Local structure and point-defect dependent selective atomic layer deposition of copper(I) oxide and metallic copper thin films

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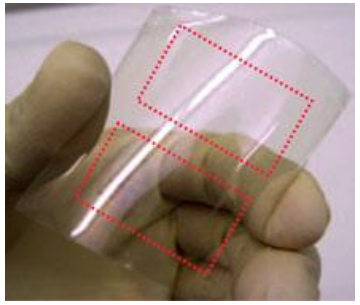
All-oxide semiconductor devices

Non-toxic, earth abundant, inexpensive

p-type semiconductor oxides → poor electrical properties

Transparent conducting oxides (TCOs)



See-Through Transistors

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p-Cu_2O

- ✓ Intrinsic p-type conductivity
- ✓ Band gap 2.1 - 2.4 eV
- ✓ High mobility (single crystal)

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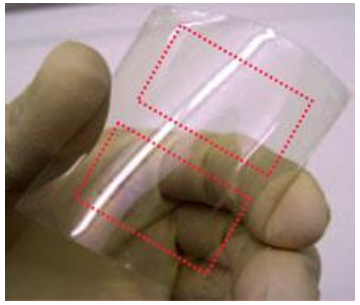

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n-ZnO

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- ✓ Wide band gap 3.4 eV
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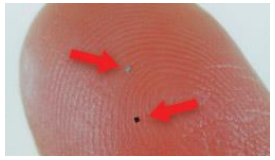
Transparent electronics

Photovoltaics

Photodetection

Area-selective deposition

Miniaturization in microelectronics



Mu-chips (IC chips).
http://global.hitachi.com

Gas sensor-NANOZ

Conventional patterning techniques are challenging

Implementation of new approaches (bottom-up)

Depositing the material directly in the desired areas

Area-selective deposition

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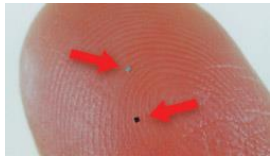

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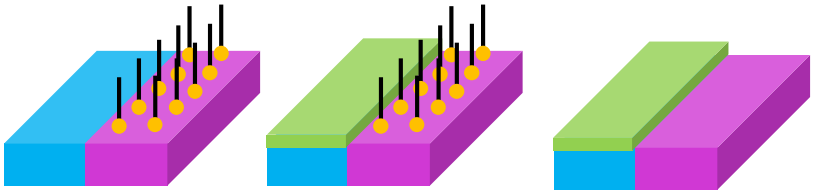
Area-selective atomic layer deposition using SAMs

Area-deactivation

SAMs



Area-selective deposition

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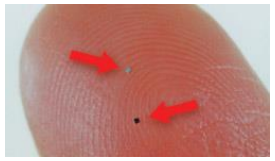

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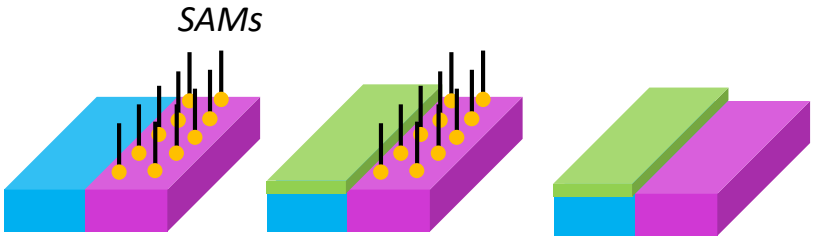


Limitations

- Poor thermal stability of SAMs
- Not compatible with plasma-assisted or ozone-based ALD
- Simultaneous deposition of different material is not possible

Developing a new SAMs-free approach for simultaneous deposition of different materials

Area-selective deposition

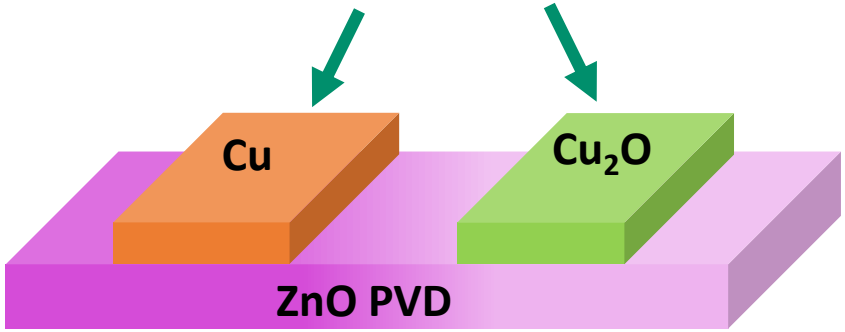
Area-selective atomic layer deposition

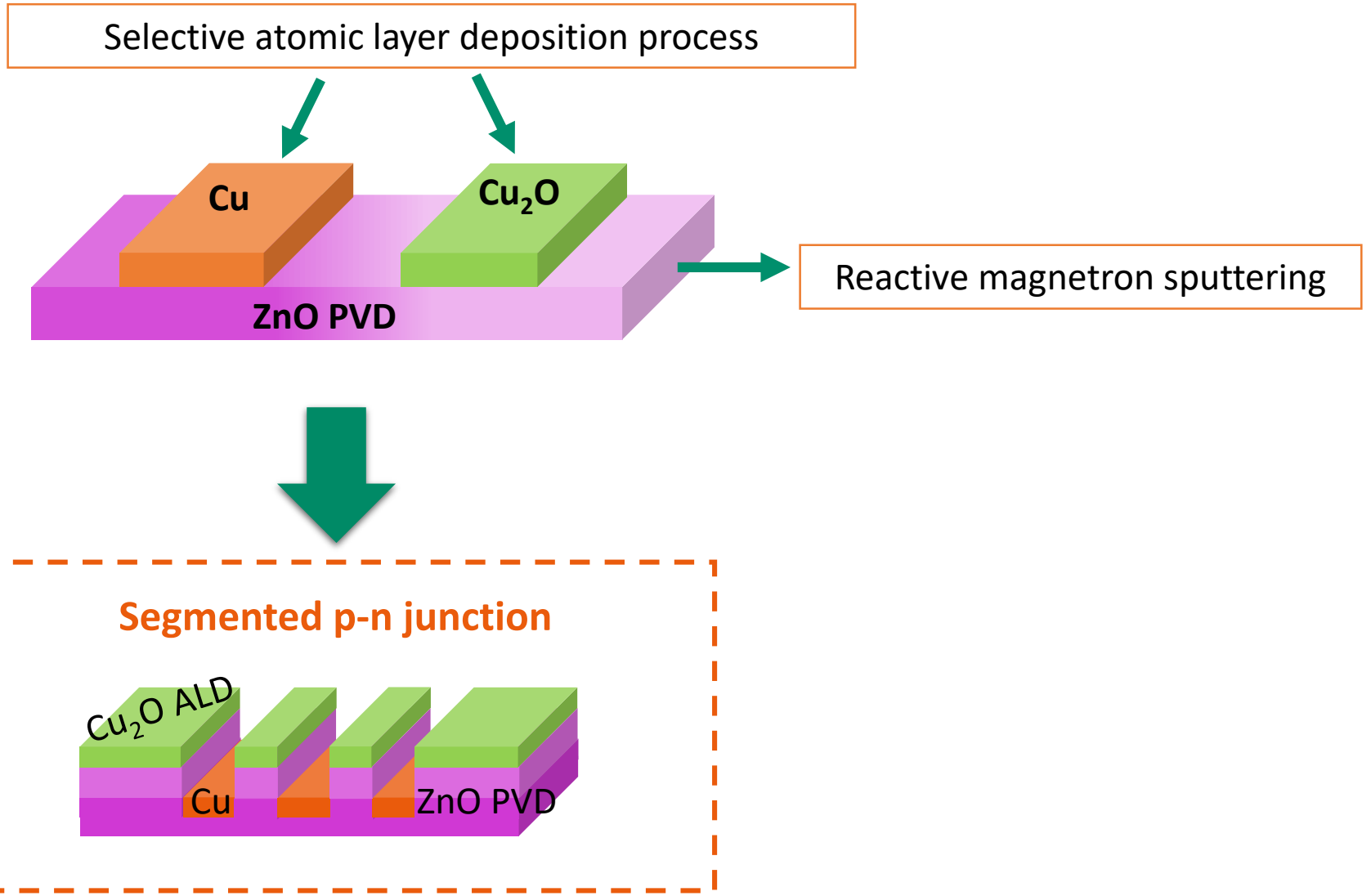
Novel approach

A property of the substrate is modulated to achieve localized growth of different materials

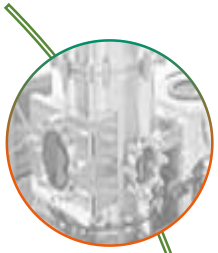
Conductivity/defects density

Cu or Cu_2O / ZnO

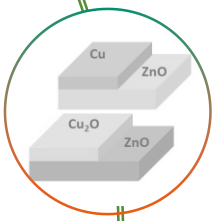



Selective atomic layer deposition process
Cu
Cu_2O
ZnO PVD
Reactive magnetron sputtering
Segmented p-n junction
Cu_2O ALD
Cu
ZnO PVD

