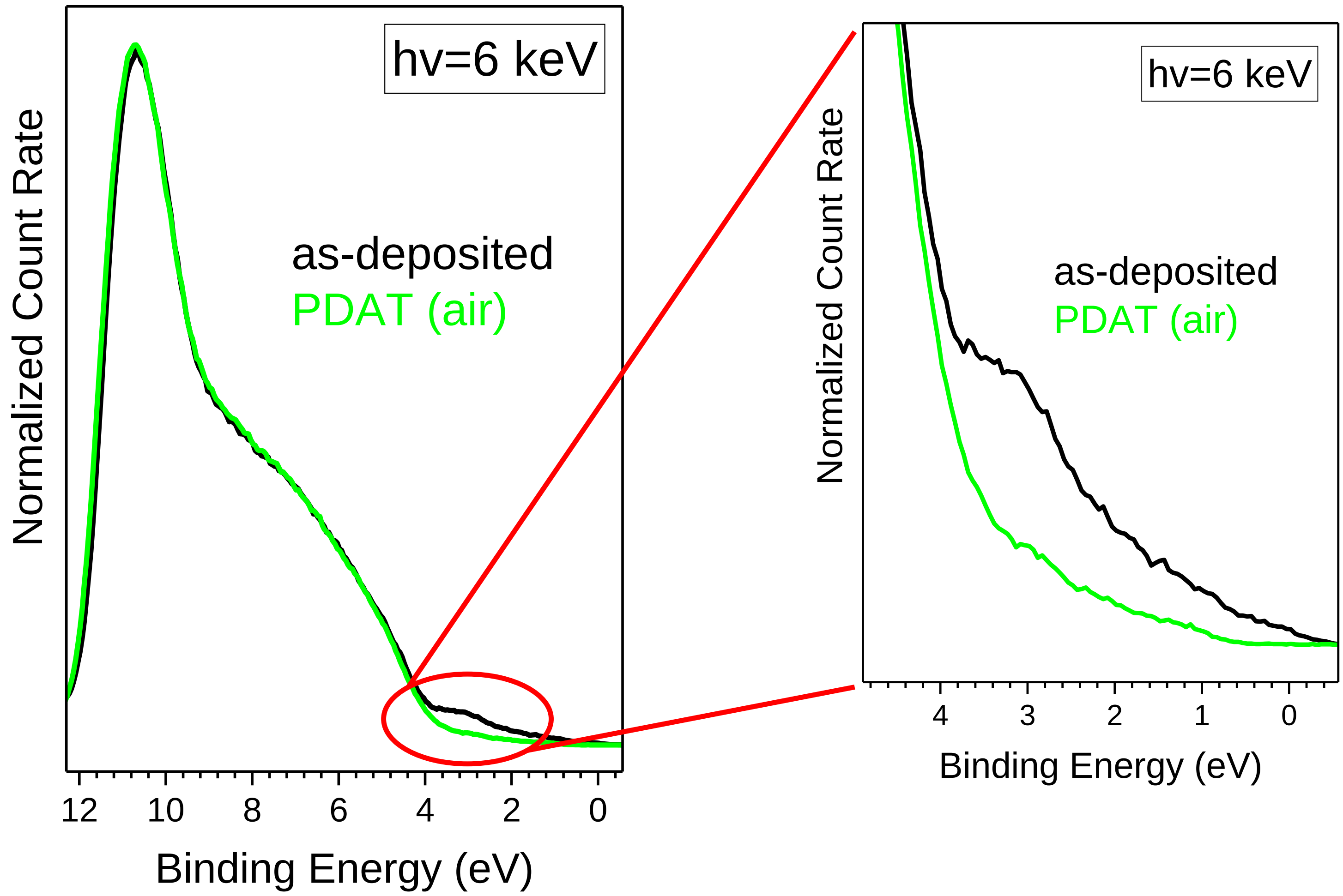
GaO_x/CIGSe

As-deposited **PDAT (air)** **As-deposited** **PDAT (air)**



- VBM shape changes with increasing buffer layer thickness
- PDAT shows no major effect on VBM position
- Spectral intensity above VBM visible for thickest as-deposited GaO_x layer

