

CuCrO₂ deposited by AA-MOCVD as p-type transparent semiconducting oxide: deposition optimization and application in CuCrO₂/ZnO junctions

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Introduction

- Transparent electronics
- CuCrO₂: Structure, properties and applications
- AA-MOCVD deposition system
- CuCrO₂ deposition optimization
- ITO/ CuCrO₂/ ZnO: An interesting case of transparent diode
- Conclusions

Transparent electronics

Electrical conductivity

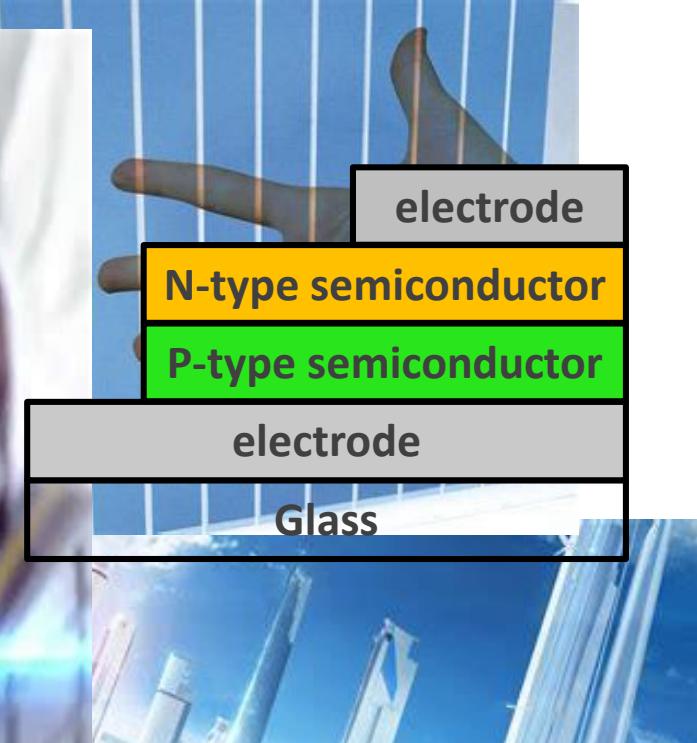
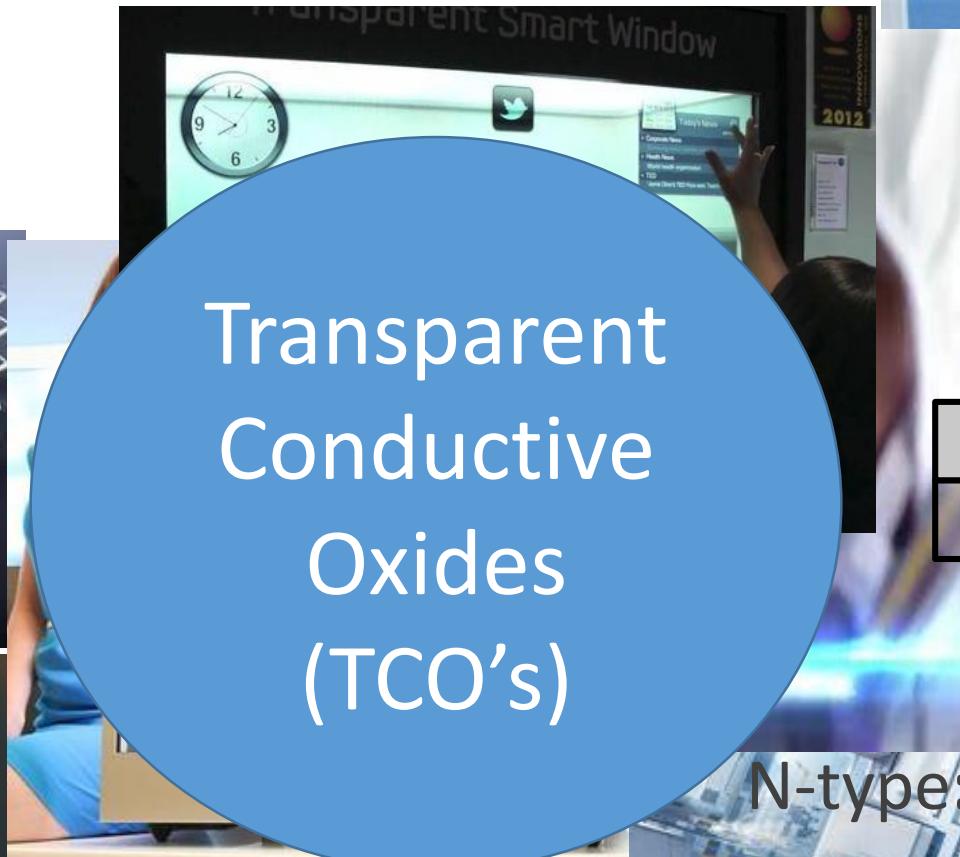
+

Transparency



Transparent
Conductive
Oxides
(TCO's)

- Transparent p-n junctions



N-type: ITO, FTO, AZO, SnO_2

Lack of performant P-type TCO → CuCrO_2



CuCrO₂:structures, properties and applications

Delafoseite structure ($A^{+1}B^{+3}O^{-2}$) → p-type TCO

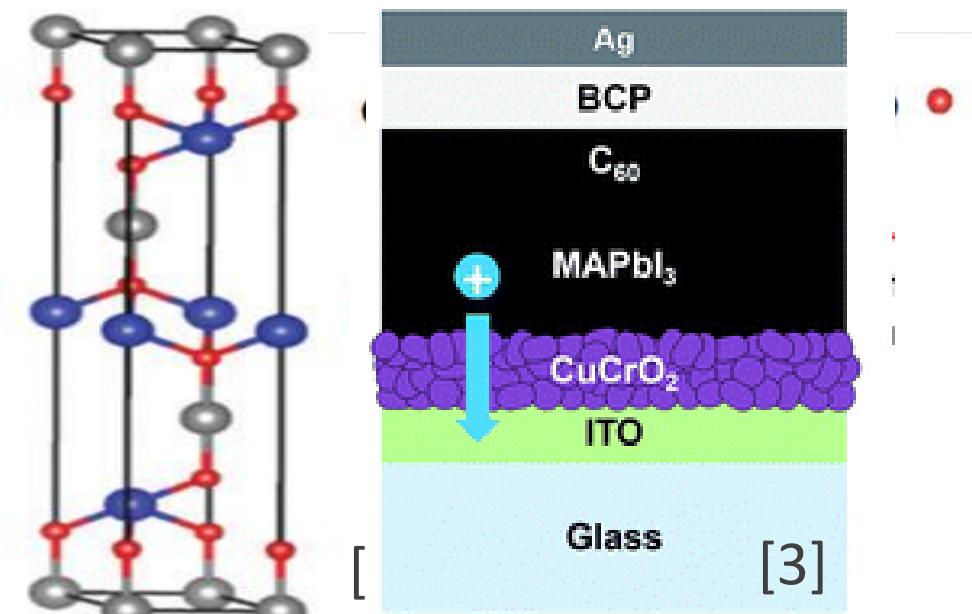
Direct energy gap: → 3.1- 3.3 eV

Resistivity : 0.1 Ω.cm

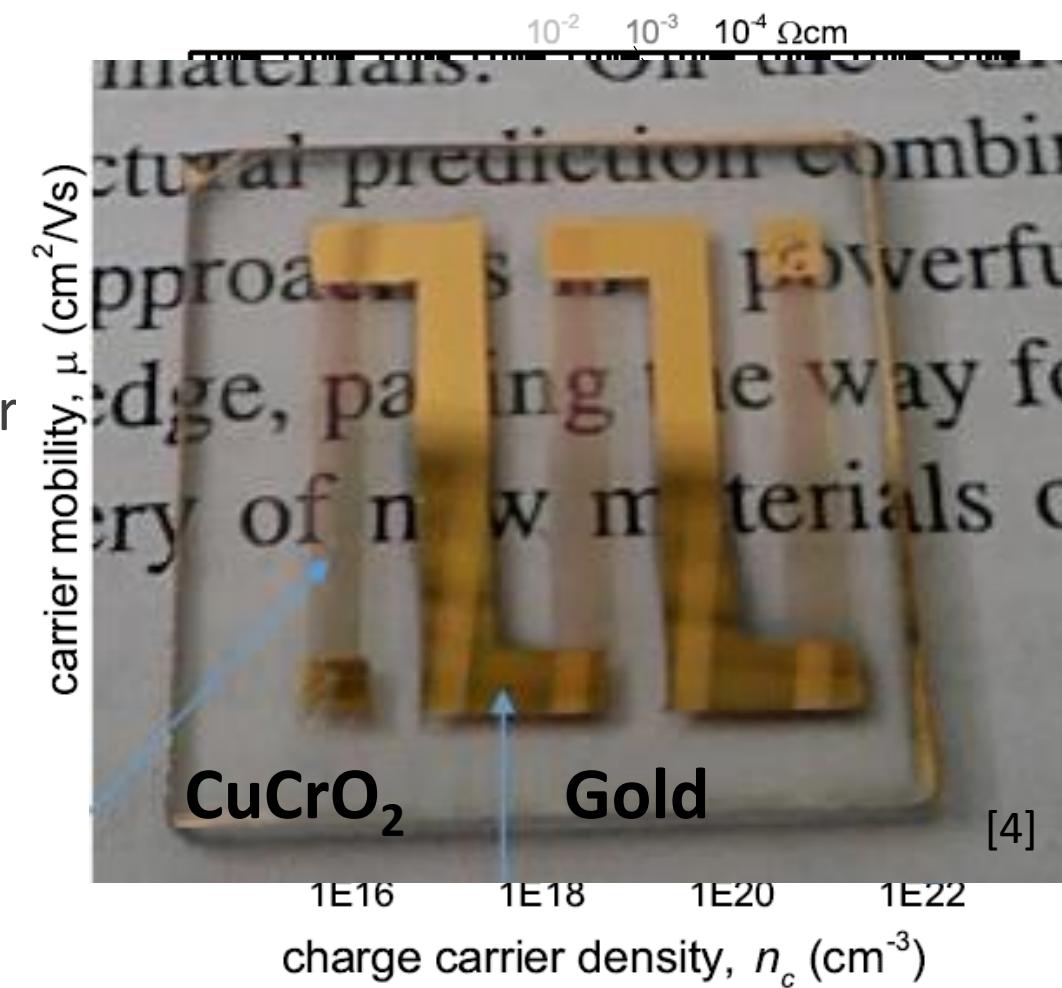
Charge carrier density: 10^{21} cm^{-3}

Applications:

transparent electrodes, TFT [2], HTL in solar cells[3], photocatalyst...



[3]



CuCrO₂

Gold

[4]

[1] Fleischer et al., Materials, 2017

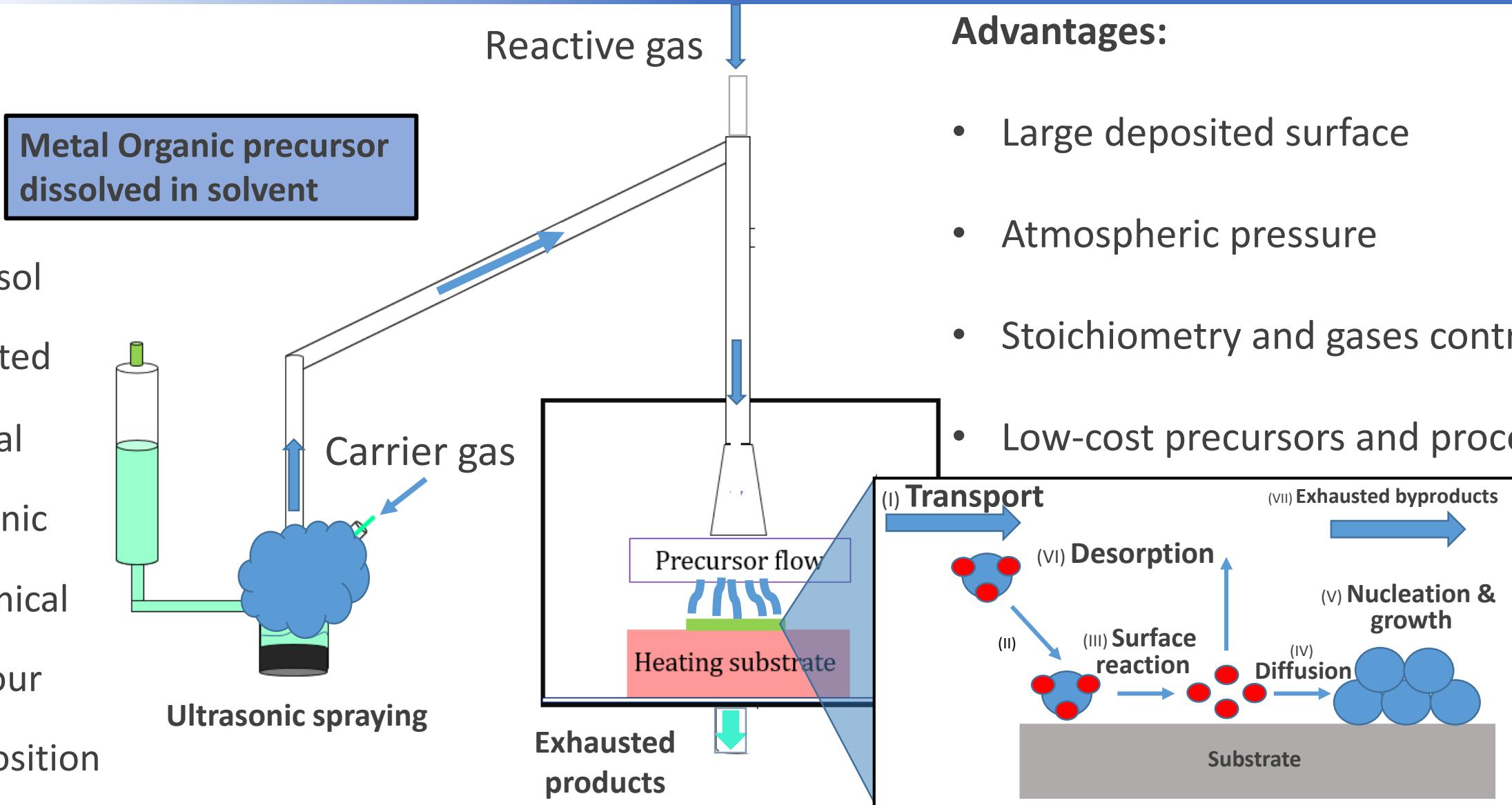
[2] Shengbin et al. *J. Mater. Chem. C*, 2018, 6, 1393