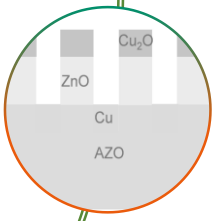
Outline



Experimental techniques



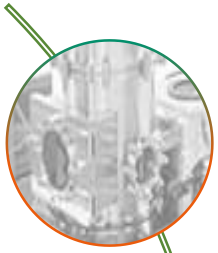
Selective Atomic Layer Deposition of Copper Oxide and Metallic Copper Thin Films



Fabrication of Cu_2O/ZnO/AZO/Cu-back electrode segmented microjunctions

Conclusions

Outline



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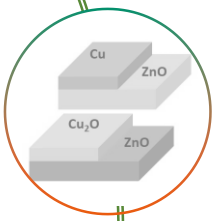

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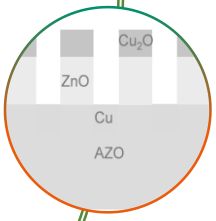

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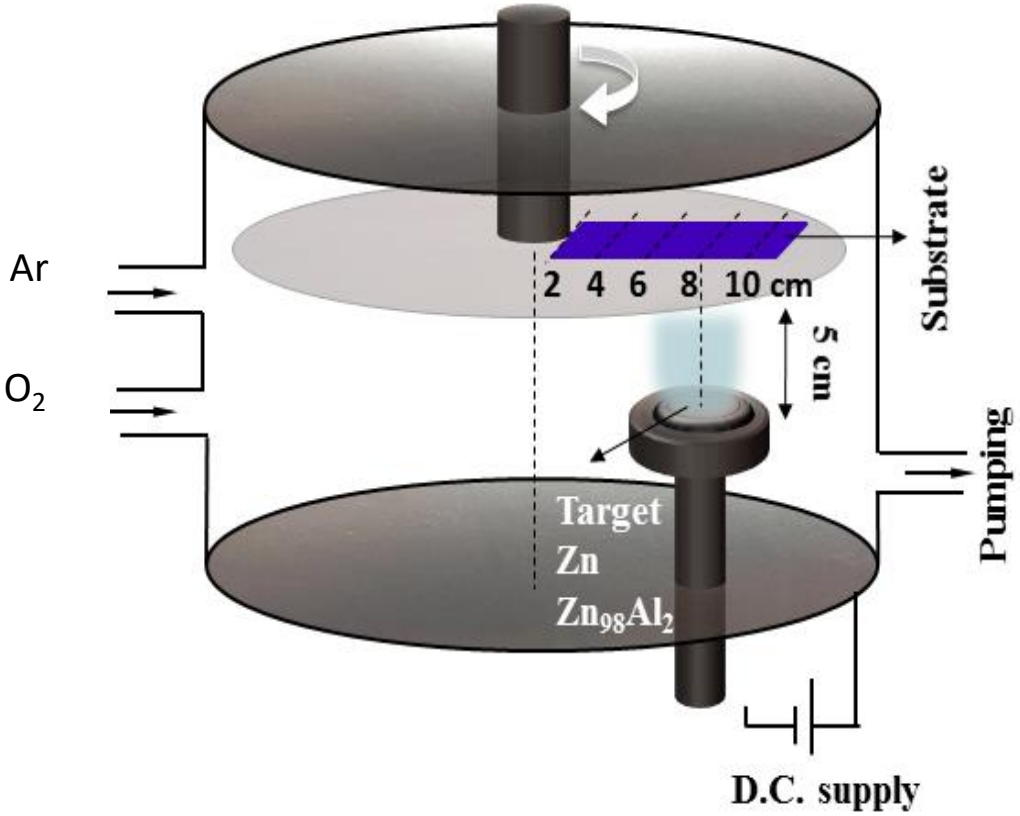
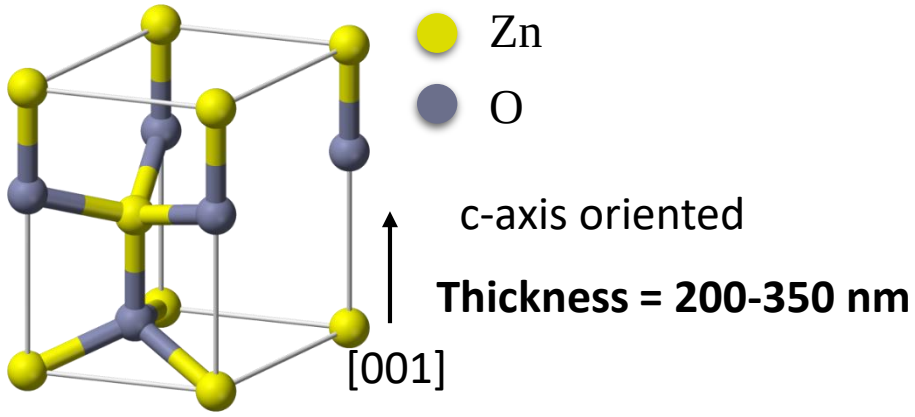
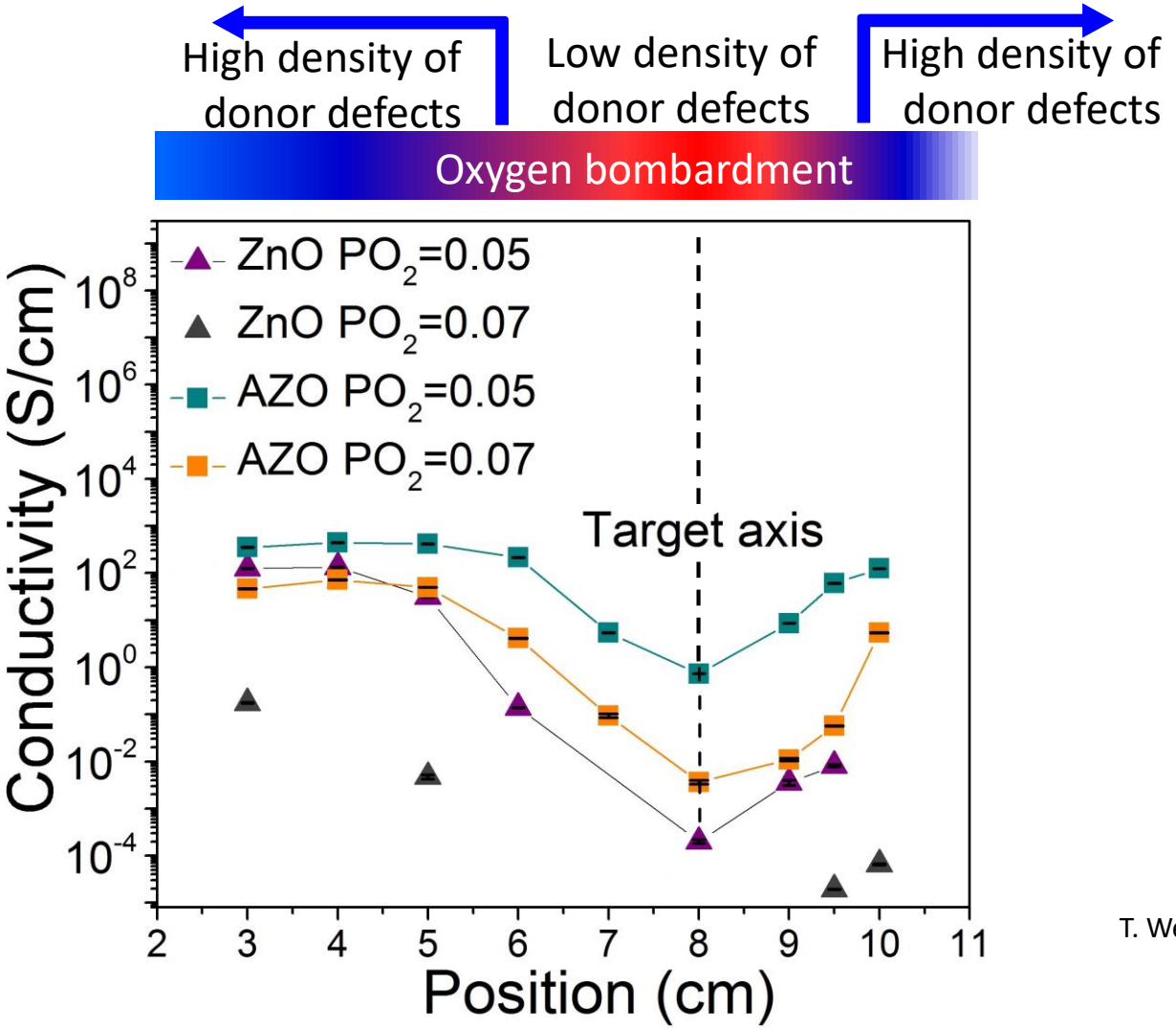
Reactive magnetron sputtering: ZnO and Al-doped ZnO

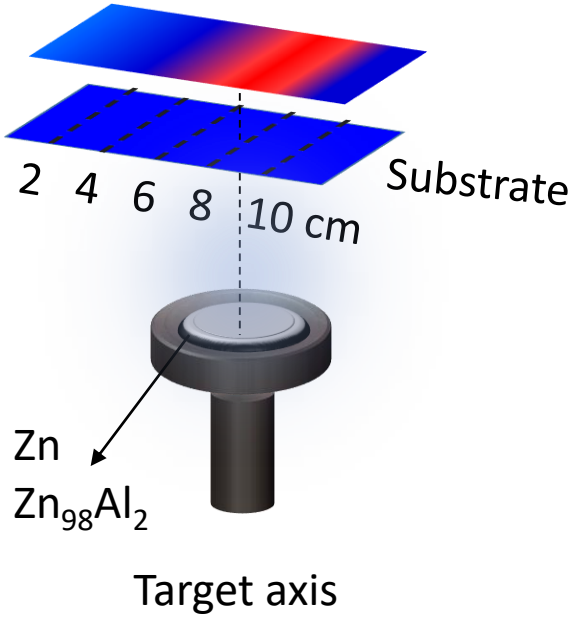


Deposition parameters	
Substrate	Si (100)
Ar flow rate (sccm)	50
O_2 flow rate (sccm)	**6, 8**
O_2 partial pressure: P_{O_2} (Pa)	**0.05, 0.07**
Position (cm)	**3 - 10 cm**
Total pressure (Pa)	0.5 Pa
Target current (A)	0.07