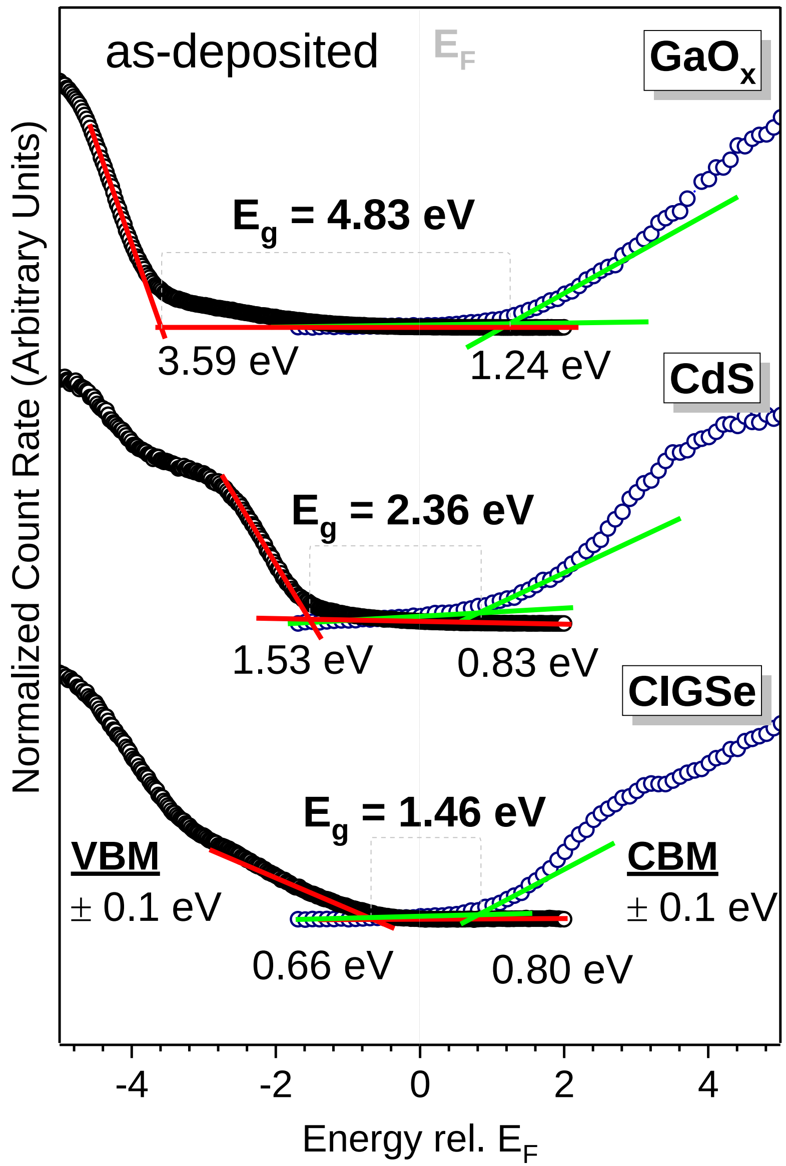
GaO_x/CIGSe: Spectral Intensity Above VBM



- Oxygen related near surface defect density visible in as-deposited GaO_x sample
- Surface defect density decreases upon PDAT

J.Kim et. al. NPG Asia Materials No. 9, e359 (2017)