[3] A. Dunlap-Shohl, *J. Mater. Chem. A*, 2018, 6, 469-477

[4] Y. Thimont et al. 2015

CuCrO₂: AA-MOCVD deposition technique

Aerosol
Assisted
Metal
Organic
Chemical
Vapour
Deposition



CuCrO₂ Deposition optimization

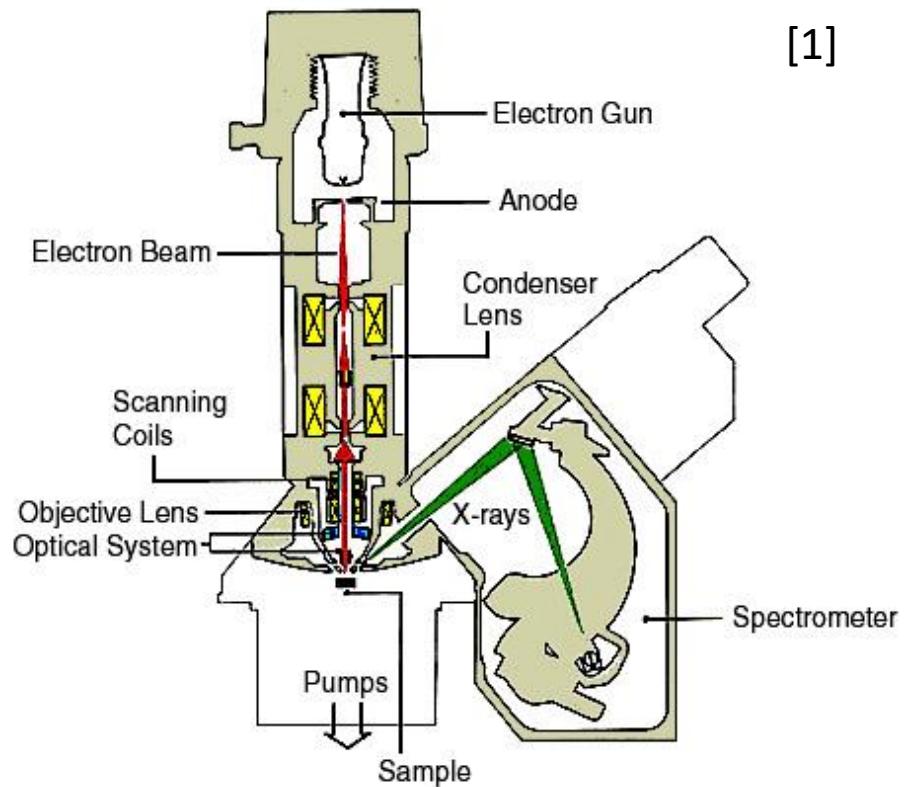
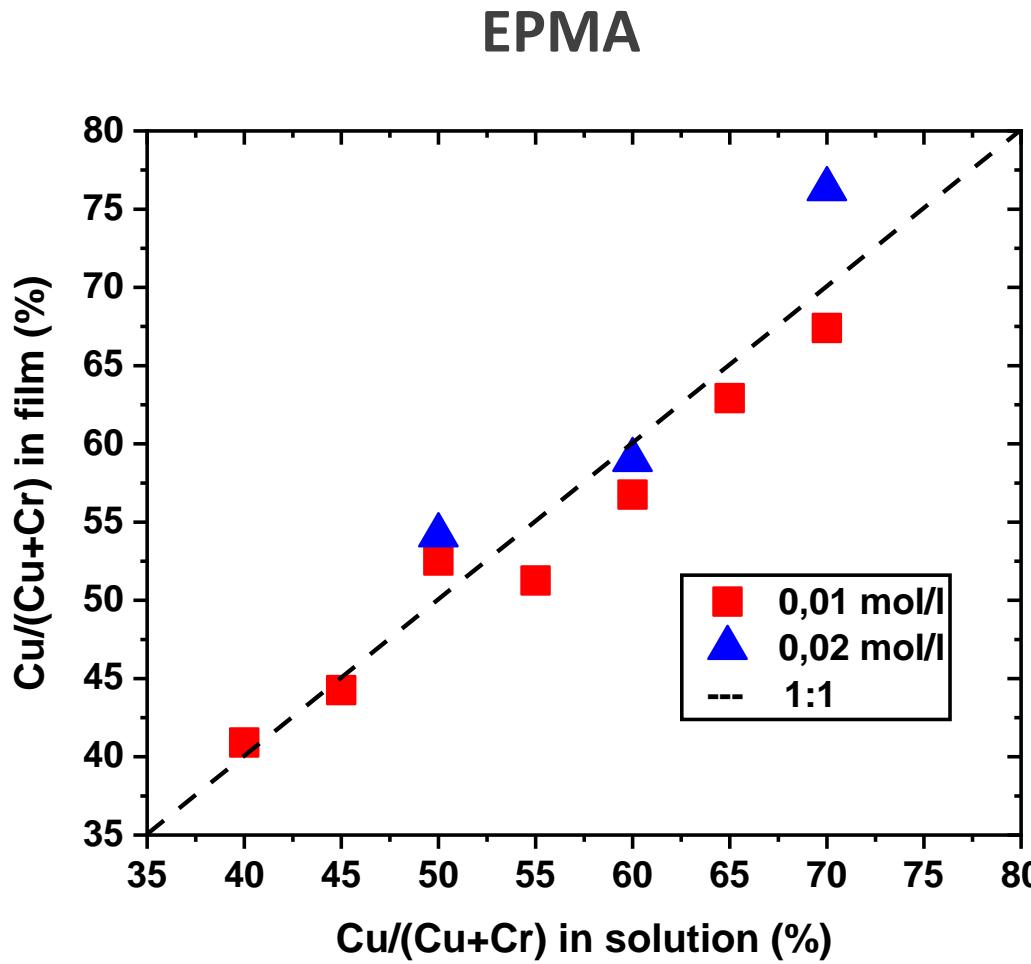
Effect of Partial concentration ($\frac{Cu}{Cu+Cr}$) and Total molar concentration (C_T)

Substrate temperature (°C)	Precursors		Total molar concentration (mol/l)	
350°C	Cu	Cr	0.01 mol/l	0.02 mol/l
	Cu (II) acac	Cr (III) acac		



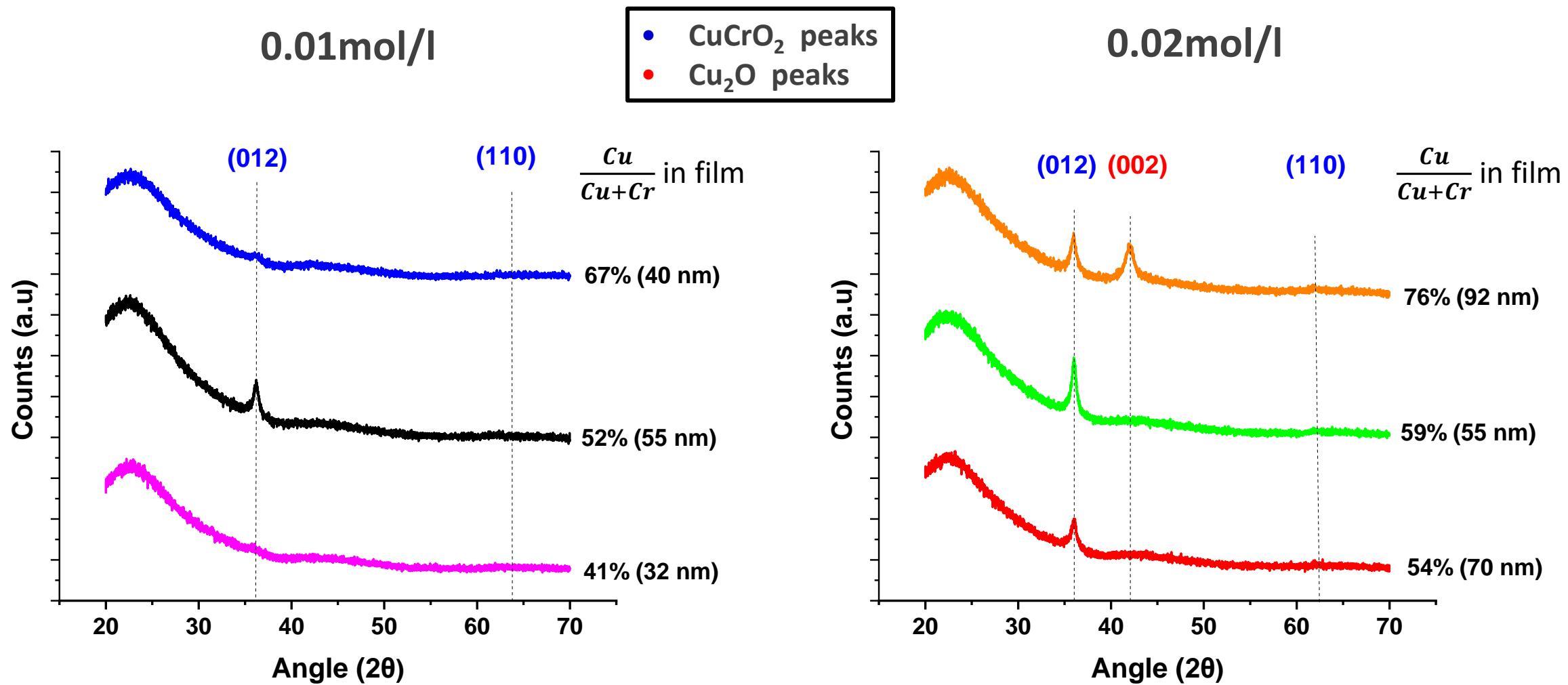
Control of film composition

- Deposited at T=350°C



Linear incorporation in film

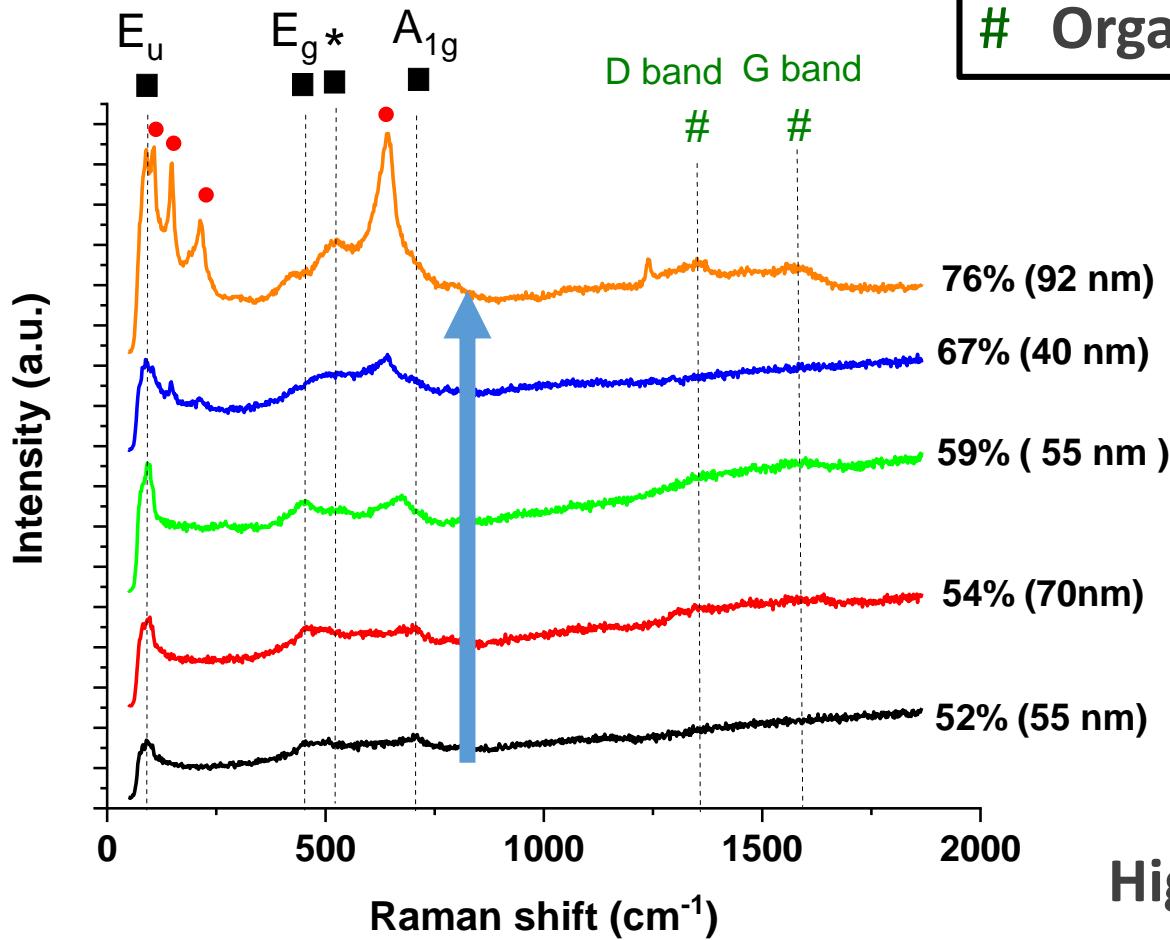
Structural properties



Influence of the thickness on crystallinity

High $\frac{Cu}{Cu+Cr} \rightarrow$ (002) peak of Cu₂O

Structural properties



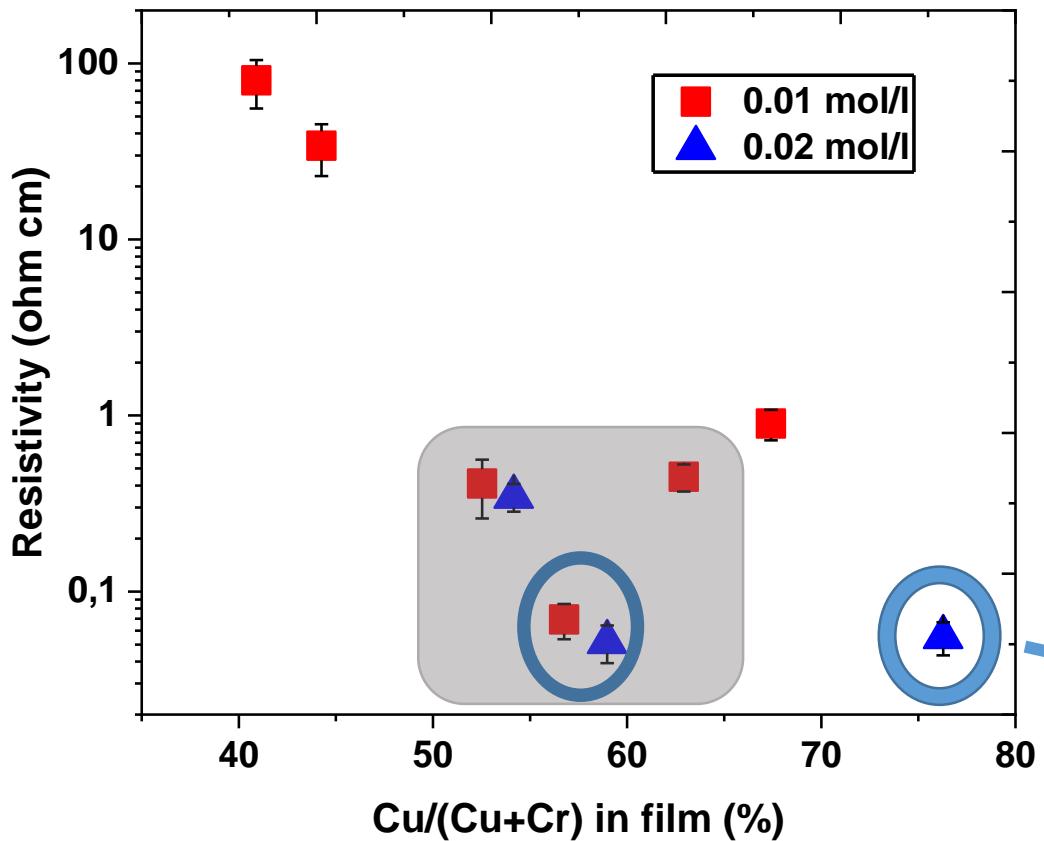
Effective deposition of CuCrO_2 phase

Evolution of the peaks with Cu content

Higher incorporation \rightarrow parasitic Cu oxide phase

Electrical properties

4-probe measurement



Effect on Cu incorporation on electrical properties

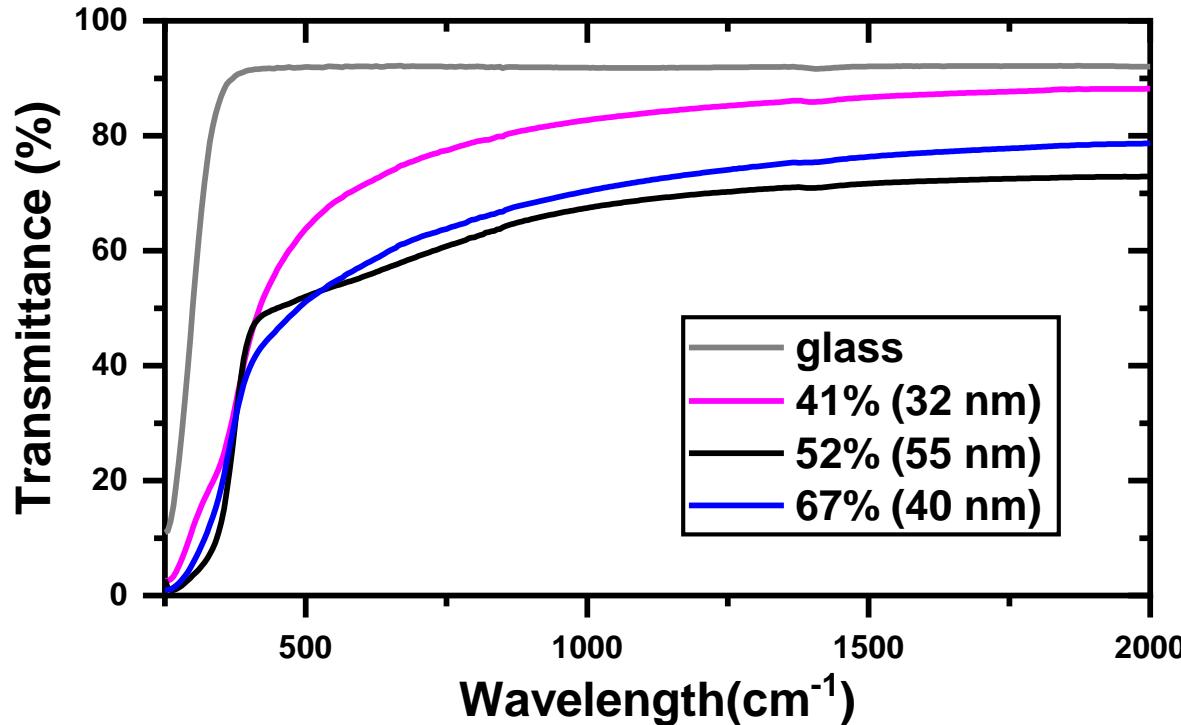
In literature $\rightarrow \rho = 5 * 10^{-2} \Omega * cm$ [1]