Evolution of ZnO and AZO conductivities

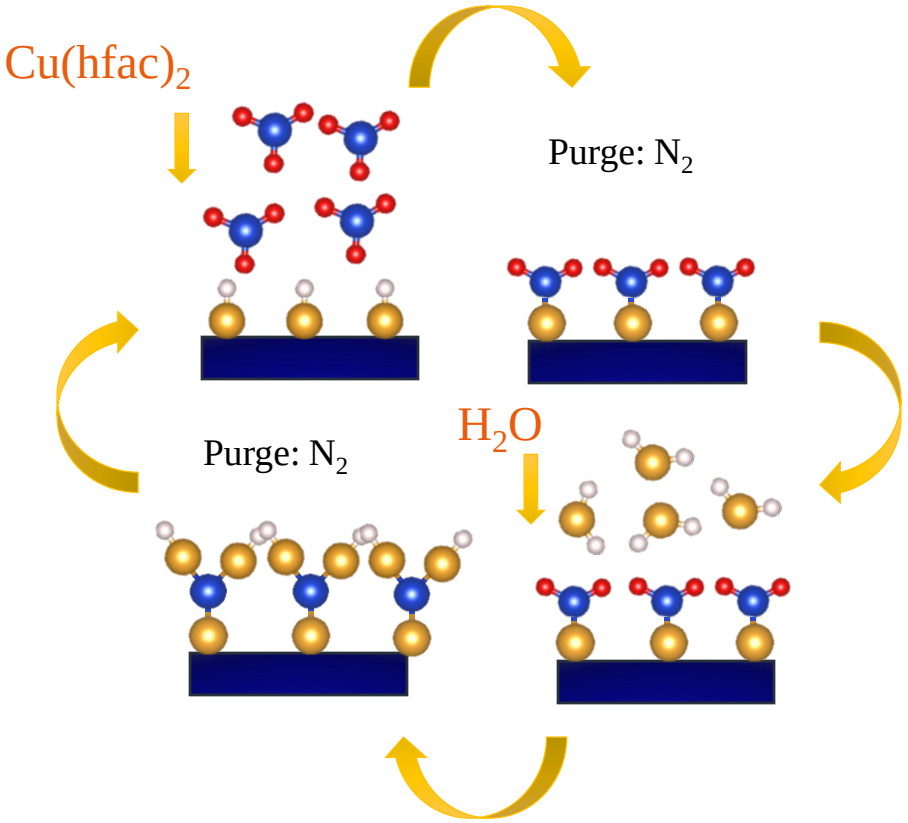




T. Welzel & K. Ellmer , Surface & Coatings Technology 205 (2011) S294.

Conductivity and majority type of defects evolve with Al-doping, position and oxygen partial pressure

Atomic layer deposition: Cu_2O and metallic Cu



ALD PICOSUN™ R-200 Advanced reactor

Precursors

- Copper (II) hexafluoro-acetyl-acetonate, $Cu(hfac)_2$ (99.99+%-Cu, Stream Chemicals)
- H_2O as reactant

N_2 as carrier gas → 300 sccm $Cu(hfac)_2$ -line
N_2 as carrier gas → 150 sccm H_2O-line

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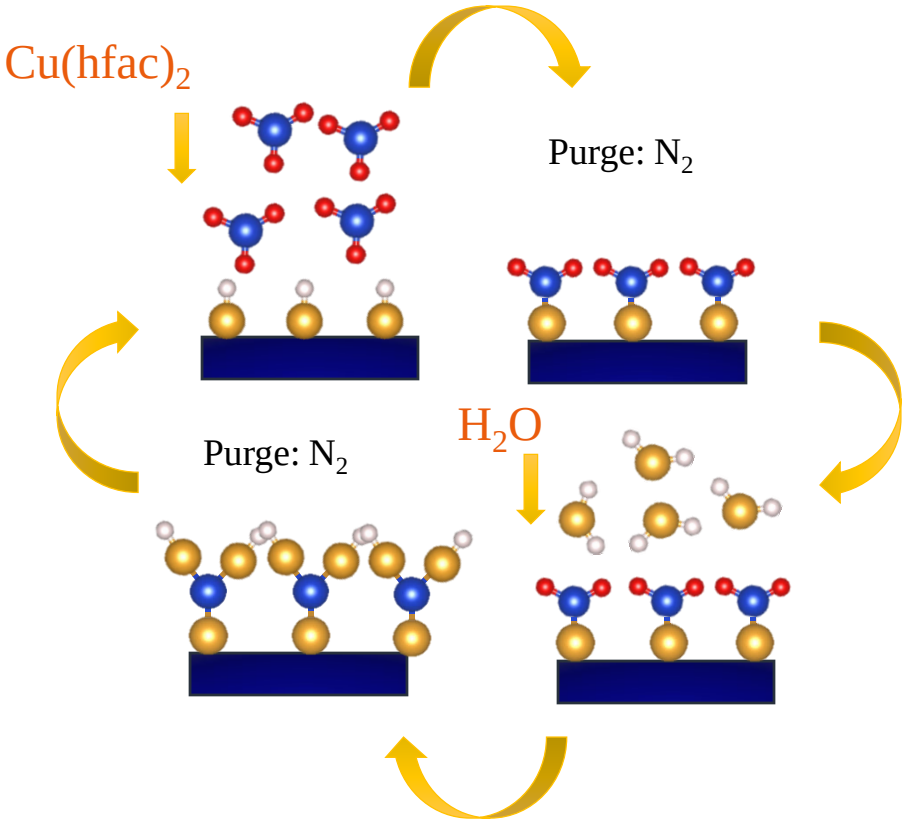

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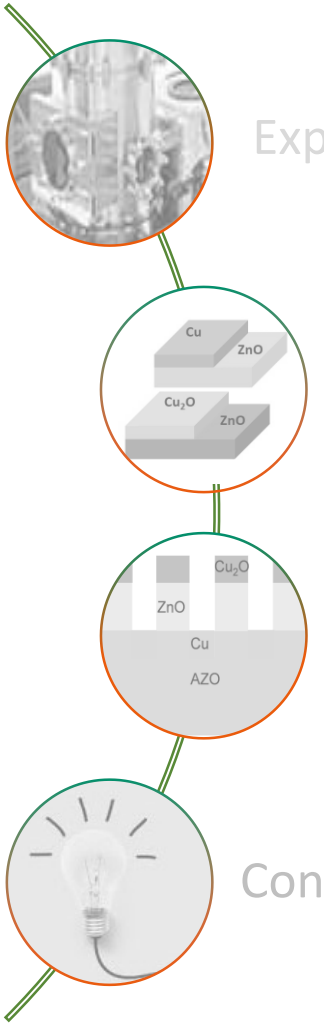
N_2 as carrier gas → 150 sccm H_2O-line

Precursor				$\sigma_{substrate}$ (S/cm)	Temp. (°C)	# cycles
	t_{pulse} (s)	t_{purge} (s)	Temp. (°C)			
$Cu(hfac)_2$	1	6	70	$10^{-4} - 10^{3}$	210 - 350	5000 - 10000
H_2O	3	6	18			

Outline



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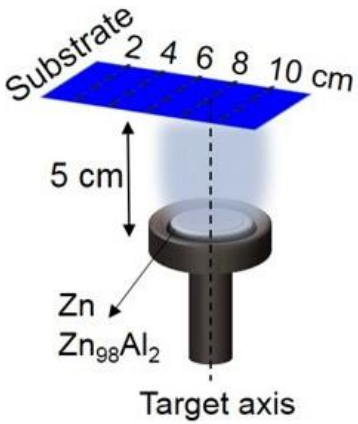
ALD and PVD growth parameters