Energy Level Positions

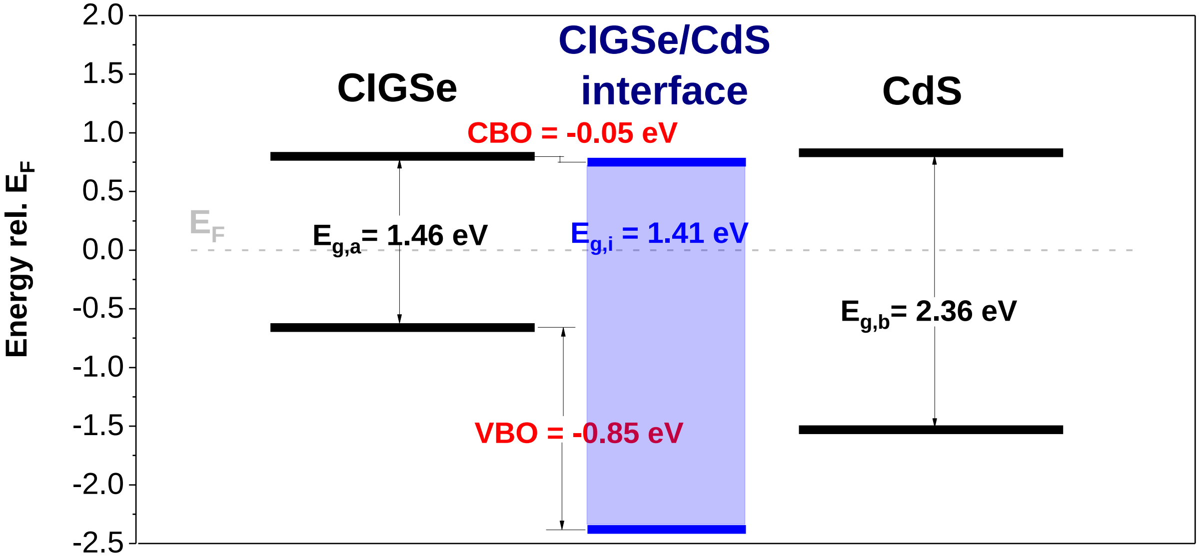


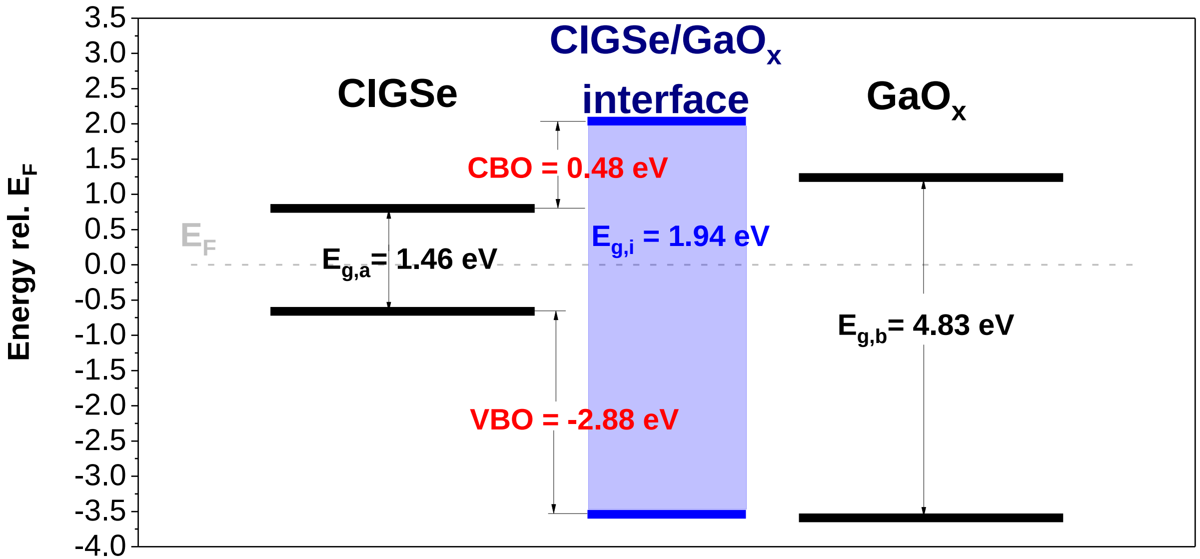
Sample	E_g (eV) UPS/IPES	Optical E_g (eV)
CdS	2.36 eV	2.42 eV*
GaO_x	4.83 eV	4.71 eV

- Positions obtained by linear extrapolation of leading edge in UPS and IPES data to estimate VBM, CBM values and energy band gap (E_g)

*A.I.Oliva at. el. Thin Solid Films, No 391, 28-35, (2001)