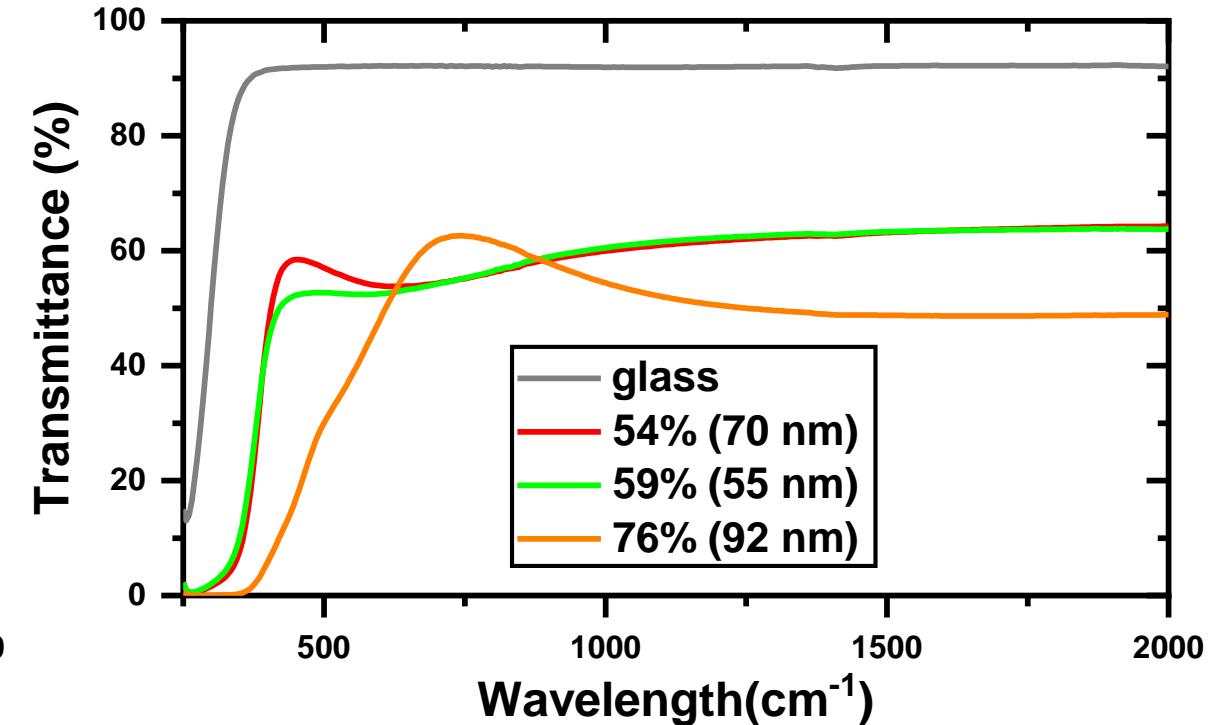
$$\rho = 7 * 10^{-2} \Omega * cm$$

Optical properties

0.01mol/l



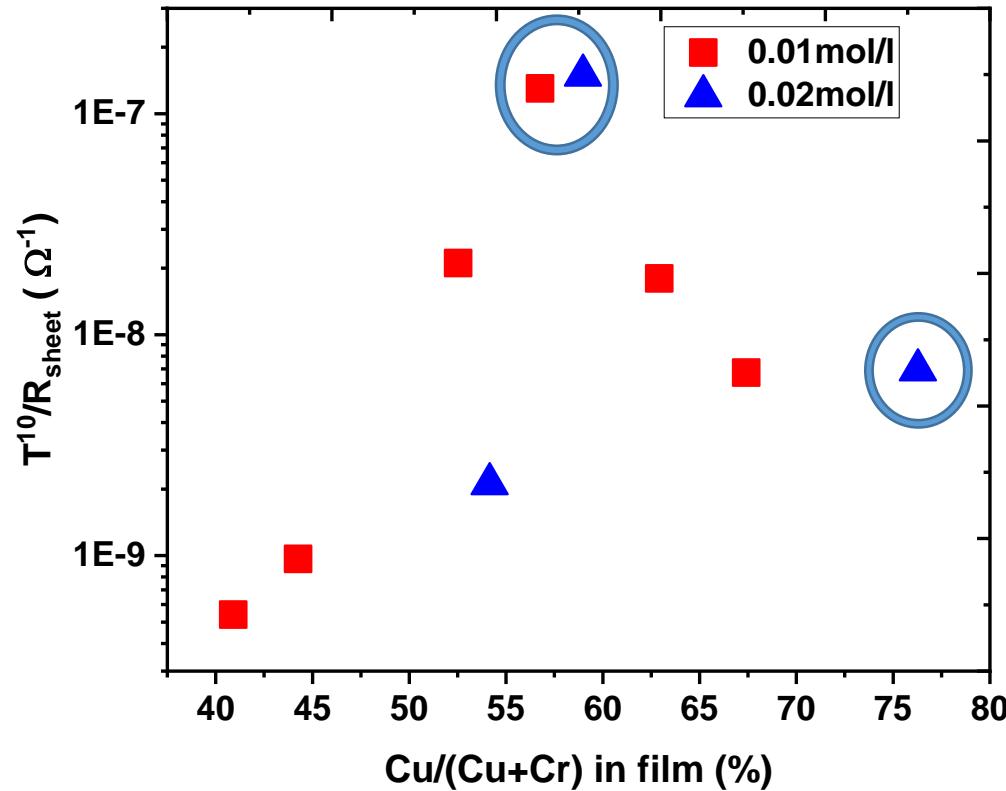
0.02mol/l



Optical properties dominated by thickness

Higher $\frac{\text{Cu}}{\text{Cu}+\text{Cr}}$ \rightarrow reduction of energy gap

Figure of Merit for TCO's



Defined by Haacke [1]

$$FoM = \frac{T^{10}}{R_{\square}} (\Omega^{-1})$$

Average transmittance in the visible range
(390 nm-700 nm)

[1] Haacke, G. (1976). New figure of merit for transparent conductors. *Journal of Applied Physics*, 47(9), 4086–4089.

Effect of $Cu/(Cu + Cr)$ and (C_T) :Summary

- CuCrO₂ Deposition optimization:

Control of the film composition with AA-MOCVD

Successfull deposition of CuCrO₂ phase for different $\frac{Cu}{Cu+Cr}$

Best performances for $59\% = \frac{Cu}{Cu+Cr} \rightarrow \rho = 7 * 10^{-2} \Omega * cm$ and an average transmittance of 52% in the visible for 55 nm film

CuCrO₂/ZnO: An interesting case of transparent diode

Performances of the basic device for future development in transparent electronic

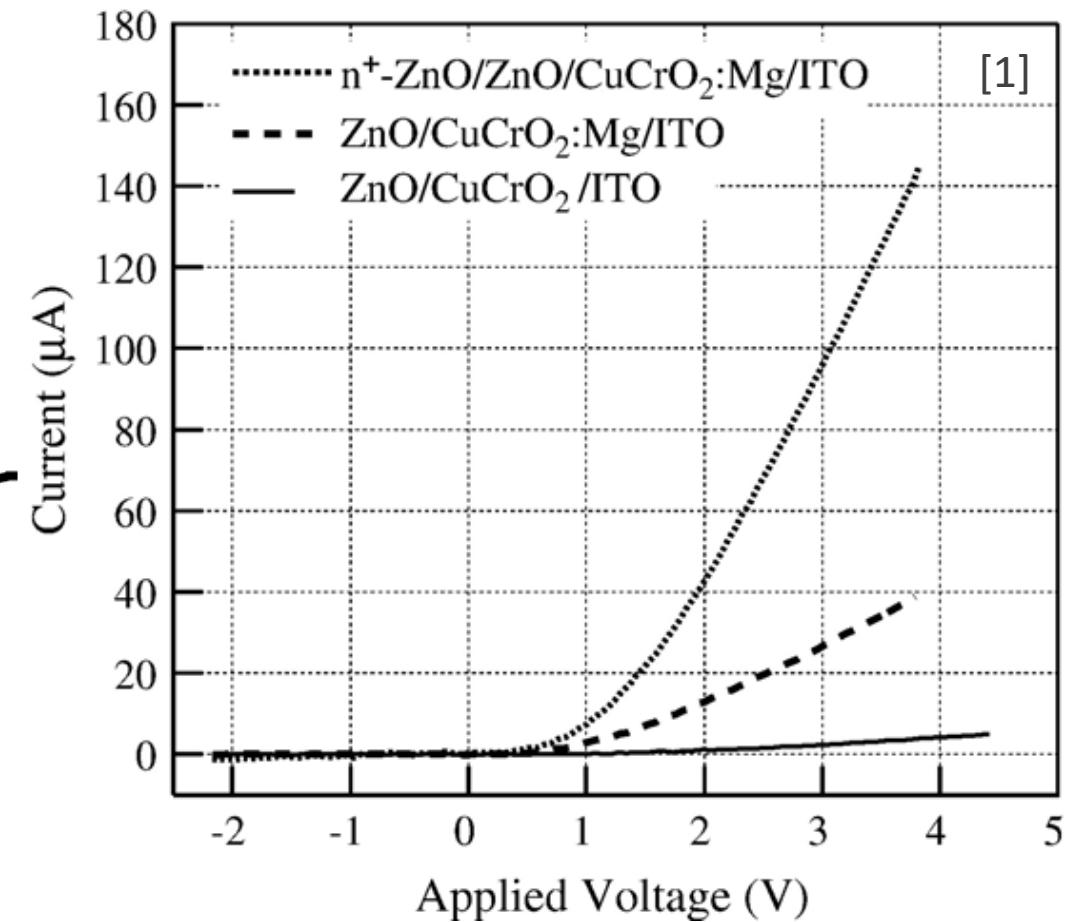
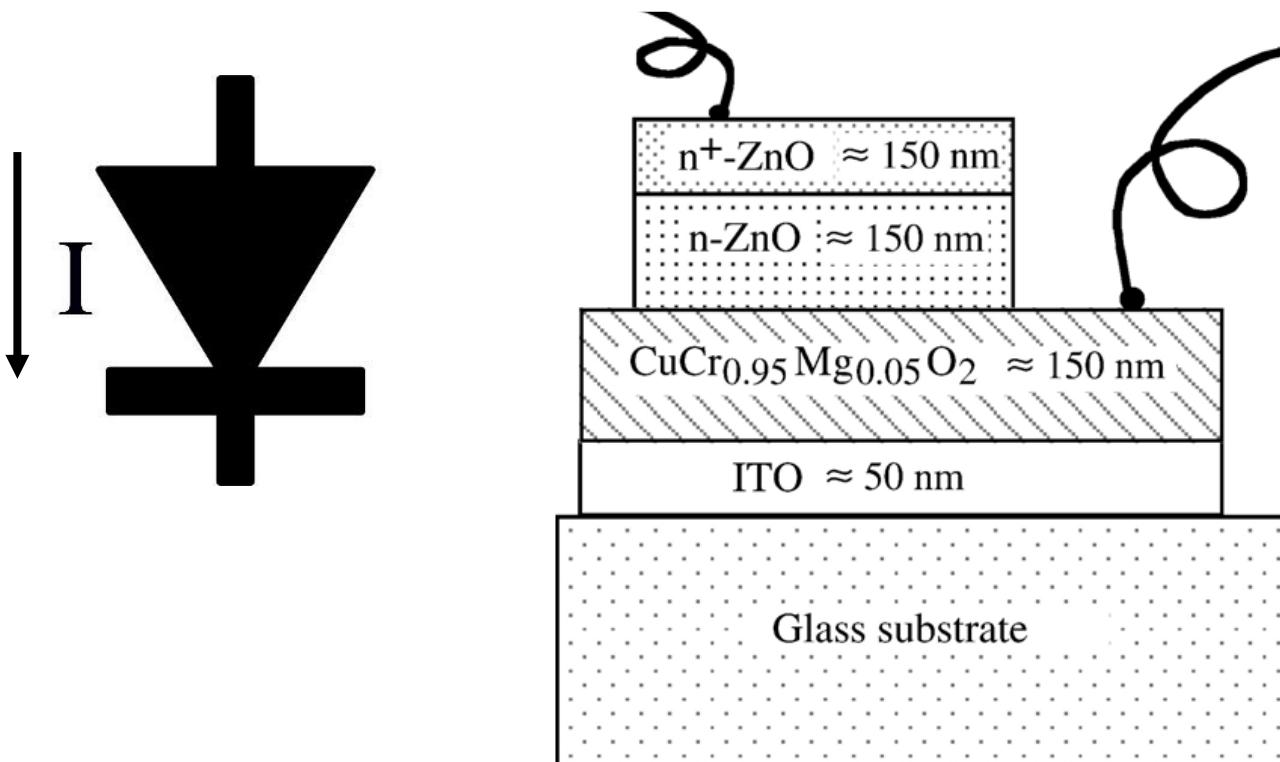


CuCrO₂/ZnO thin films: Transparent diode

Transparent *pn* junction ITO/CuCrO₂/ZnO:

CuCrO₂ deposited by AA-MOCVD

ZnO deposited by SALD



CuCrO₂/ZnO properties and applications

CuCrO₂

Delafoseite structure ($A^{-1}B^{+3}O^{-2}$) → p-type TCO

Energy gap: → 3.1- 3.3 eV

Resistivity : 1 Ω.cm

Charge carrier density: 10^{21} cm^{-3}

ZnO

Wurtzite lattice → n-type TCO

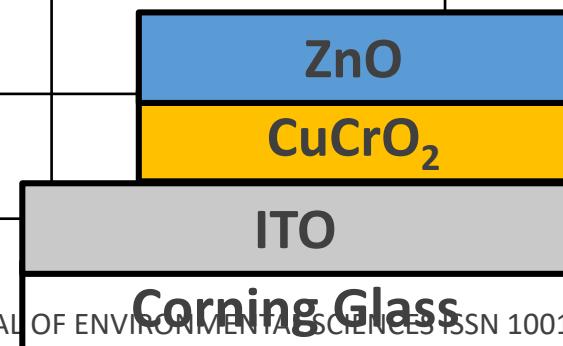
Energy gap : 3.4eV

Resistivity : $2.8 \times 10^4 \Omega.\text{cm}$

Charge carrier density: $1.10^{19} \text{ cm}^{-3}$

Type II band alignment

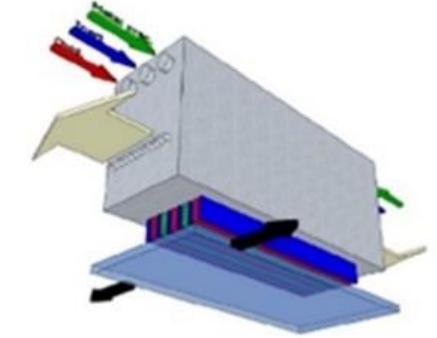
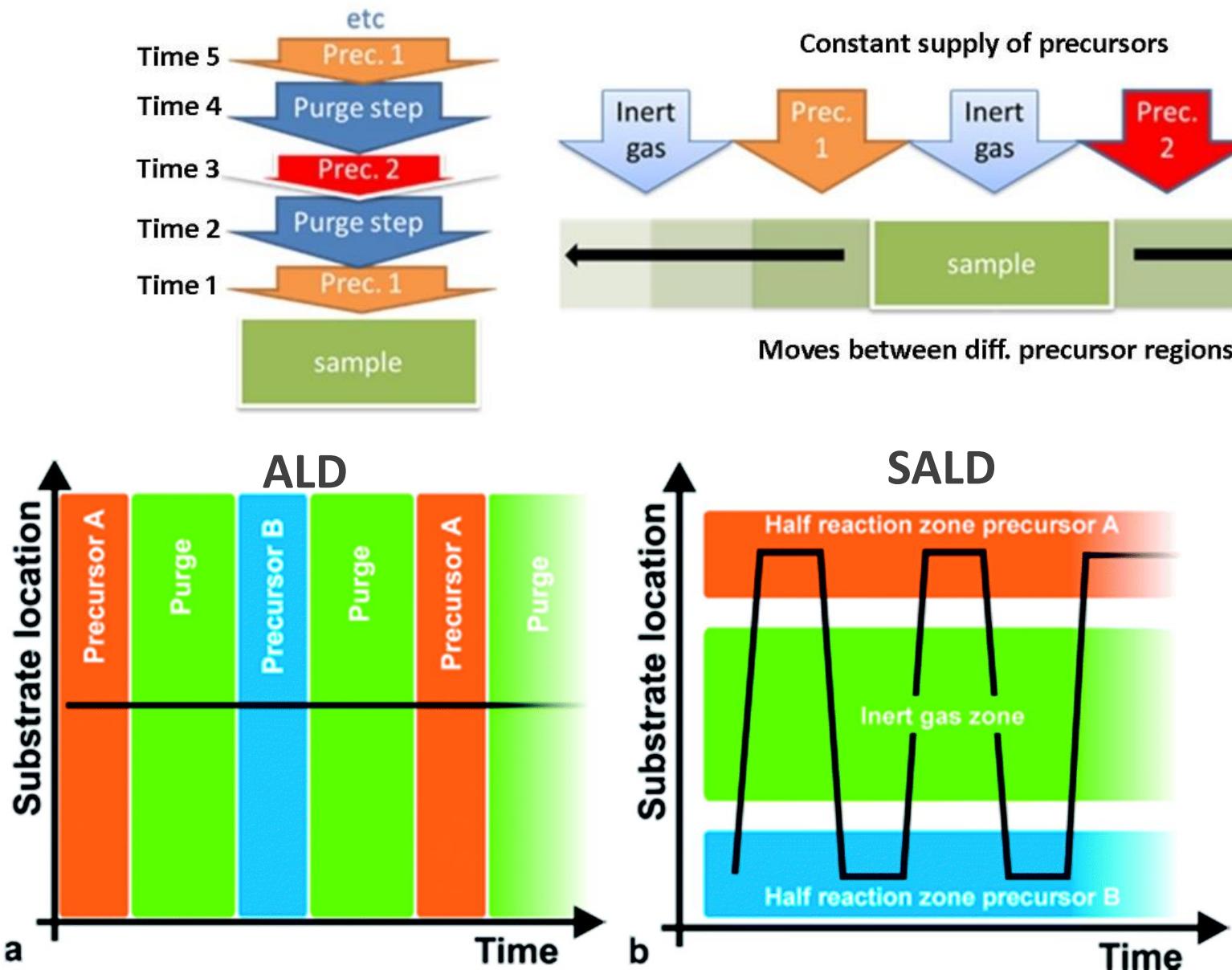
ZnO/CuCrO ₂ growth technique	ZnO growth technique	Structure	Rectification ratio (I_{ON}/I_{OFF})	Transmittance (390nm-700nm)	Reference
Solar cell, UV sensor , the photoreduction of chromate[1], magnetoresistances[2]	PLD 500°C	ZnO/ZnO/CuCrO ₂ :Mg/ITO	-1.5 to 1.5 V 70	>80%	Tonooka, K. et al. <i>Thin Solid Films</i> 2006 , 515, 2415–2418..
PLD 500°C	PLD	CuCrO ₂ :Mg/ZnO/AZO/ITO	-5 to +5 V 120	>70%	Chiu, T.-W. et al. <i>Vacuum</i> 2008 , 83, 614–617.
Sputtering		CuCrO ₂ :Mg/ZnO/ITO	-4 to +4 V 85.9	>75%	Chen, L. et al. <i>Japanese Journal of applied physics</i> 2013 , 52, 2–5.



[1] W ketir et al. JOURNAL OF ENVIRONMENTAL SCIENCES ISSN 1001-074{2012}

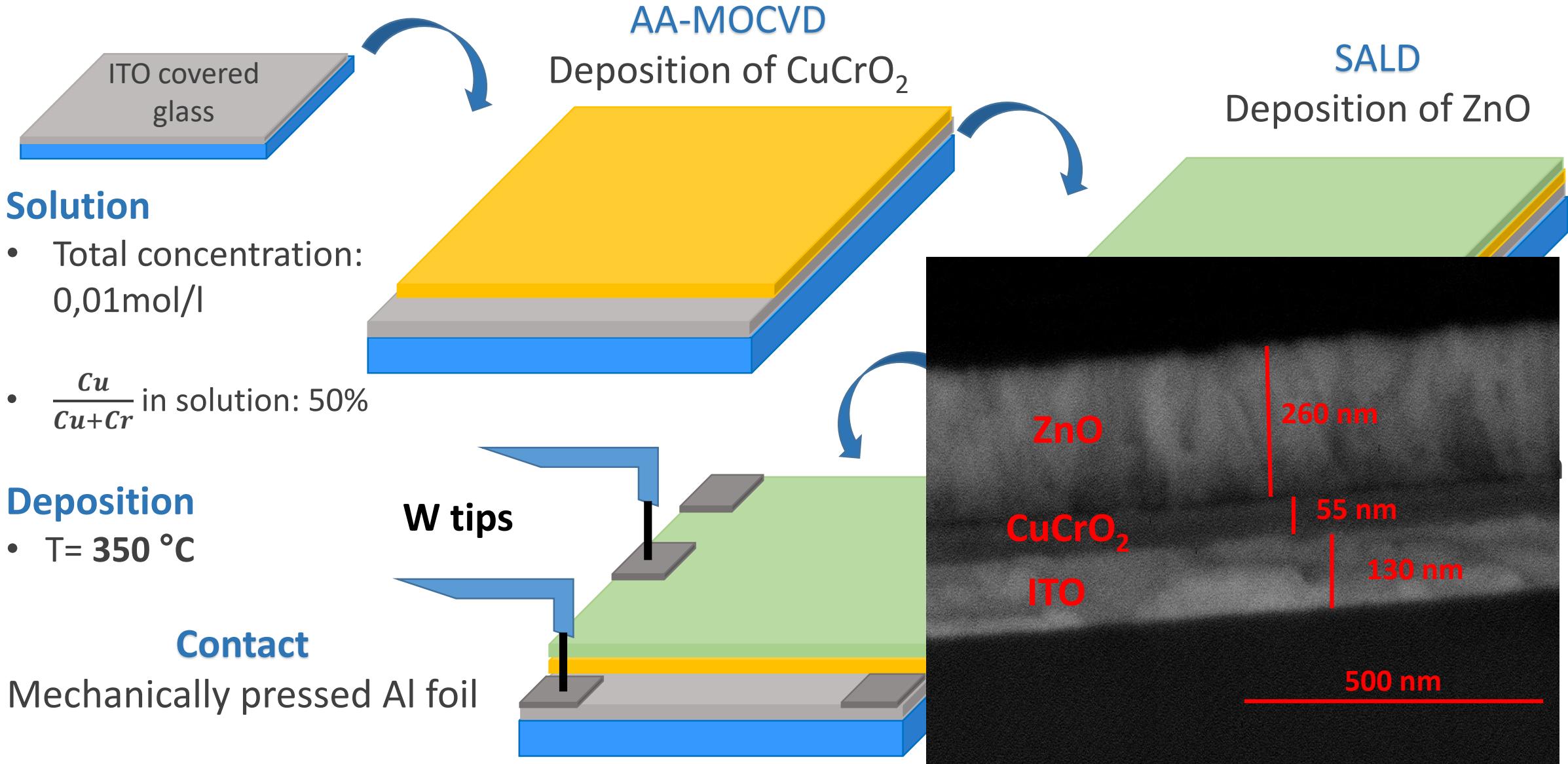
[2] X. R. Li. Journal of Applied Physics **116**, 223701 (2014)

ZnO: SALD deposition technique

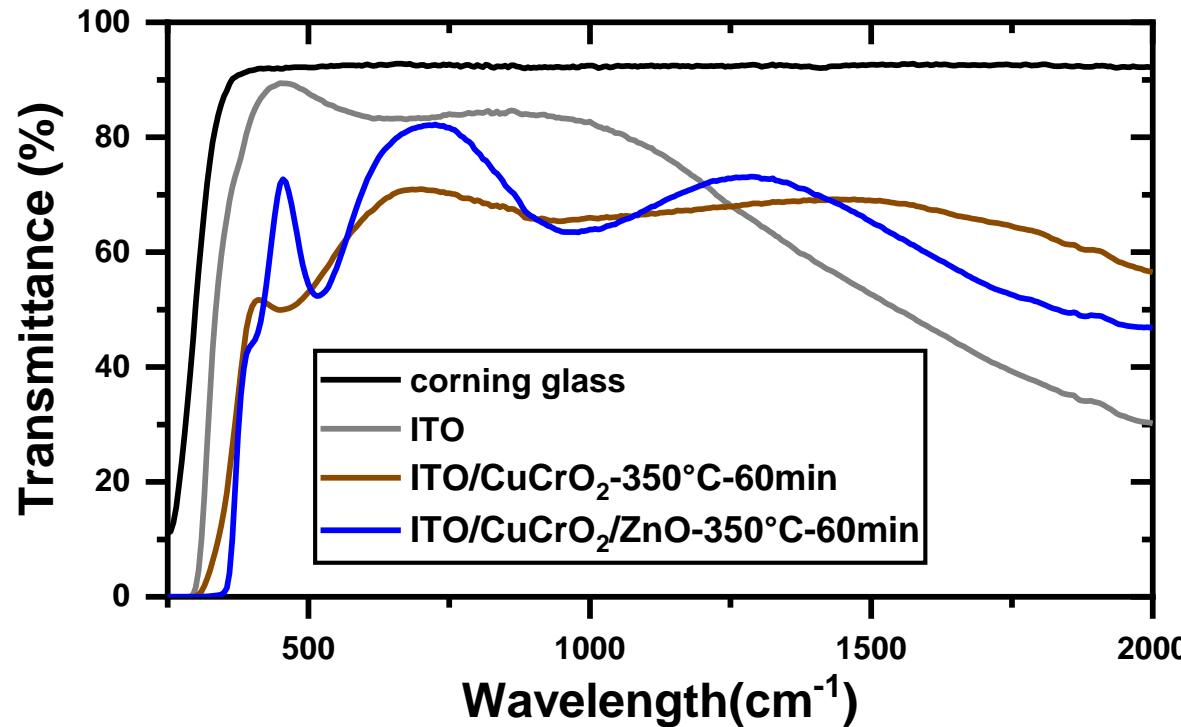


- Surface limited reaction
- High conformality
- High film quality
- Atmospheric pressure
- Easily scalable
- Faster than ALD

CuCrO₂/ZnO thin films: Processes step

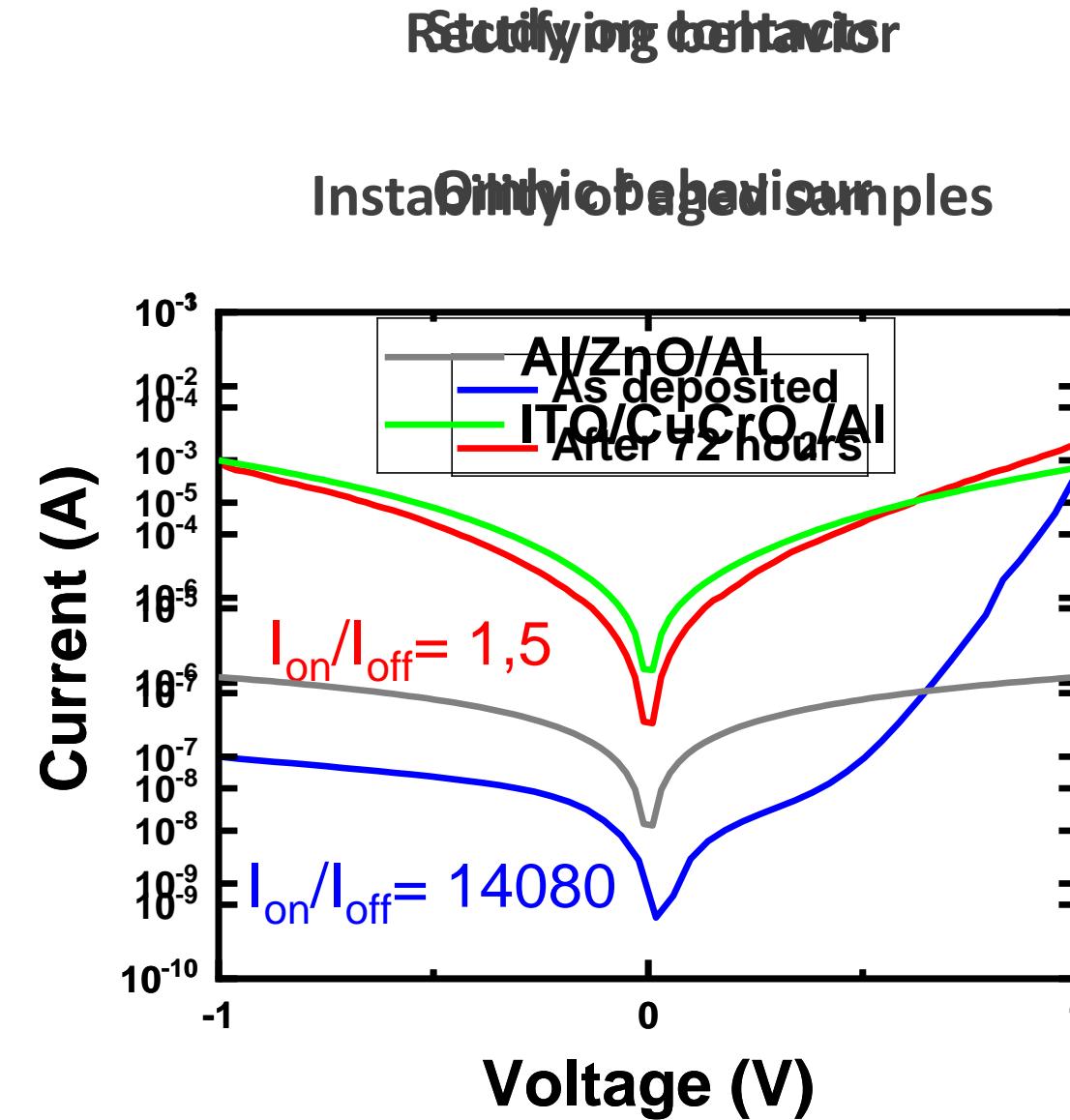


CuCrO₂/ZnO thin films: Performances



Junctions with 65% transmittance in the visible range (390nm-700nm)

ZnO as anti-reflection layer



Summary

- ITO/CuCrO₂/ZnO thin films:

ZnO as antireflection layer improving optical properties

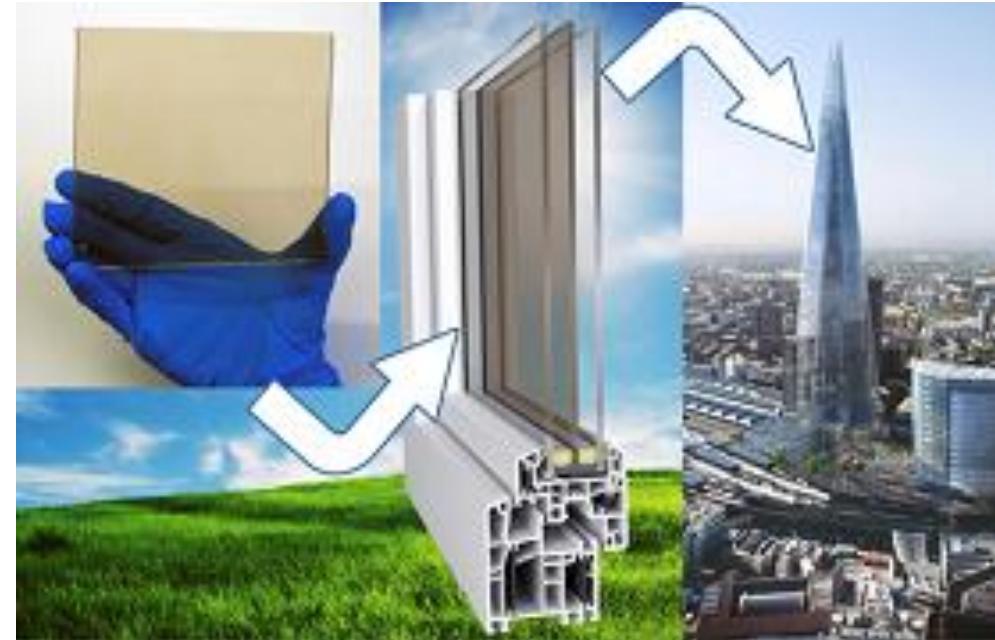
Rectifying behaviour $I_{on}/I_{off} (\pm 1V) \approx 14000$