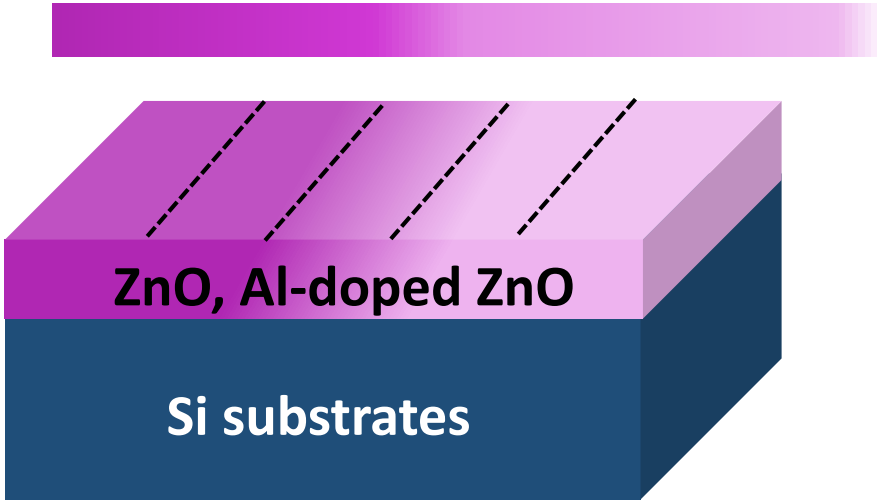
Reactive Magnetron Sputtering



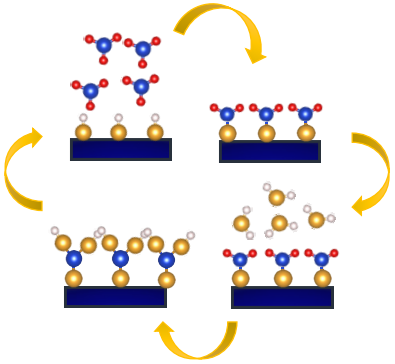
Different P_{O_2}

High density of donor defects

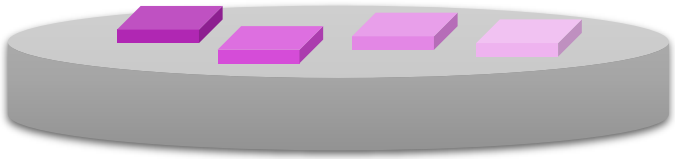
Low density of donor defects



Atomic layer deposition

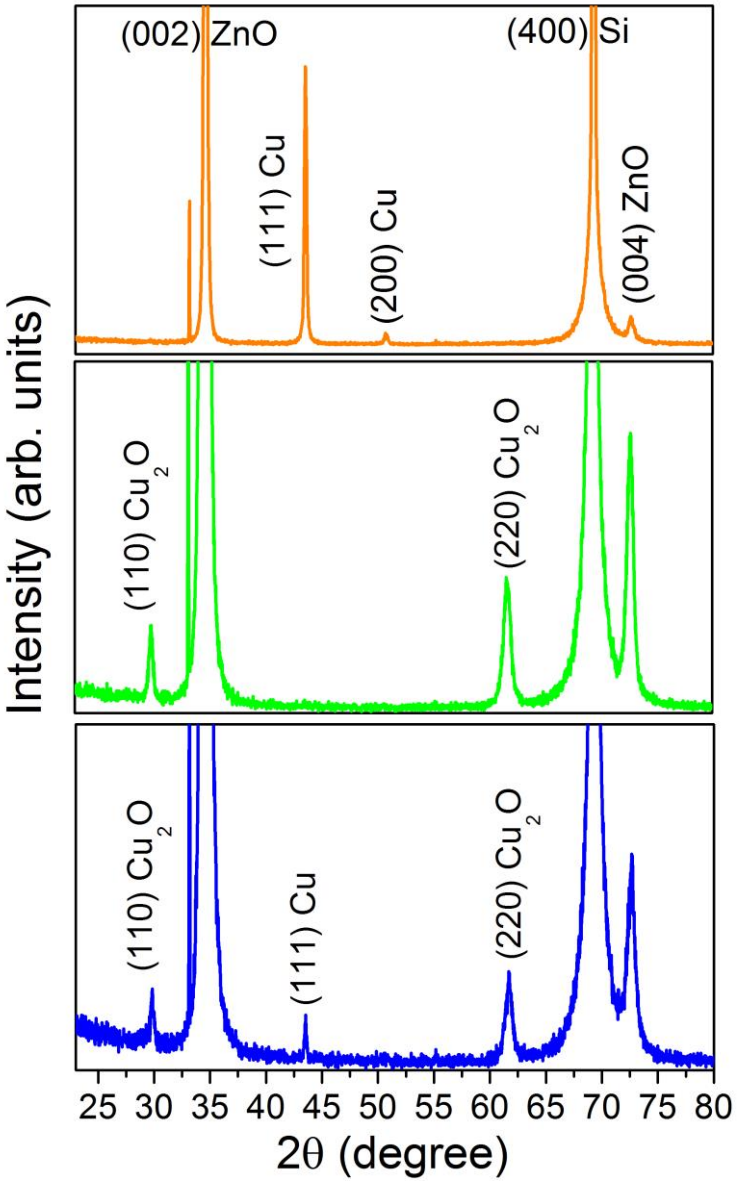


Cu/ Cu_2O ?



T = 280°C
$\sigma_{ZnO,\ AZO} = 10^{-4} - 10^{3}$ S/cm
10 000 ALD cycles

Conductivity-driven selectivity on ZnO



Cu

Cu_2O

Cu + Cu_2O

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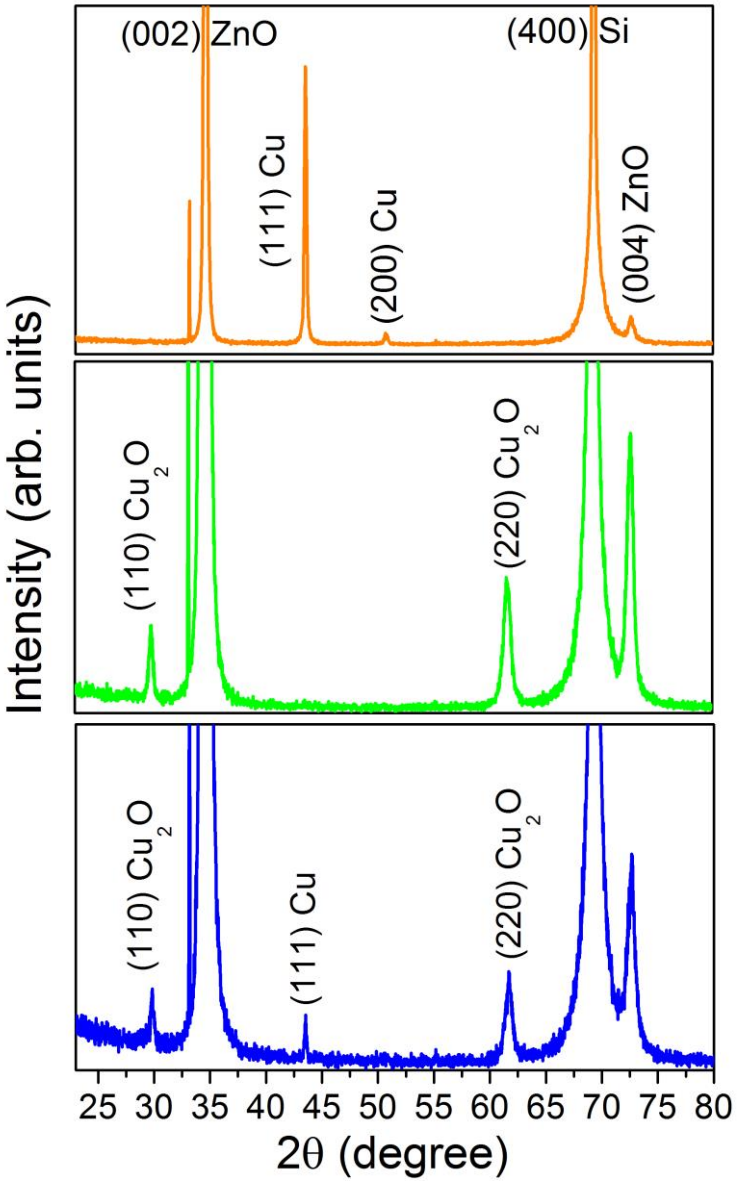

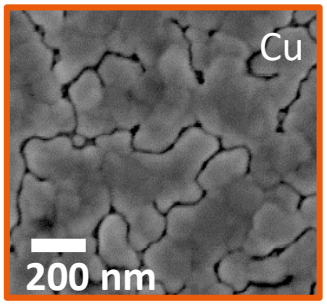

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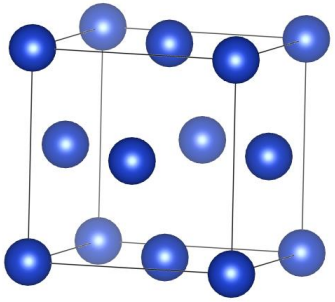
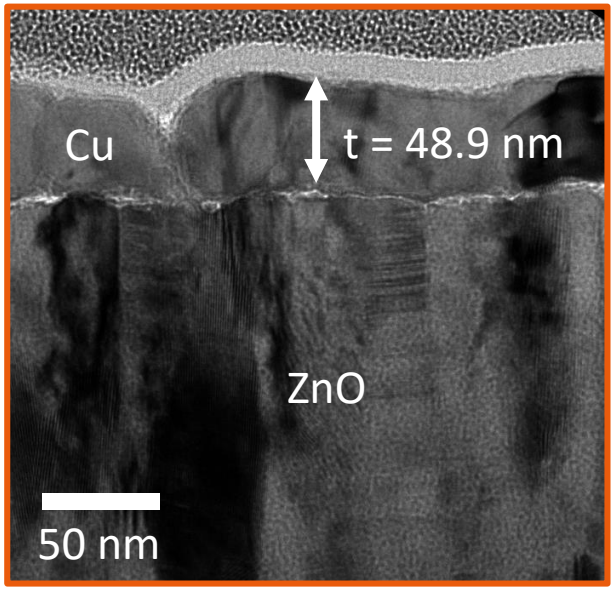
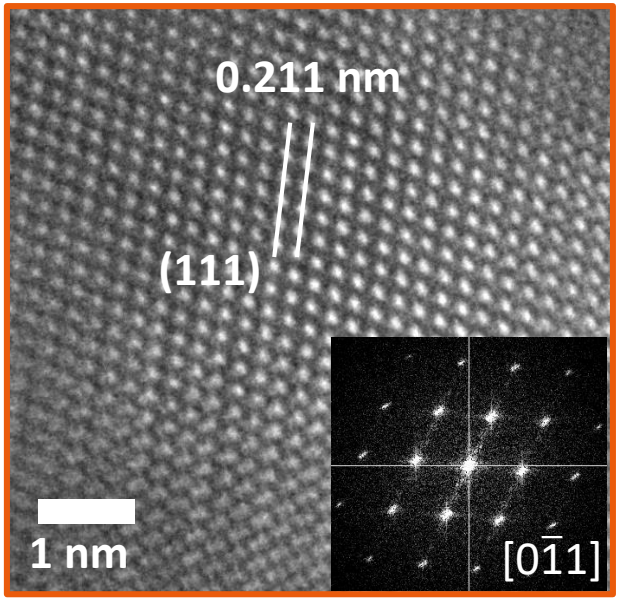