Band Level Alignment



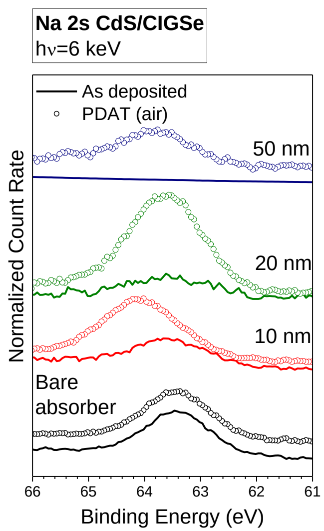


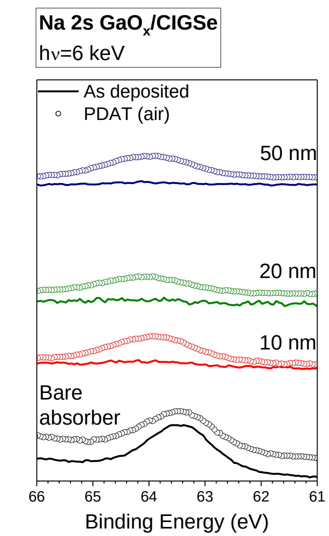
- CBM alignment at the CdS/CIGSe interface in alignment with achieving high efficiencies
- Increase of energetic barrier for charge carrier transport at CIGSe/GaO_x interface
- Replacement of CdS with GaO_x increases interface band gap, the energy barrier for recombination across the (defect rich) buffer/absorber interface
- GaO_x (if designed properly) could be used as passivation layer in CIGSe-based solar cells*

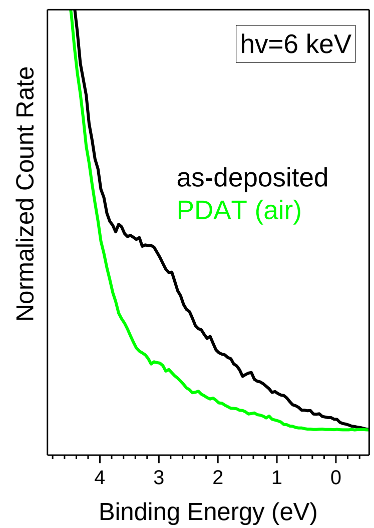
*S.Garud at. el. Phys Status Solidi A, No 215, 1700826 (2018)

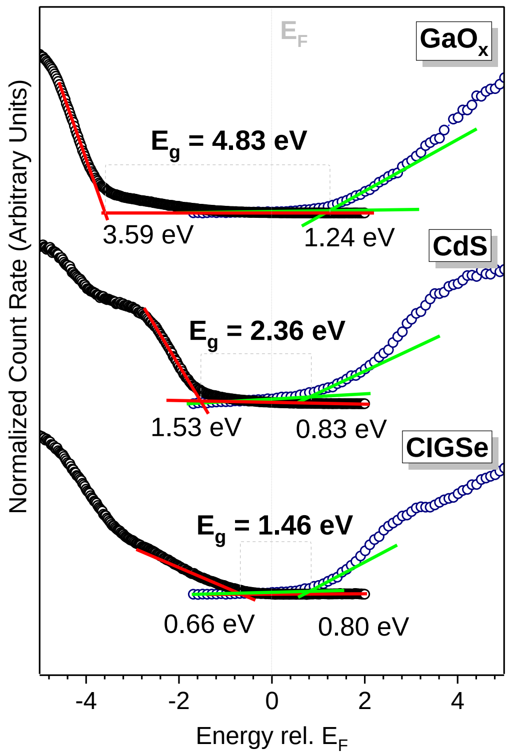
Summary

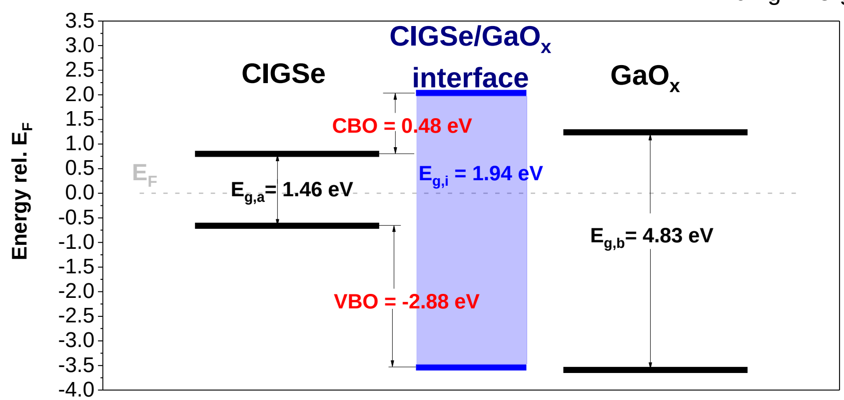
- Na diffusion in GaO_x less pronounced than in the CdS/CIGSe samples
- No prominent PDAT influence on VBM values except to the defect related states in GaO_x
- PDAT passivates oxygen related defects GaO_x in VBM
- Derived energy level alignment suggest the application of GaO_x as passivation layer in CIGSe based solar cells