Degradation of the performances with time



THANK YOU

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Communauté
UNIVERSITÉ Grenoble Alpes



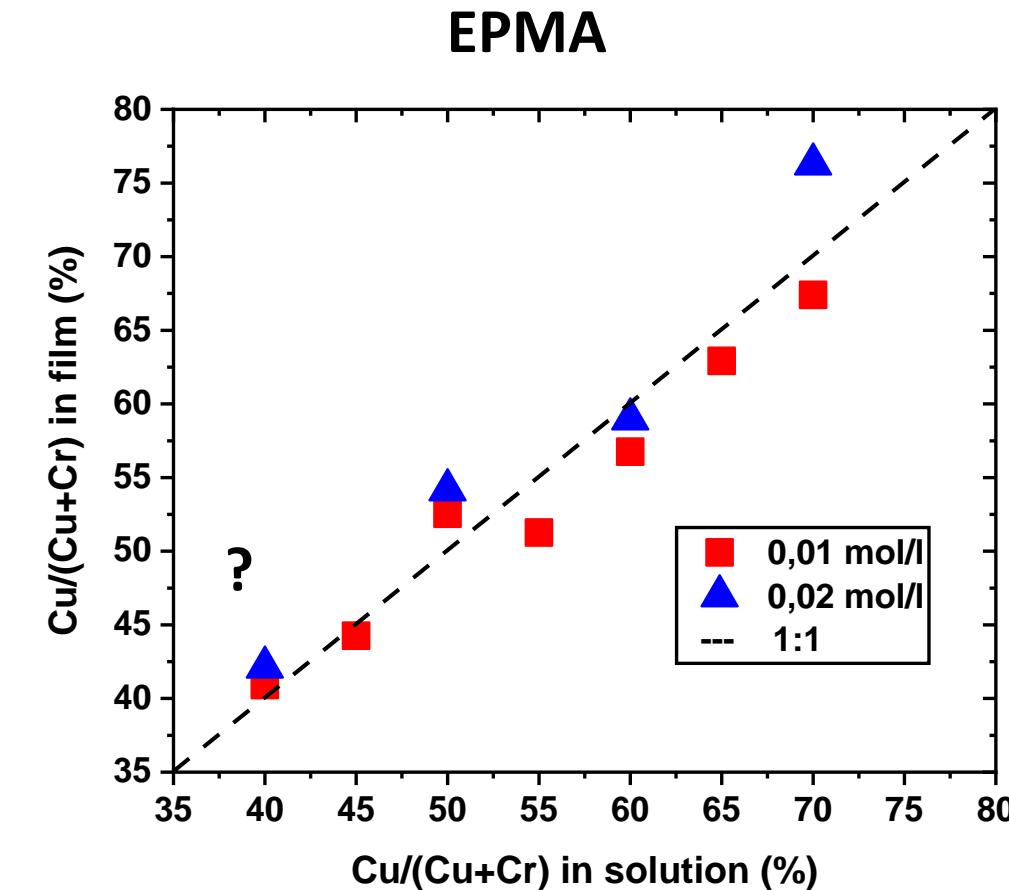
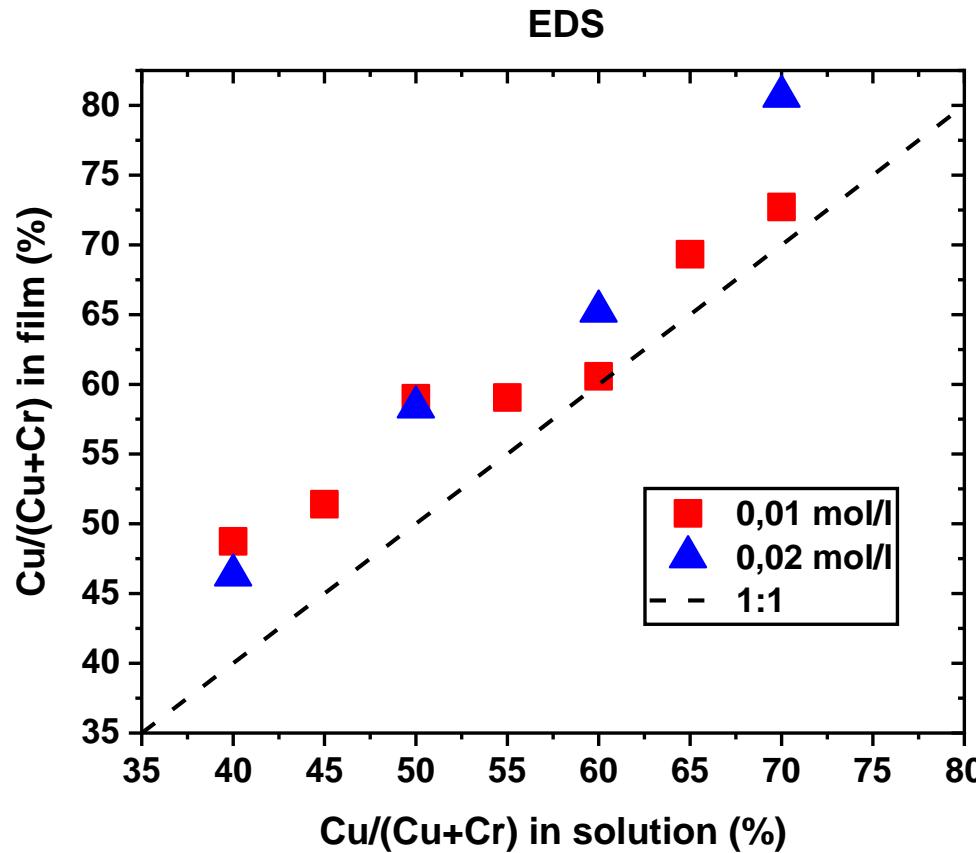
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La recherche

pour l'innovation
des entreprises

Supporting information

Incorporation



Morphology

0.01 mol/l

41% (32 nm)

52% (55 nm)

1 μm

HV | mag | WD | spot | det | 1 μm
5.00 kV | 50 000 x | 9.6 mm | 3.0 | ETD |

bl-p-cucro-57-40

56% (77 nm)

67% (40 nm)

HV | mag | WD | spot | det | 1 μm
9.00 kV | 50 000 x | 8.7 mm | 2.0 | ETD |

cucro56-60

0.02 mol/l

???

54% (70 nm)

1 μm

HV | mag | WD | spot | det | 1 μm
9.00 kV | 50 000 x | 9.0 mm | 2.5 | ETD |

CUCRO74-40

59% (50 nm)

76% (92 nm)

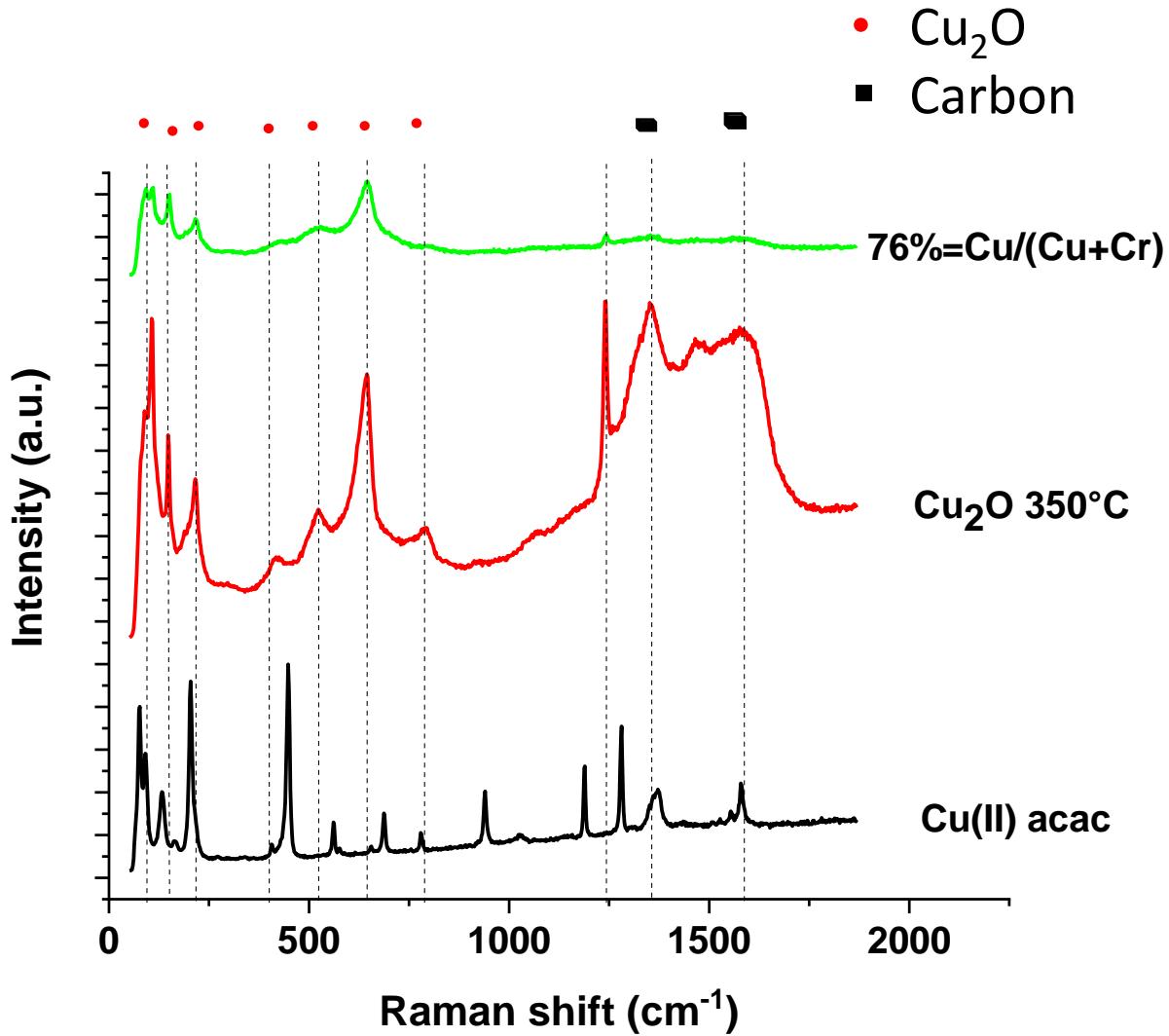
HV | mag | WD | spot | det | 1 μm
9.00 kV | 50 000 x | 9.4 mm | 2.0 | ETD |

CUCRO65-60

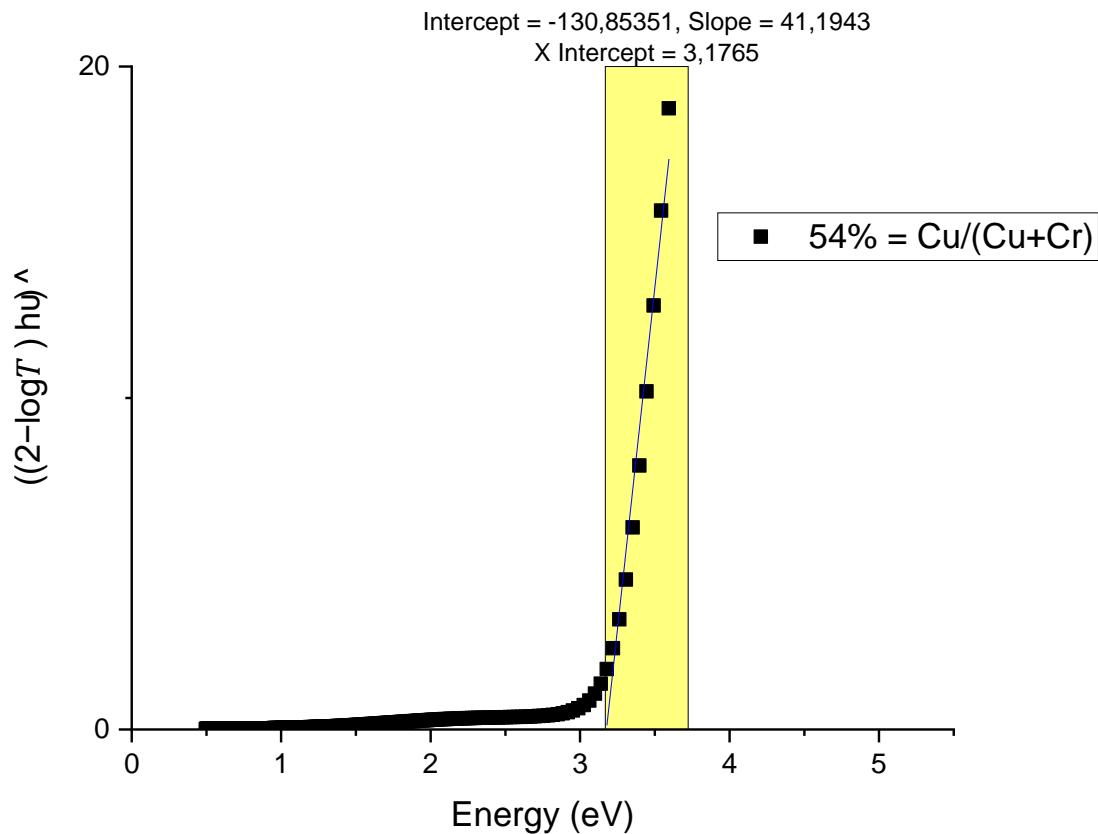
HV | mag | WD | spot | det | 1 μm
8.70 kV | 50 000 x | 8.2 mm | 2.5 | ETD |

CUCRO66-70

Supporting information



Supporting information



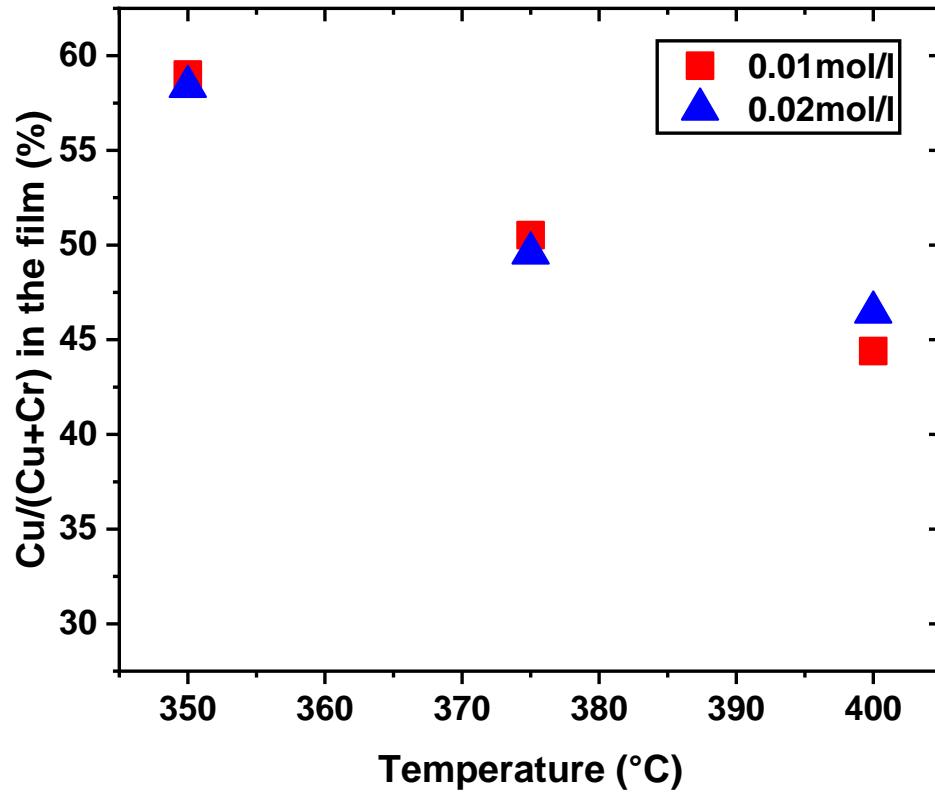
Calculation of the energy gap by Tauc Relation