$a = 3.615$ Å





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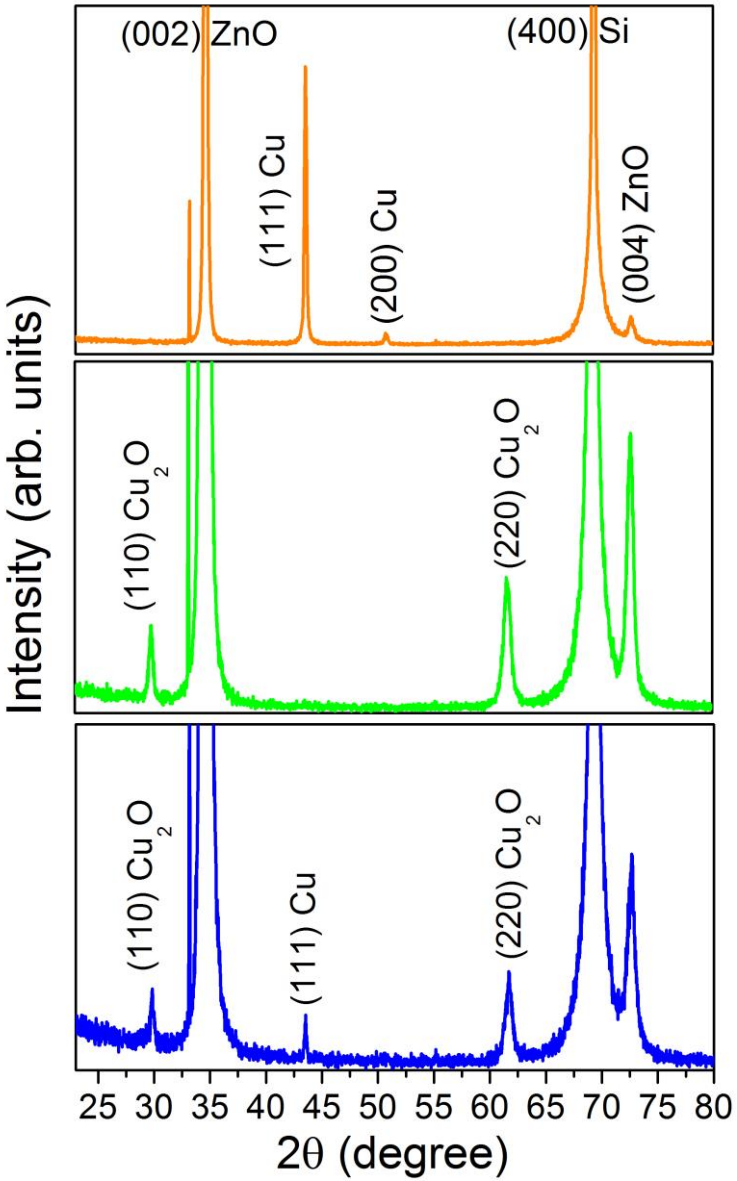

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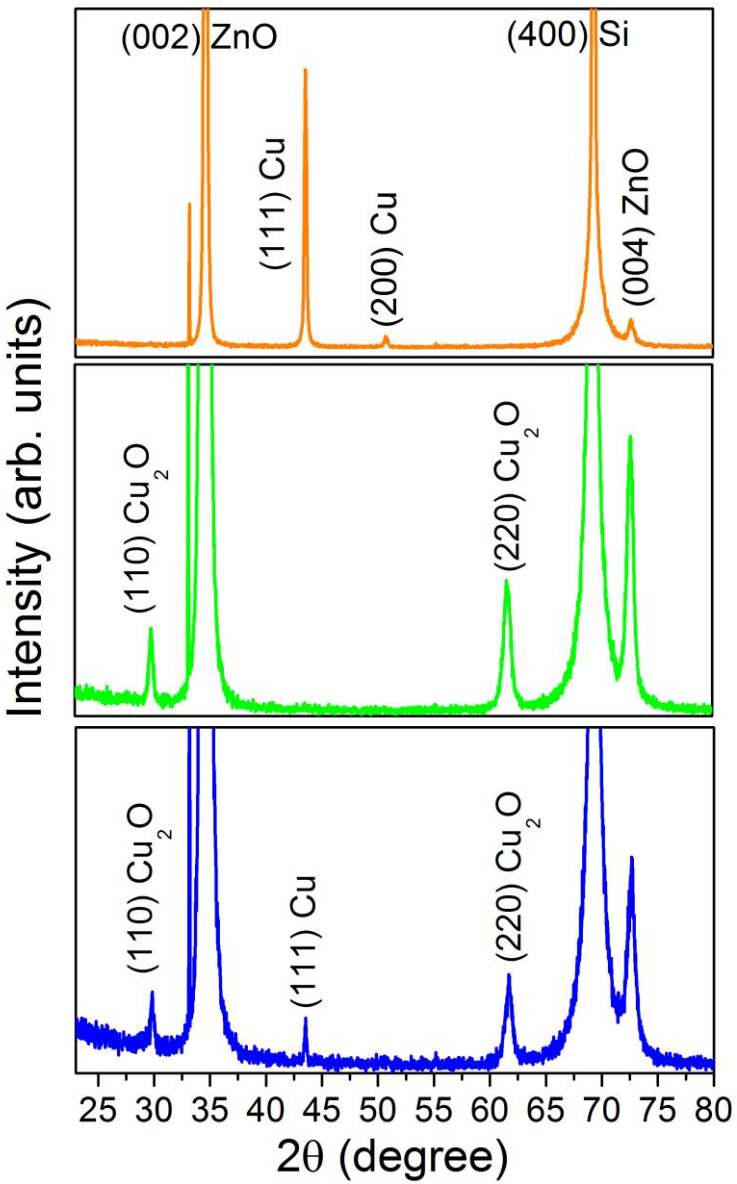

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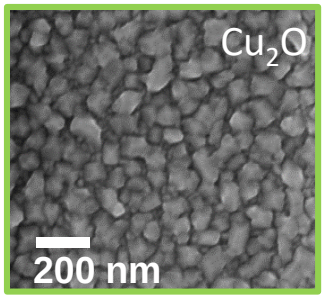