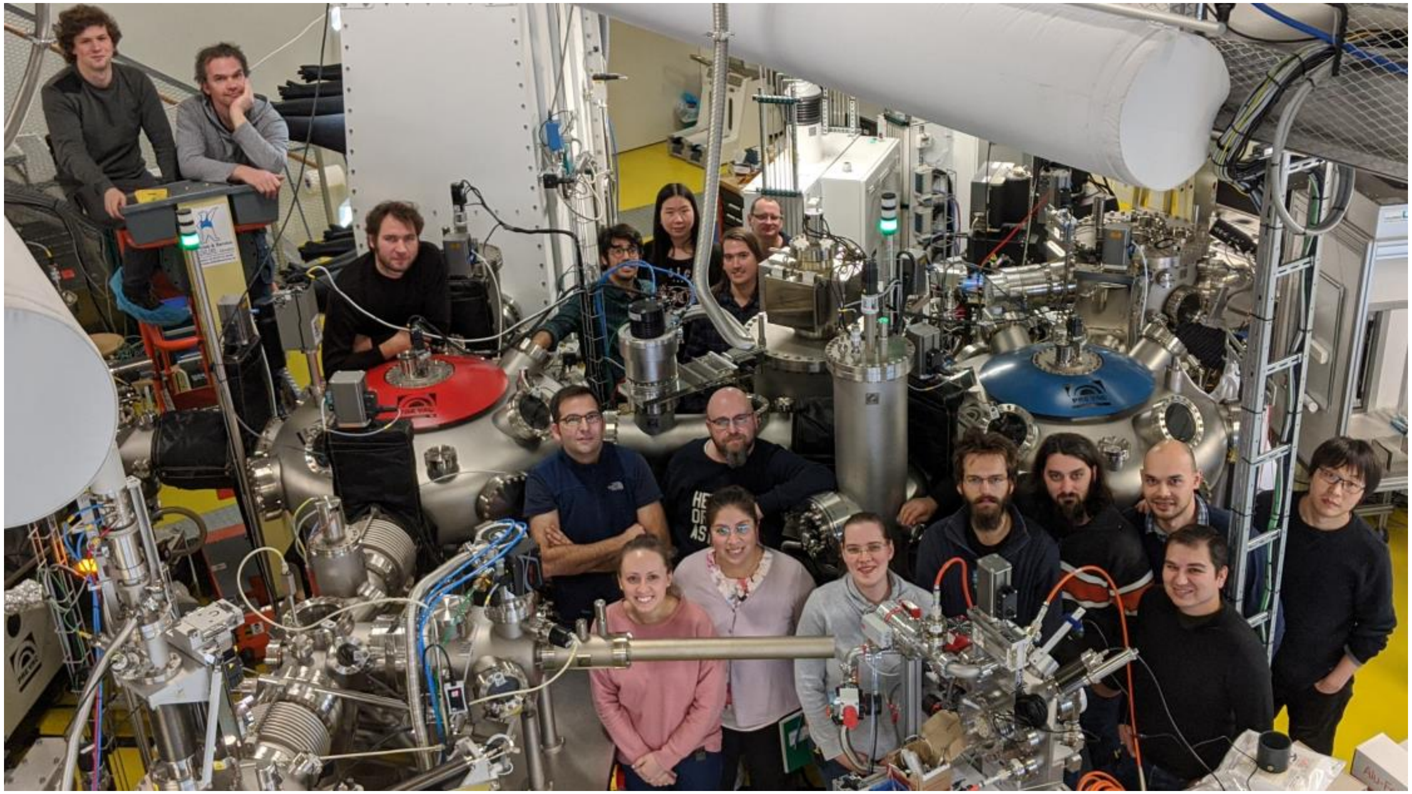






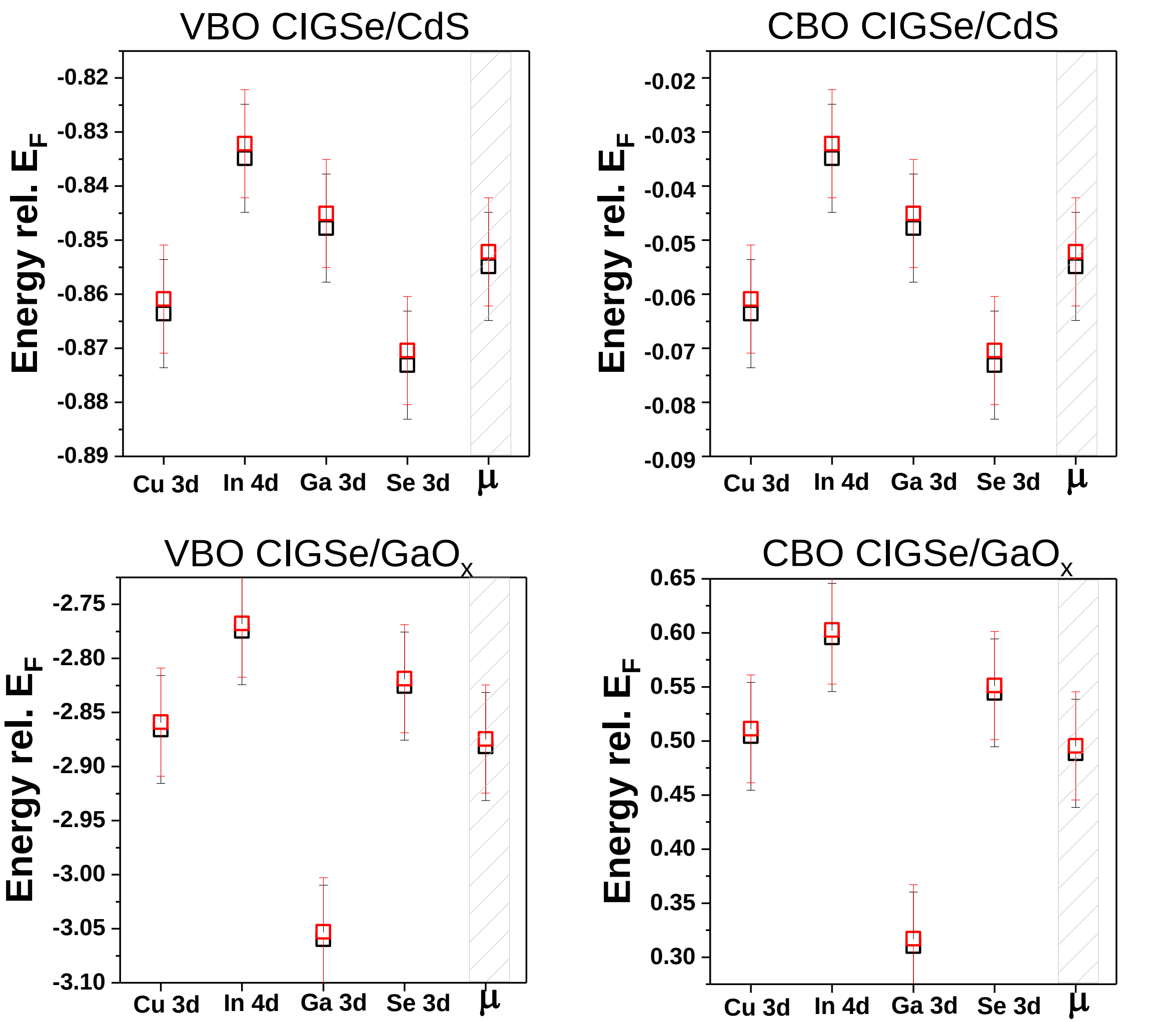
Acknowledgment

HZB Helmholtz Zentrum Berlin　EMIL　PVcomB　SPring-8



THANKS FOR YOUR ATTENTION!

Interface Induced Band Bending



$$VBO = (CL_{cap} - VBM_{cap}) - (CL_{sub} - VBM_{sub}) - (CL_{cap}^{int} - CL_{sub}^{int}) \quad (1)$$

$$CBO = (E_g^{cap} - E_g^{sub}) + VBO \quad (2)$$