$$K' \cdot ((2 - \log T)hv)^2 = (hv - E_g)$$

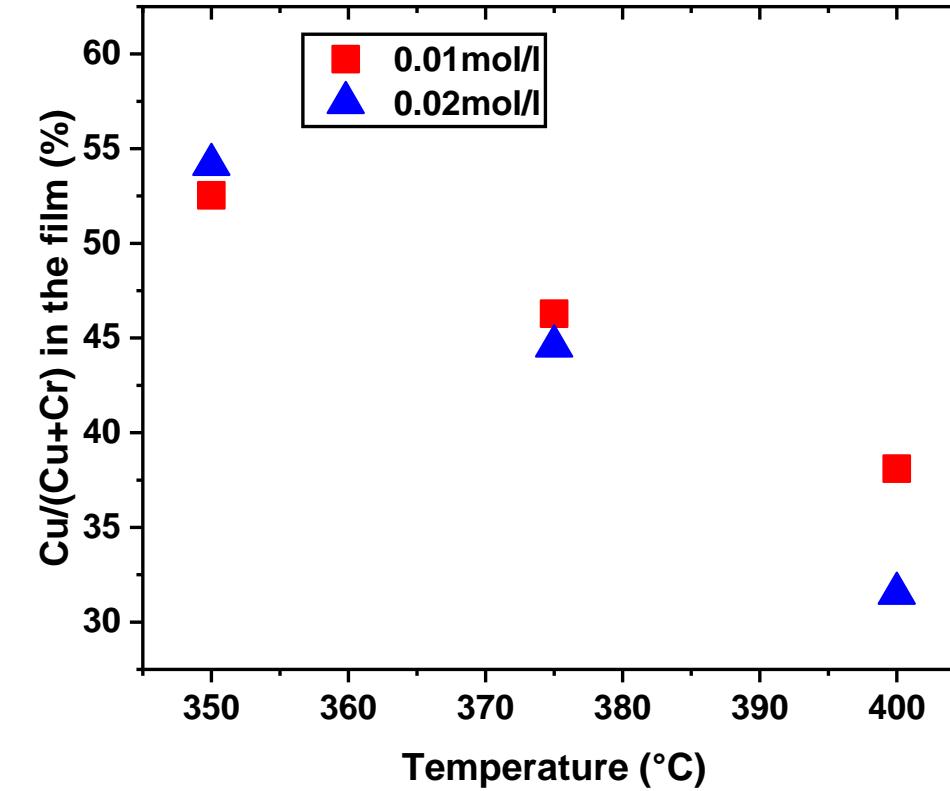
Supporting information

Incorporation in T

EDS



EPMA



Supporting information

P-type: CuCrO₂ by AA-MOCVD at 400°C

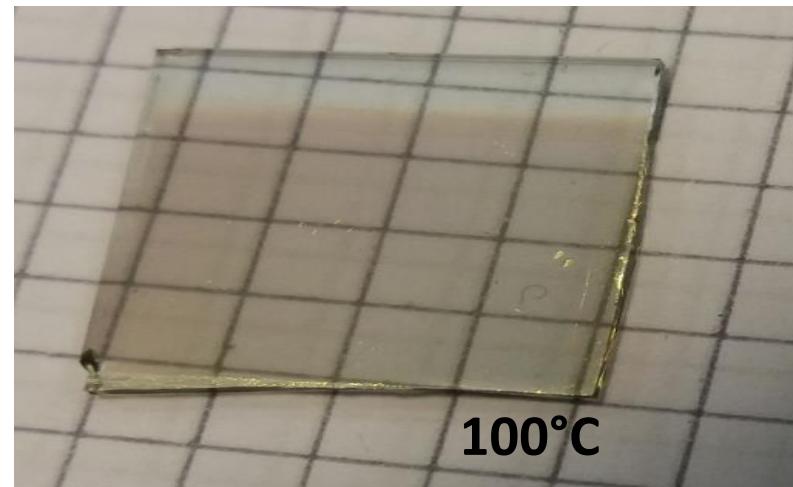
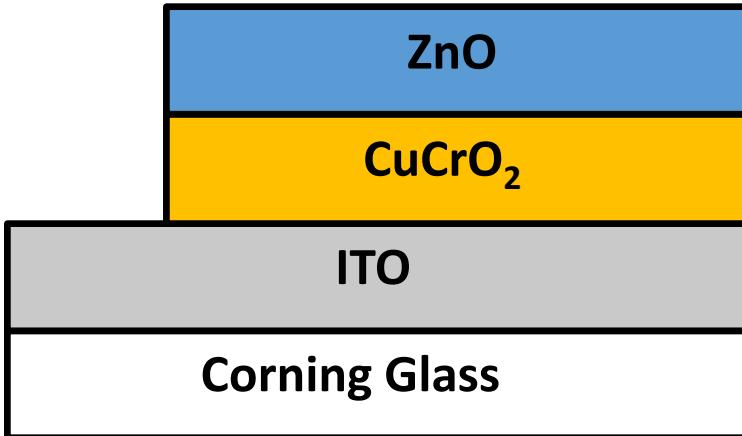
N-type: ZnO by SALD

1) 200 cycles at 100°C

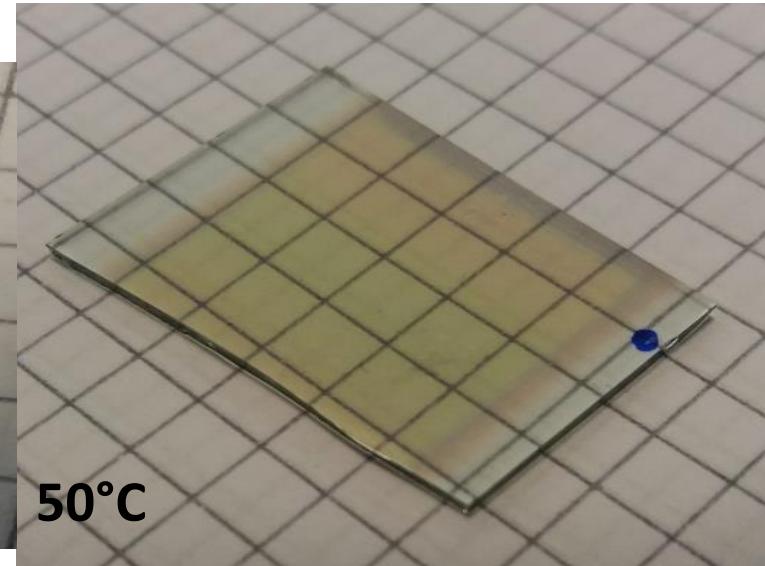
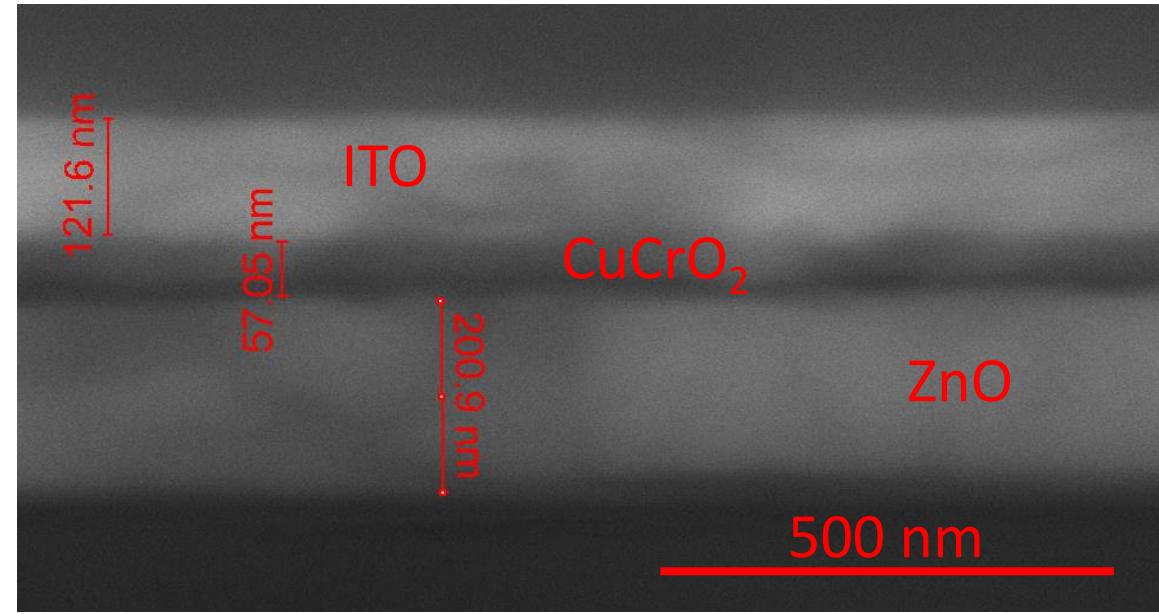
2) 100 cycles at 50°C

+

200 cycles at 100°C

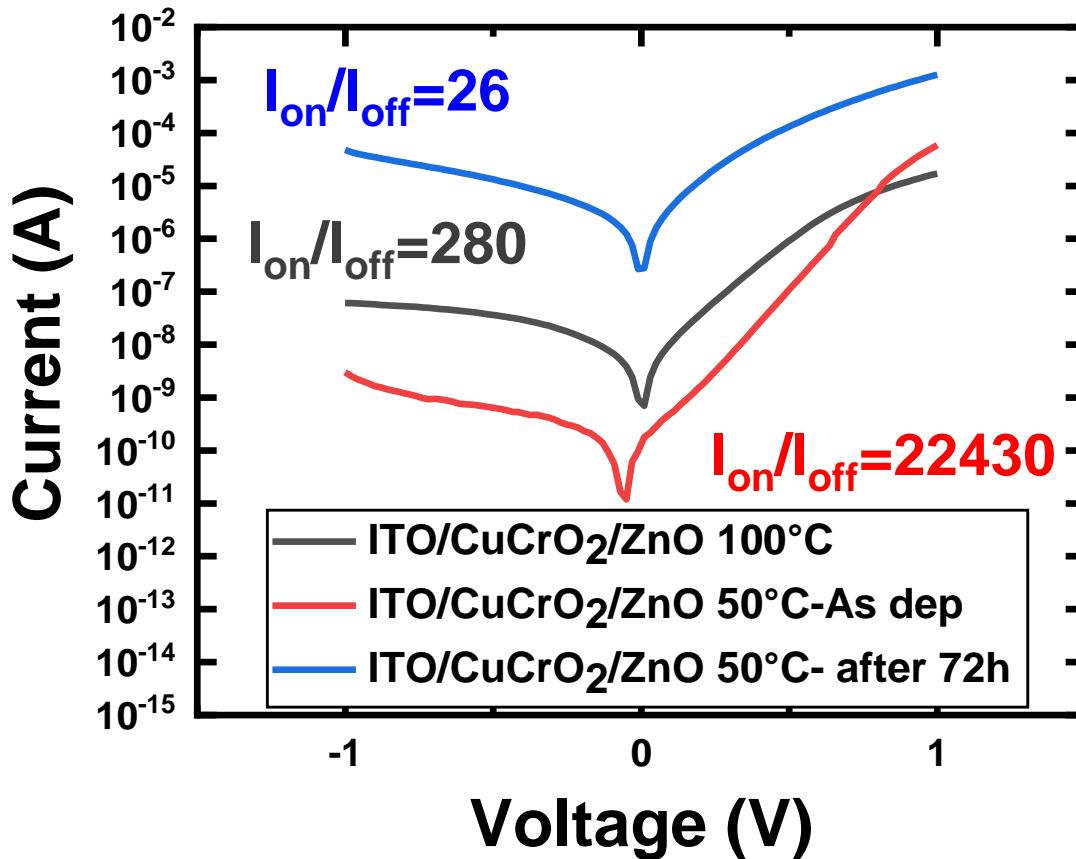


100°C



50°C

Supporting information

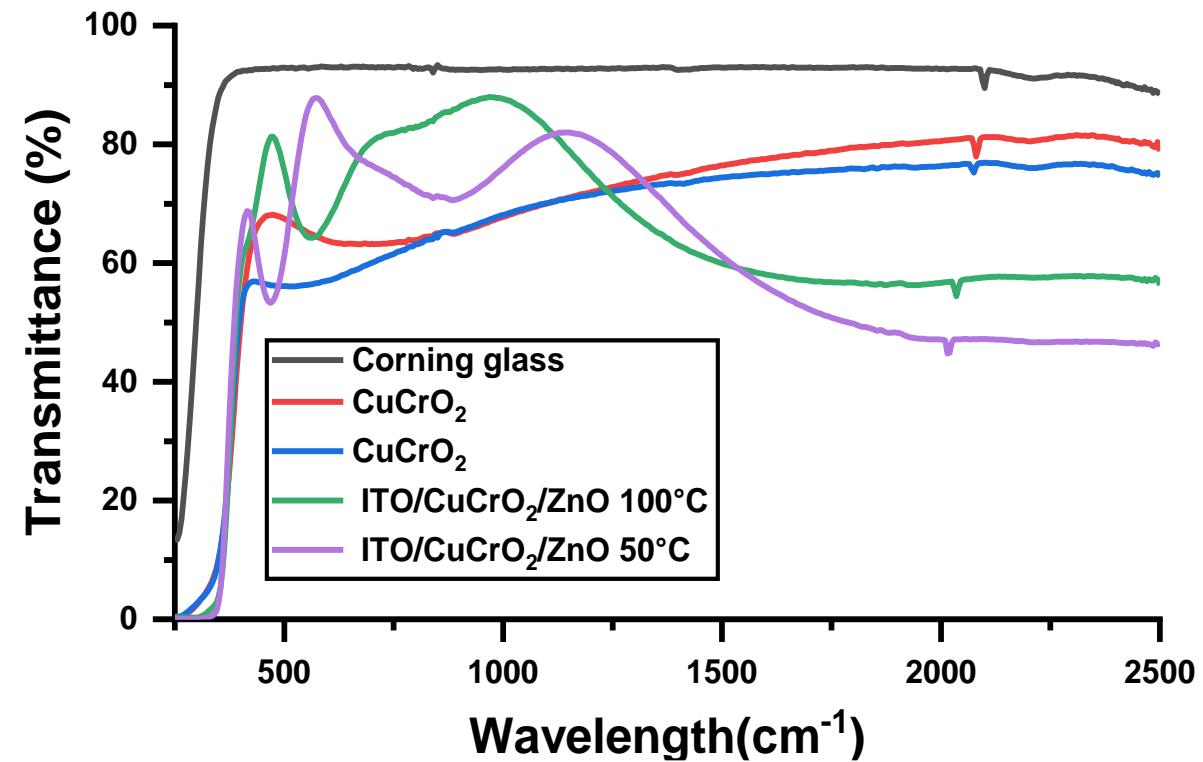


Rectifying behavior

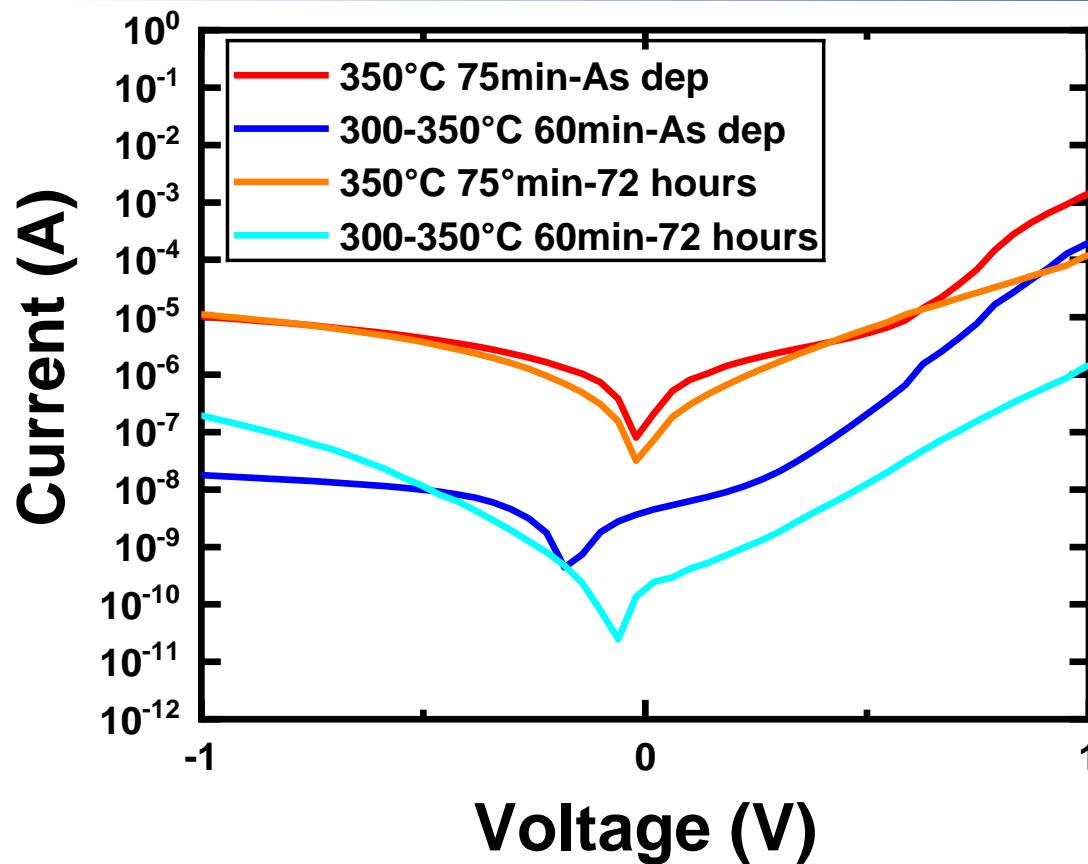
Instability under air

Junctions with 70% transmittance in the visible range (390nm-700nm)