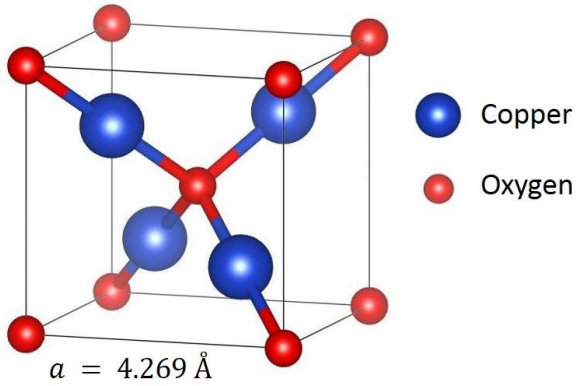

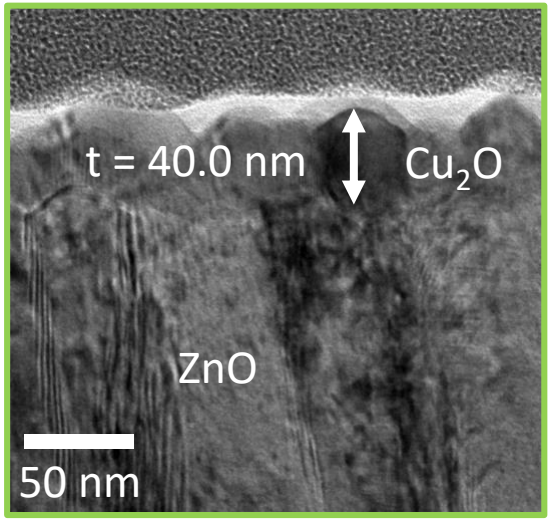

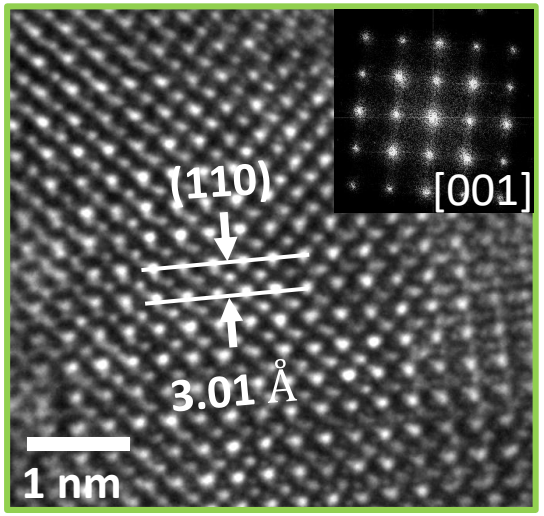

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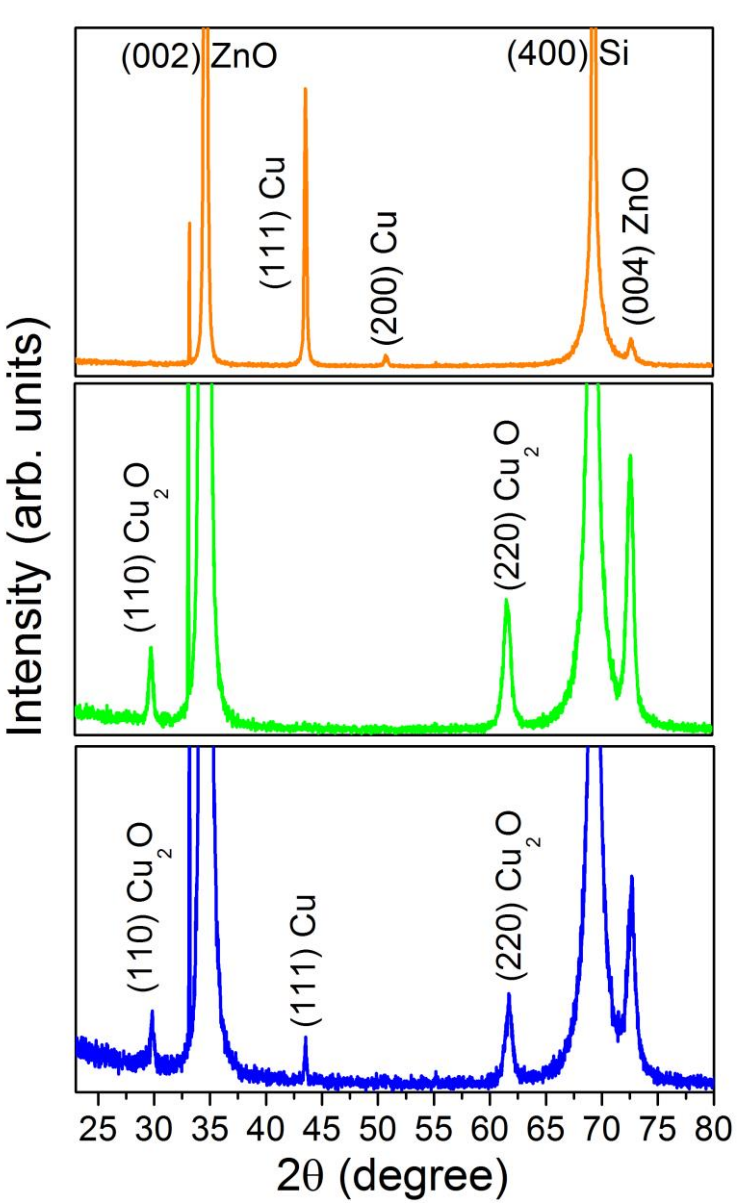
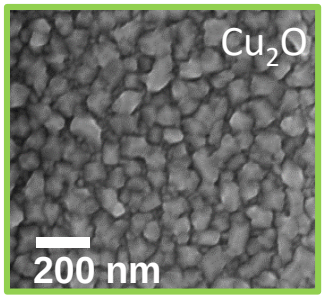
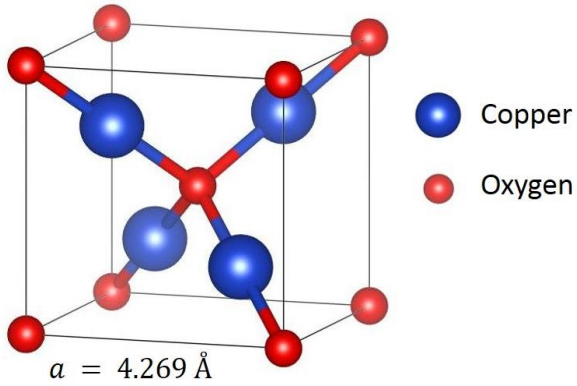


Cu

Cu_2O

Cu + Cu_2O





Typical texture of Cu_2O films grown on ZnO → [111] || [001] ZnO

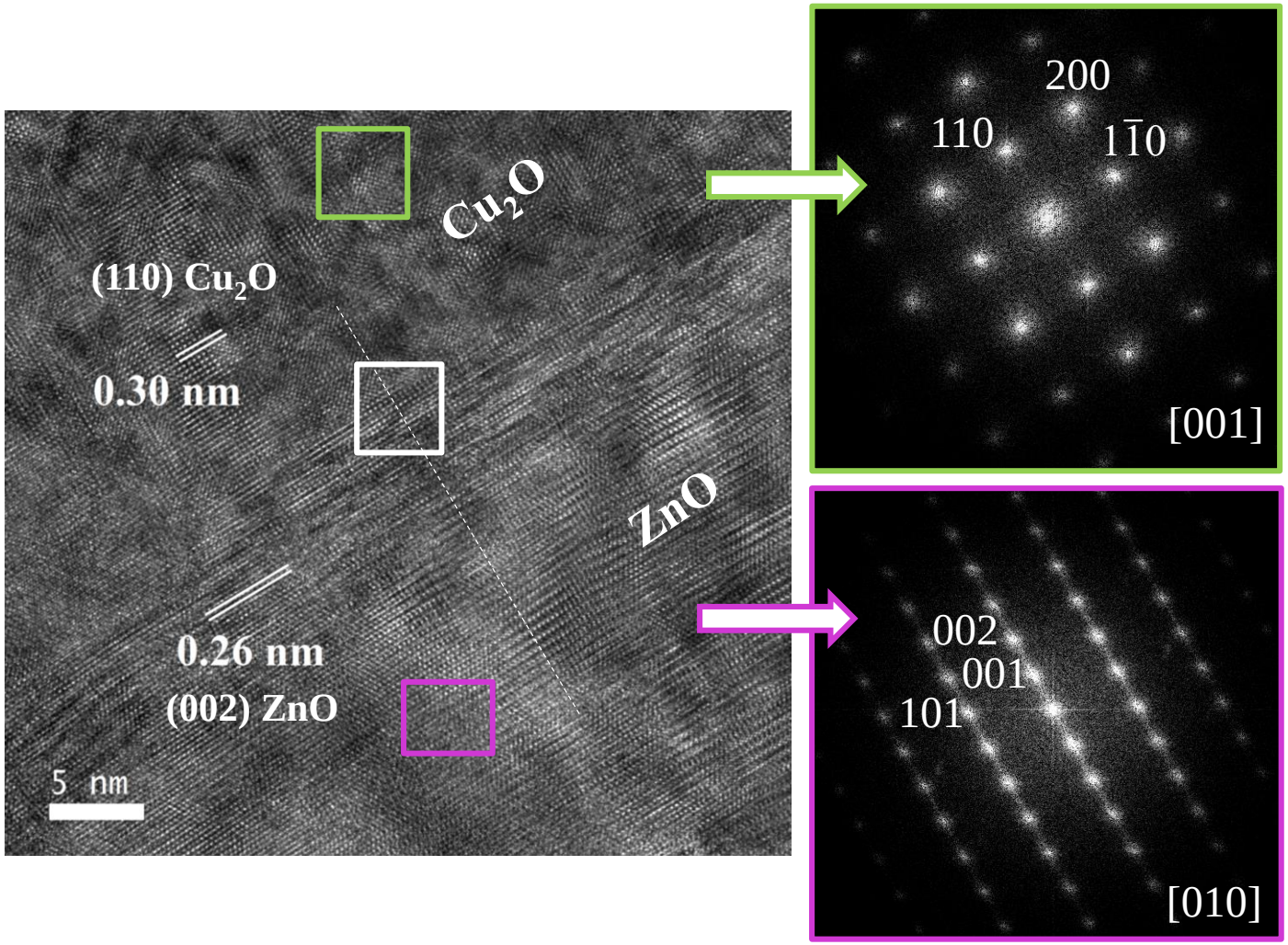
S. Jeong et al., J. Cryst. Growth **311**, 4188 (2009)

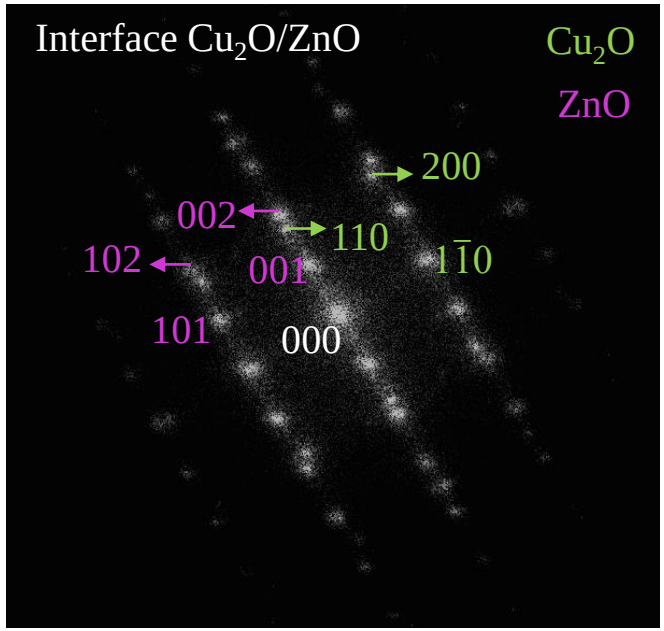
Y. Wang et al., Acta Mater. **76**, 207 (2014)