ZnO as anti-reflection layer



Supporting information



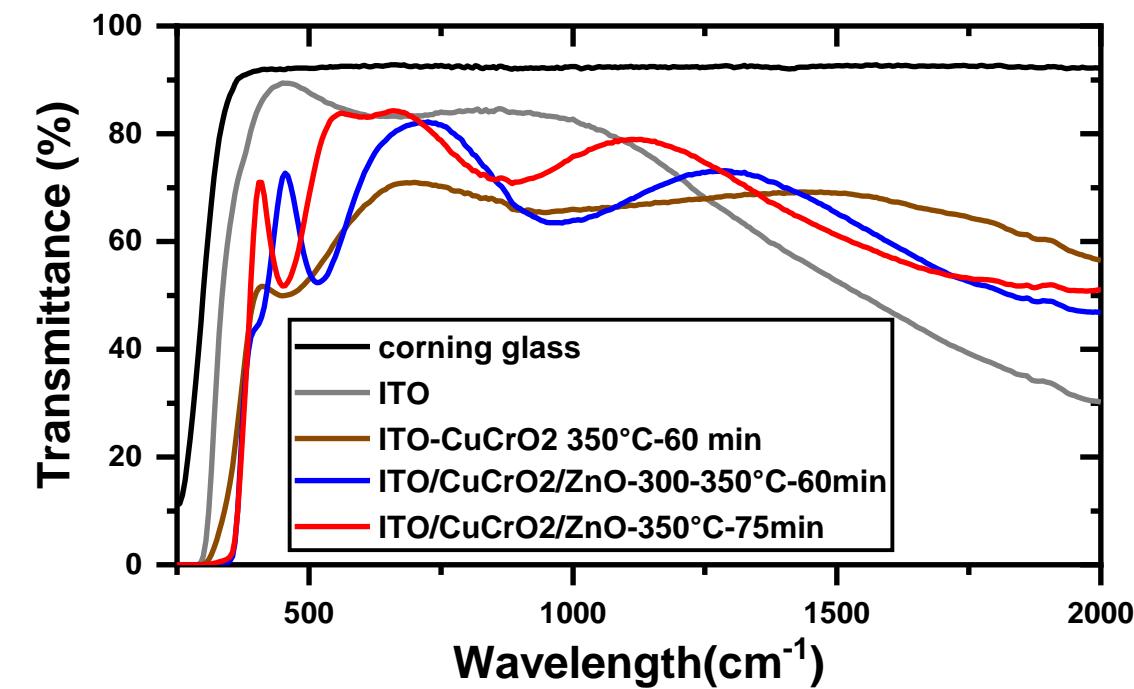
Rectifying behavior

Instability of aged samples

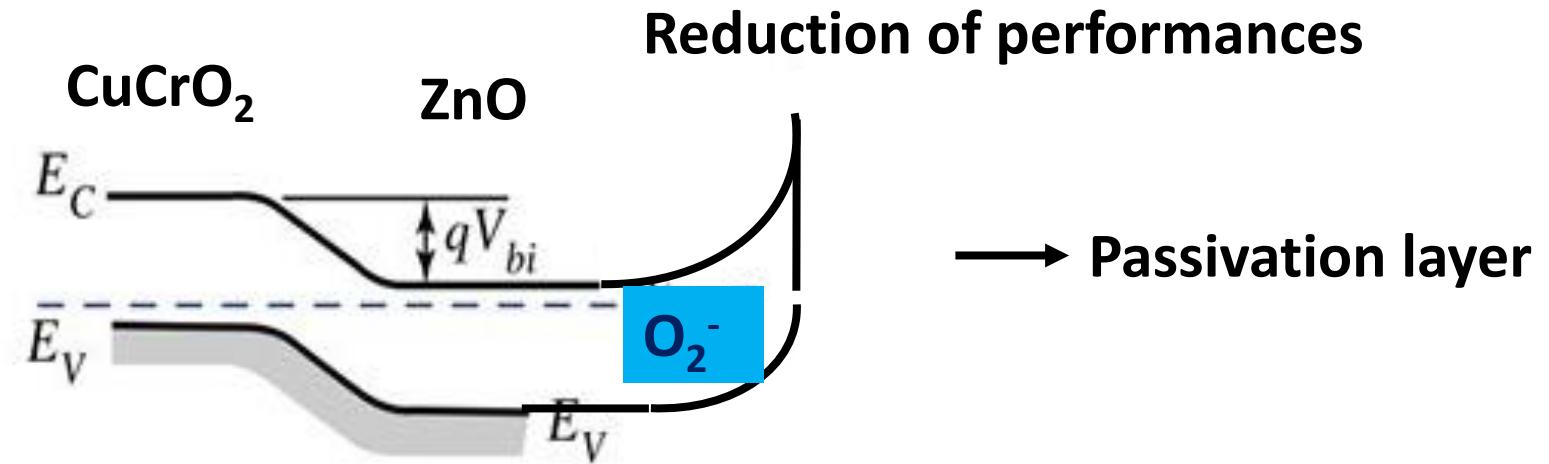
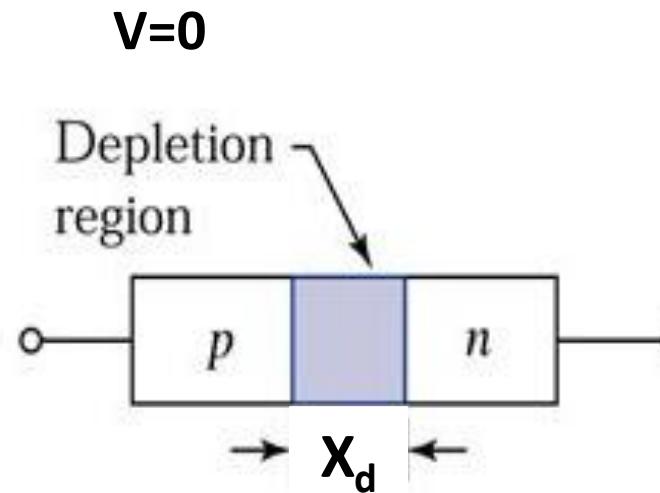
Junction	As dep $I_{on}/I_{off} \pm 1\text{V}$	72 hours $I_{on}/I_{off} \pm 1\text{V}$
$300-350^\circ\text{C}$ 60 min	7010	4
350°C 75°min	90	7

Junctions with 70% transmittance in the visible range (390nm-700nm)