[110] Cu_2O|| [001] ZnO texture

Suggests the influence of the substrate structure on Cu_2O growth

Local epitaxy of Cu_2O on ZnO

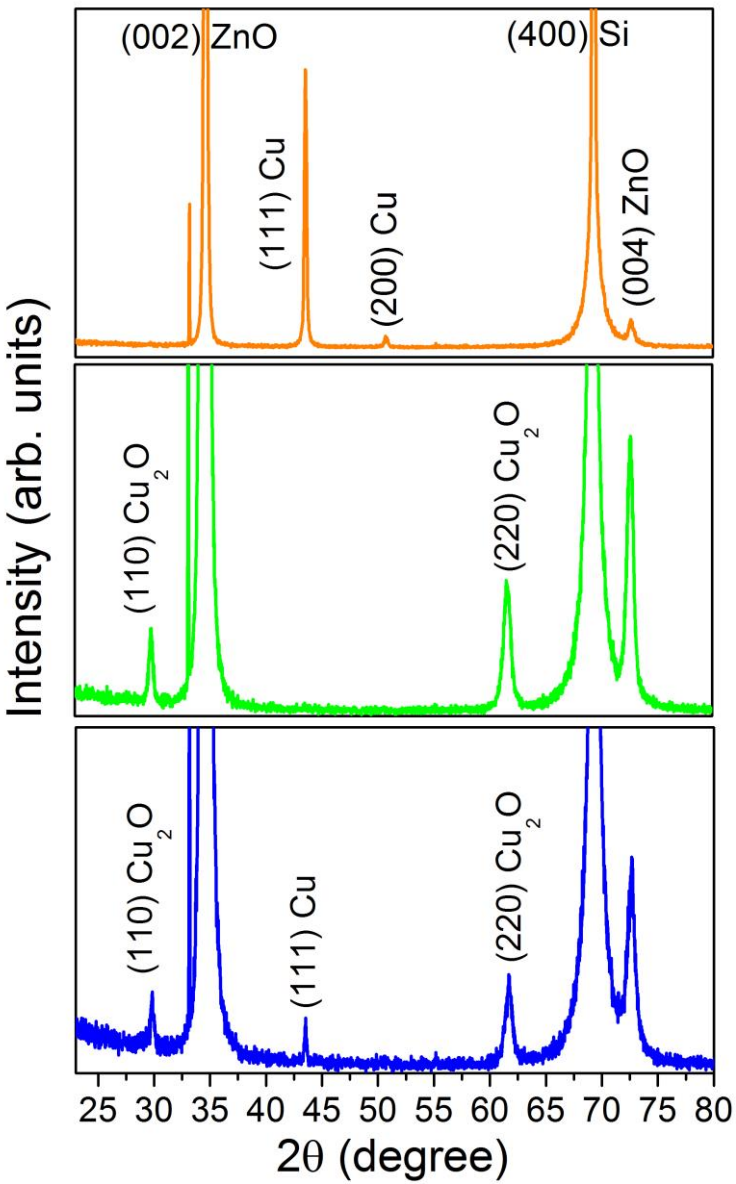


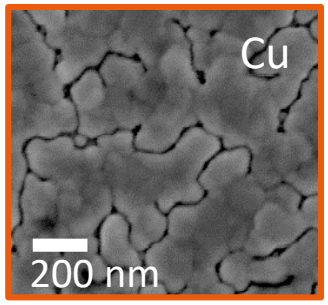


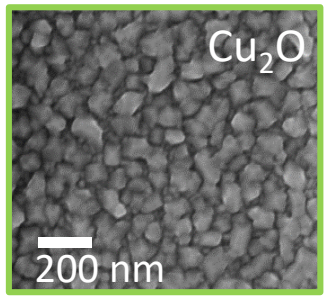
ALD enables local epitaxial growth of Cu_2O on ZnO

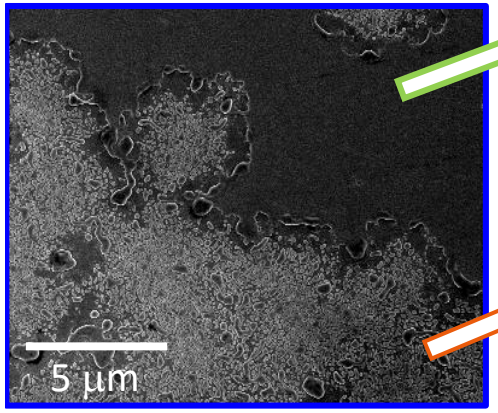
[110] Cu_2O ∥ [001] ZnO (out-of-plane); [001] Cu_2O ∥ [010] ZnO (in-plane)