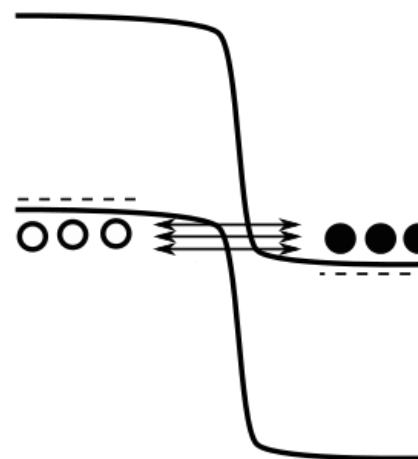
ZnO as anti-reflection layer



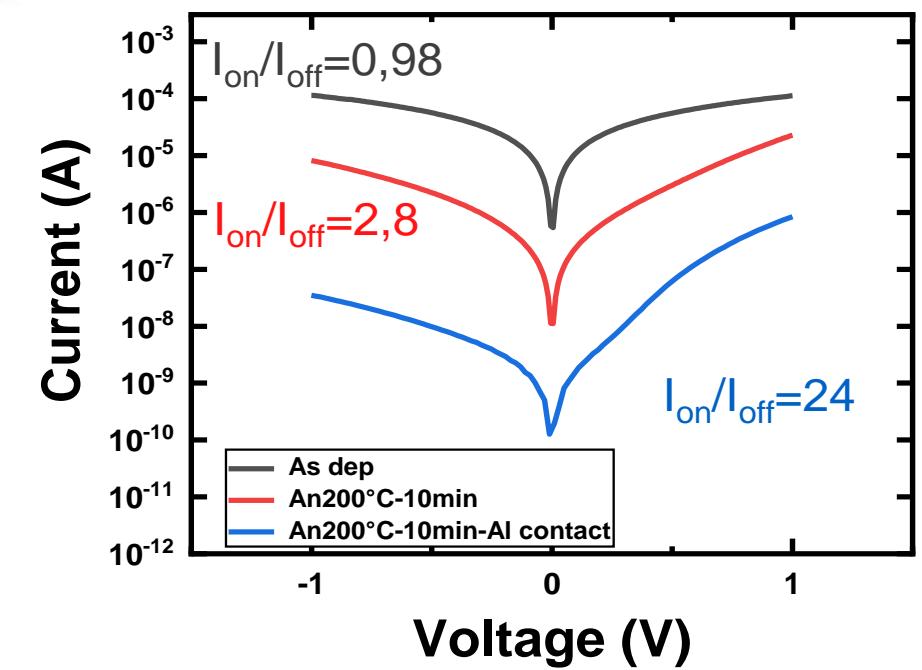
Supporting information



Very thin CuCrO_2 film



- Ohmic behaviour
- Quantum tunneling
- Interface defects

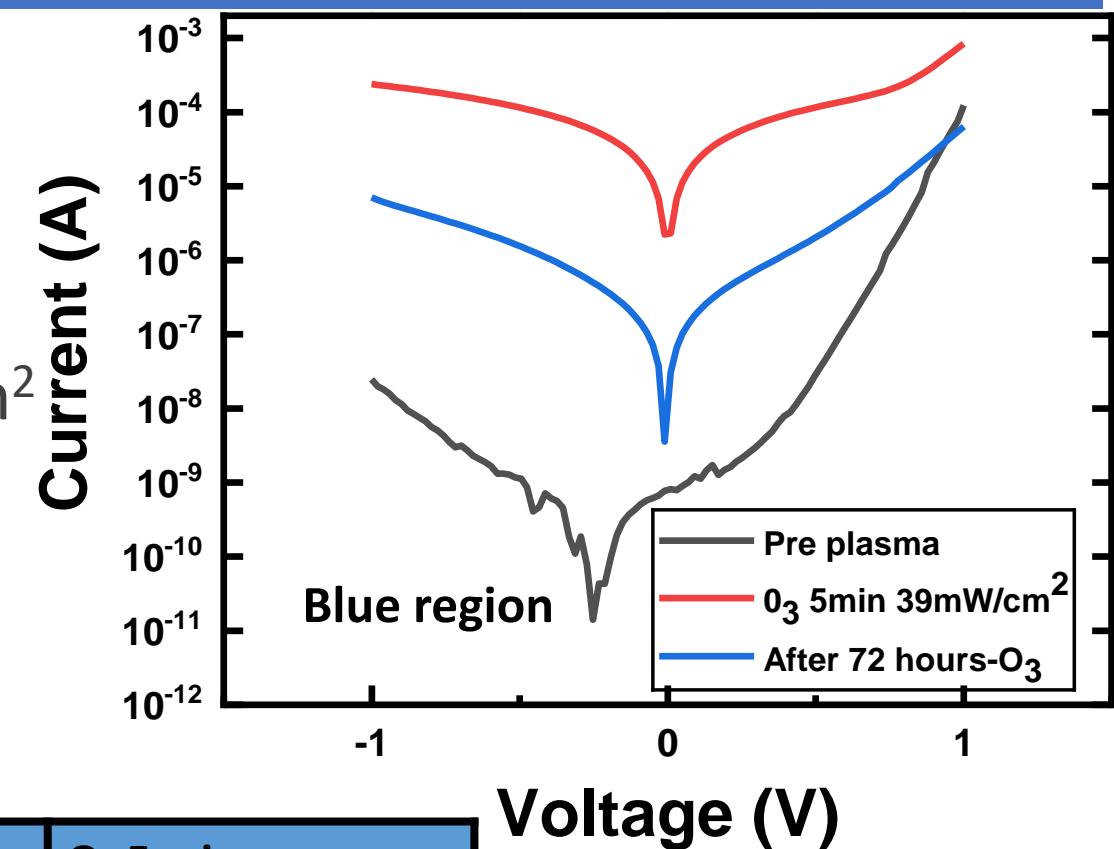


Supporting information

350 °C 60 min

- Non uniform samples
- UV-O₃ treatment-5 min at 39mW/cm²

Degradation by O₃ treatment

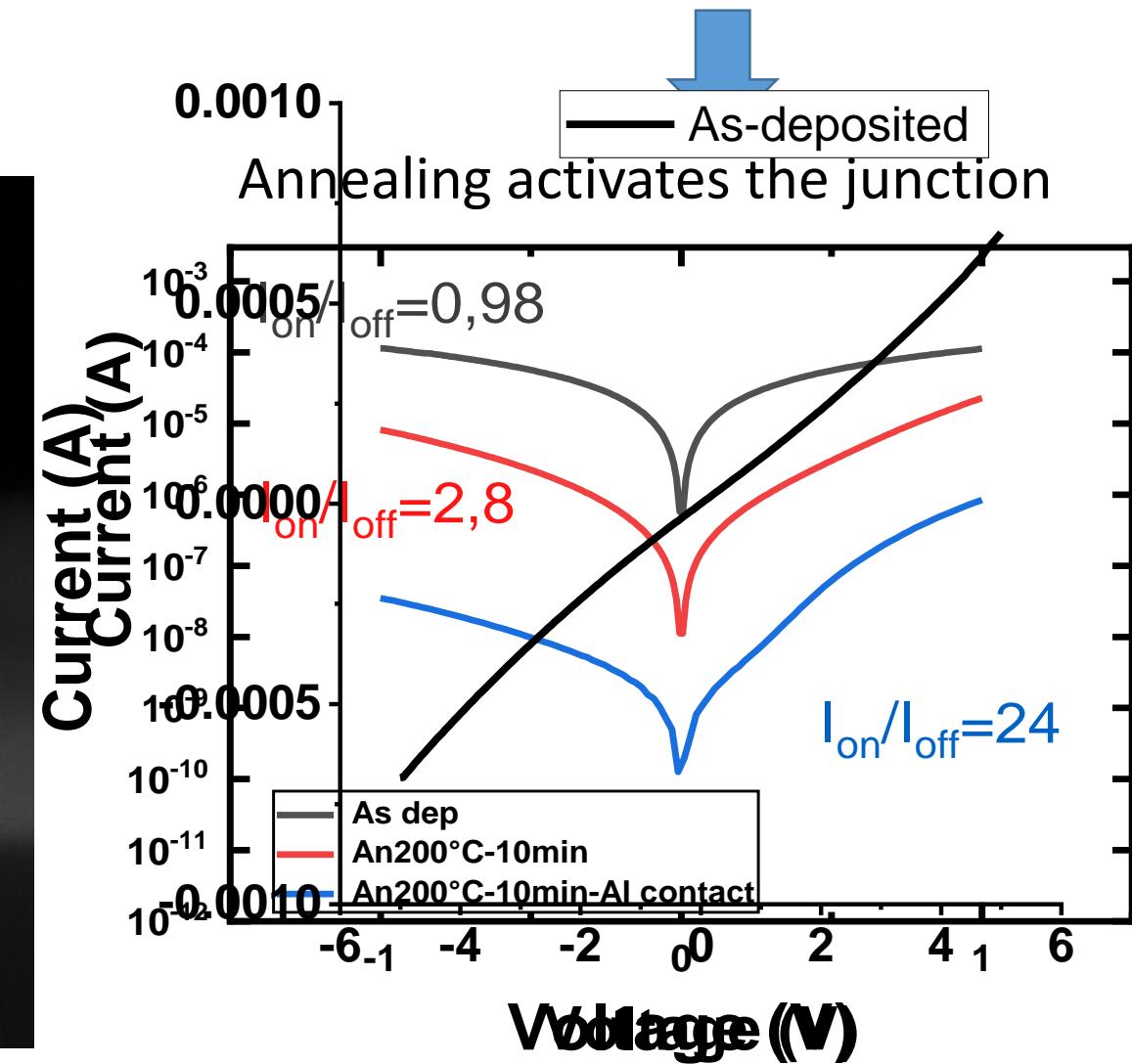
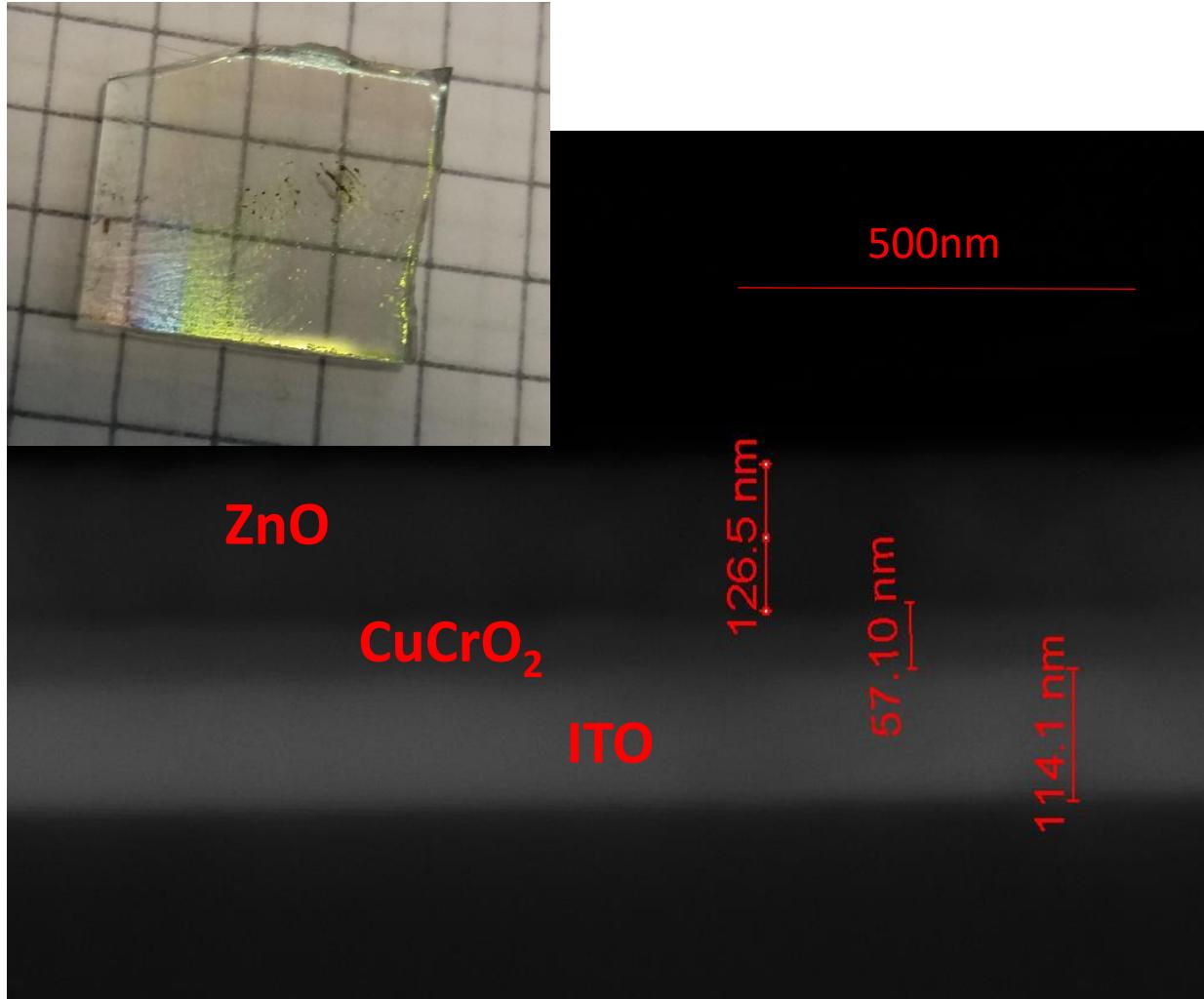


Region	As- dep	O ₃ 5 min 39mW/cm ² -As dep	O ₃ 5 min 39mW/cm ² -72h
Purple	37	4,4	9,7
Blue	5000	3,5	9
Green	449	2,6	4,7



CuCrO₂/ZnO thin film: creation of pn junction

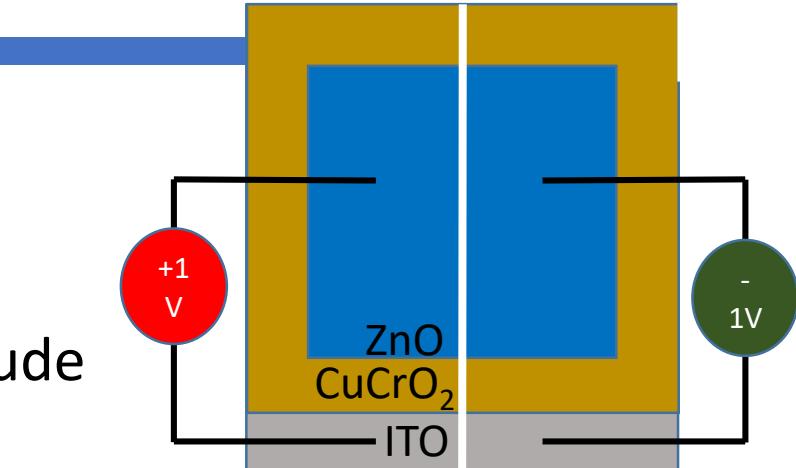
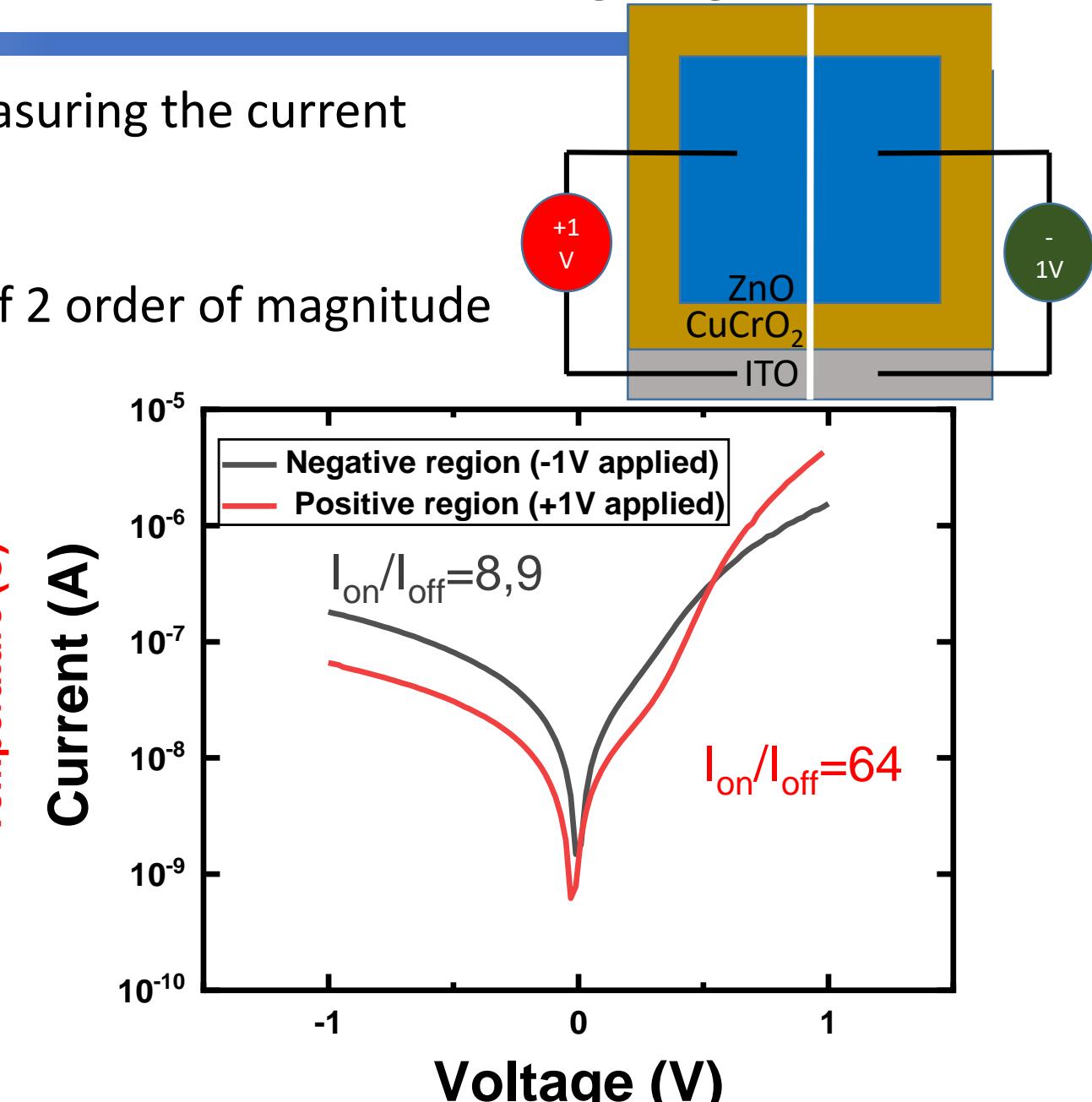
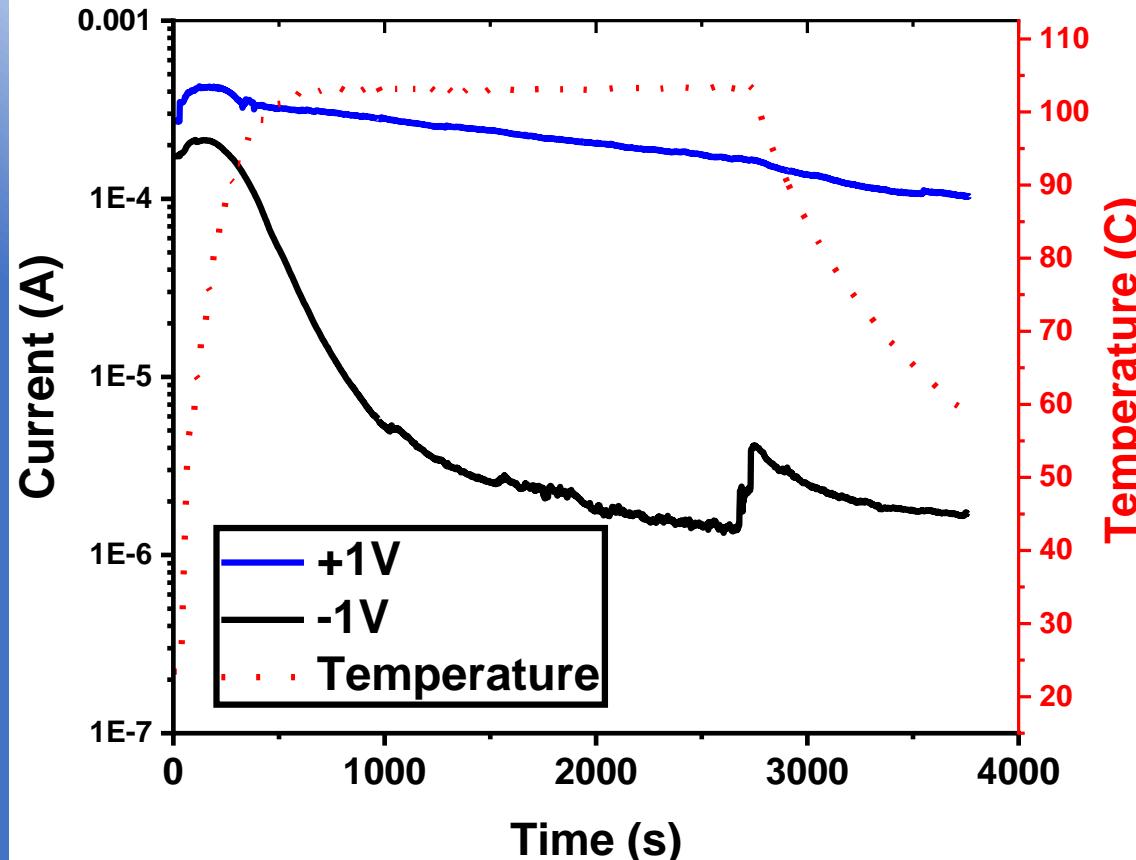
ZnO as top layer by SALD at 150 °C with 150 cycles → As deposited → Ohmic contact



CuCrO₂/ZnO thin film: In situ creation pn junction

Division in two regions and bias ($\pm 1V$) measuring the current during the thermal annealing

Current in negative region (-1V) reduced of 2 order of magnitude



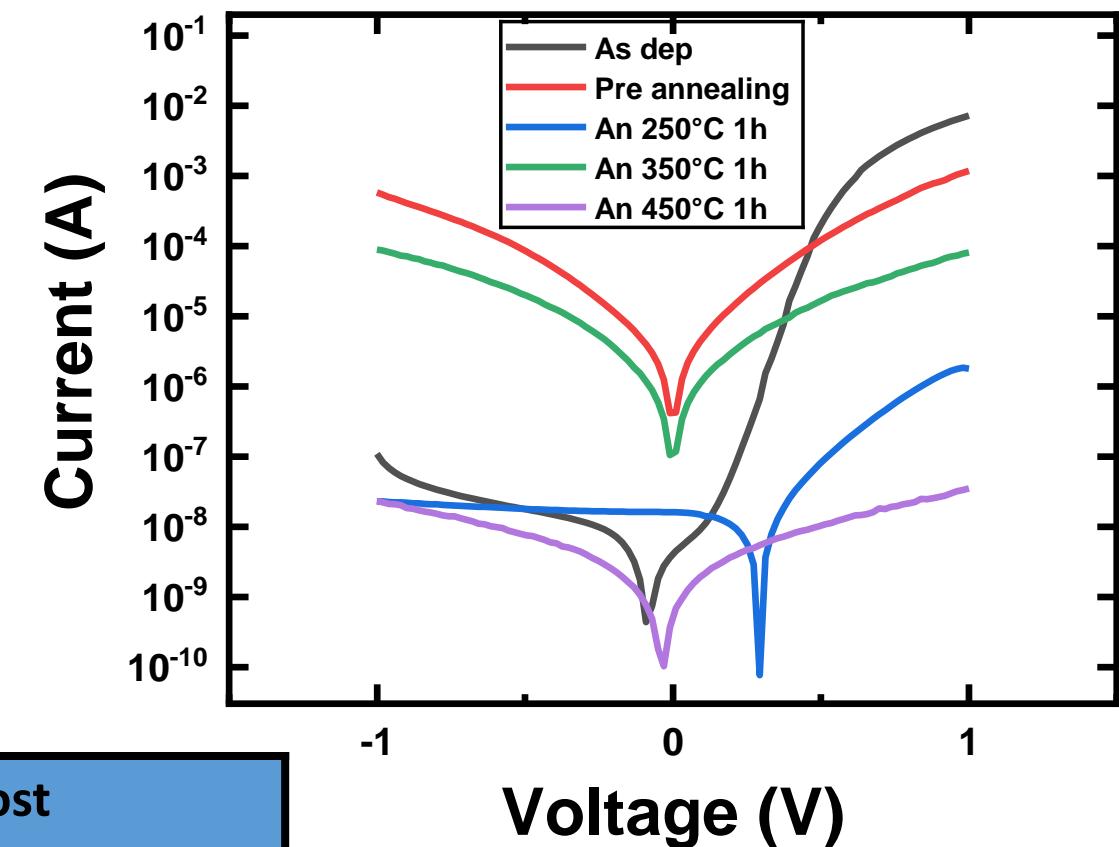
Supporting information

300- 350 °C 60min (42) annealed:

1h-250°C

1h-350°C

1h-450°C



Annealing Temperature (°C)	I_{on}/I_{off} Pre annealing	I_{on}/I_{off} Post annealing
250°C	2,03	77,5
350°C	2,02	0,9
450°C	2,9	1,5