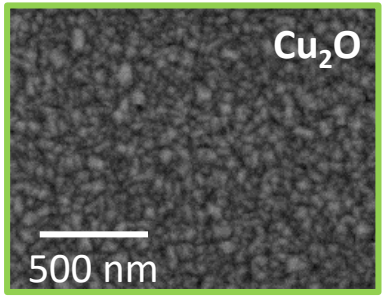
Conductivity-driven selectivity on ZnO

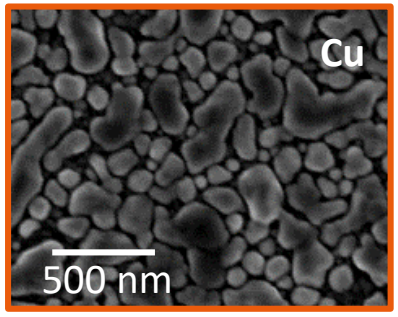












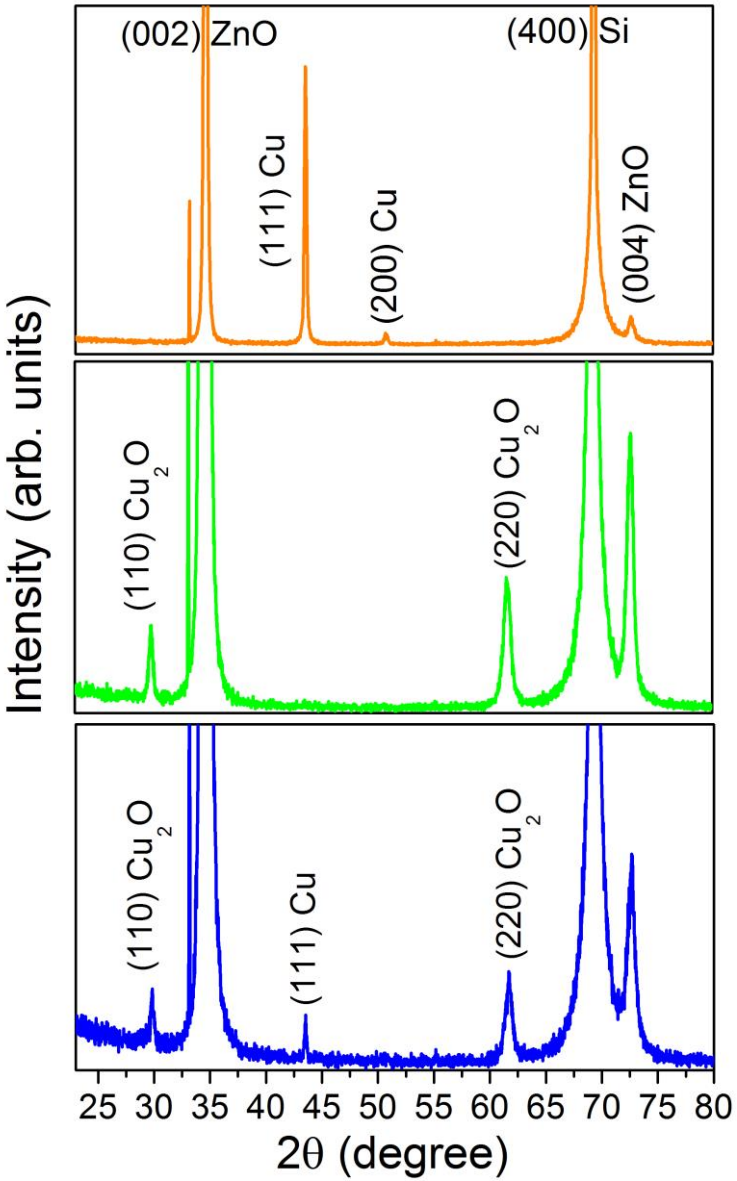
Cu

Cu_2O

Cu + Cu_2O

Sensitivity of Cu_2O and Cu growth to local conditions

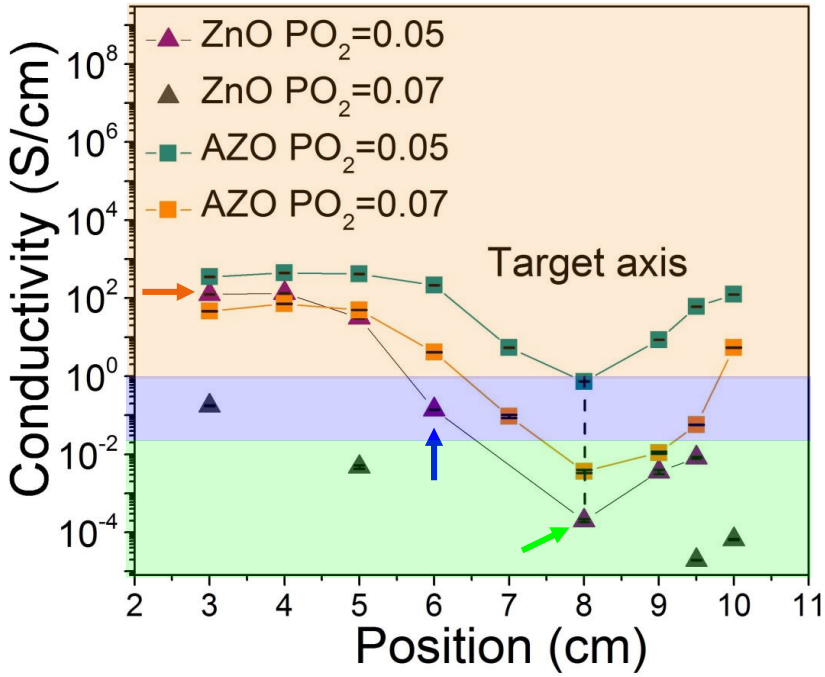
Conductivity-driven selectivity on ZnO



Cu

Cu_2O

Cu + Cu_2O

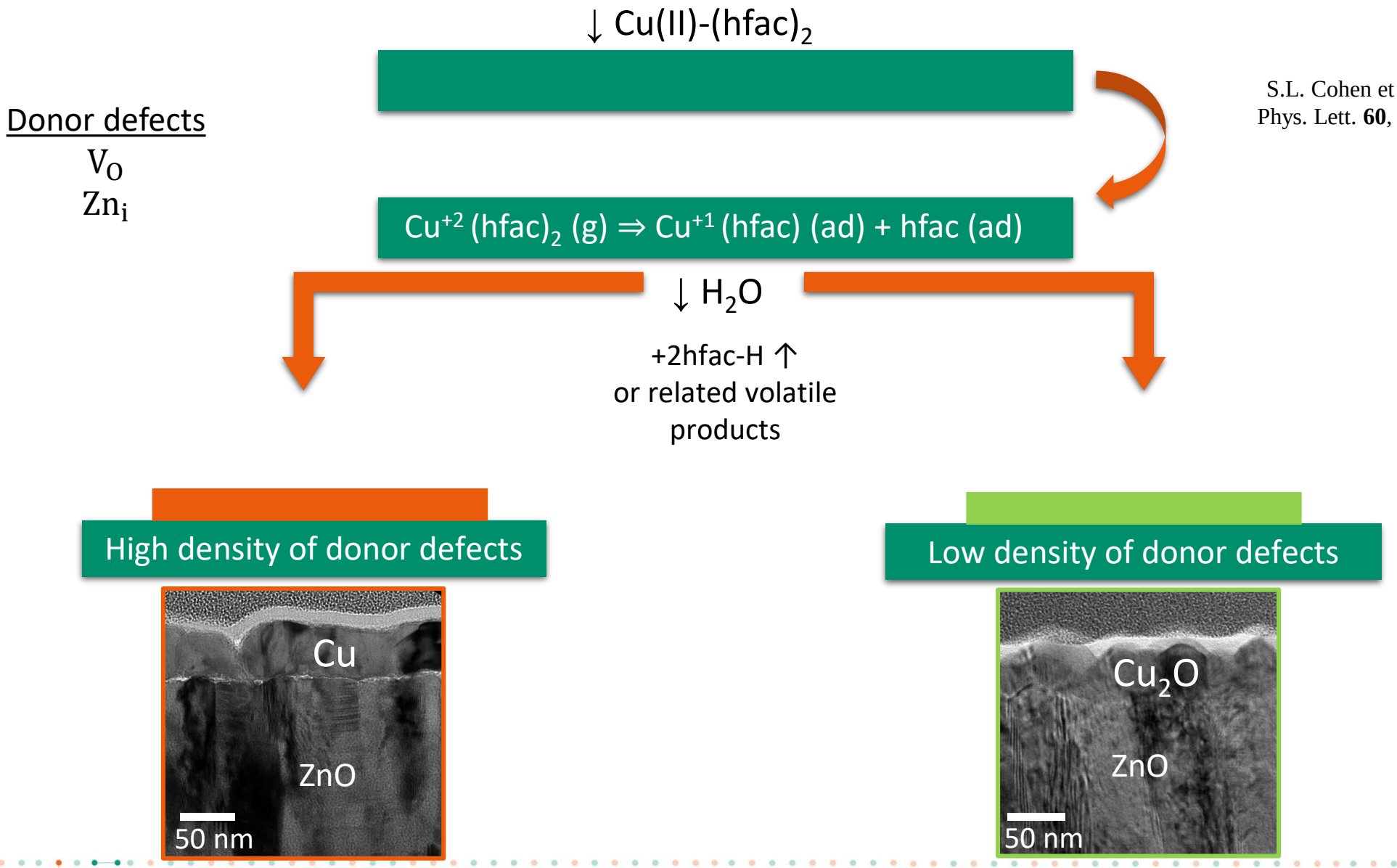


Cu — High conductivity — $\sigma > 10\ S/cm$

mixture

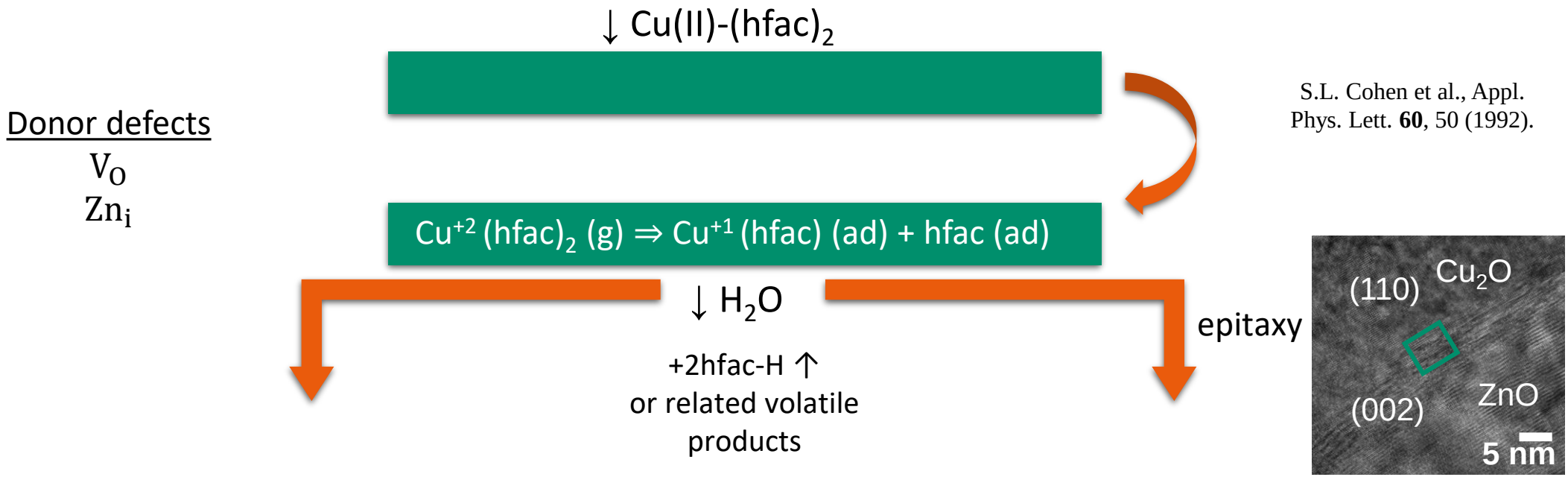
Cu_2O — Low conductivity — $\sigma < 10^{-2}\ S/cm$

Selective growth mechanism



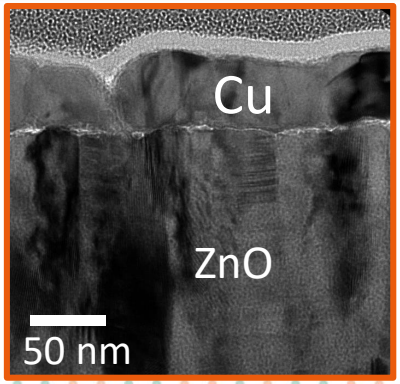
S.L. Cohen et al., Appl. Phys. Lett. **60**, 50 (1992).

Selective growth mechanism

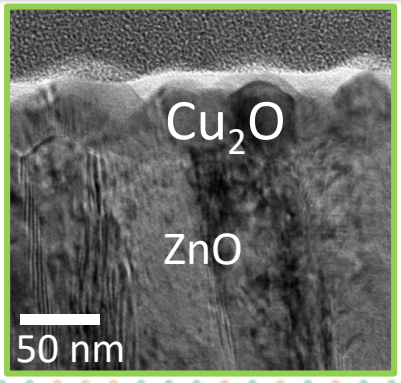


S.L. Cohen et al., Appl. Phys. Lett. **60**, 50 (1992).

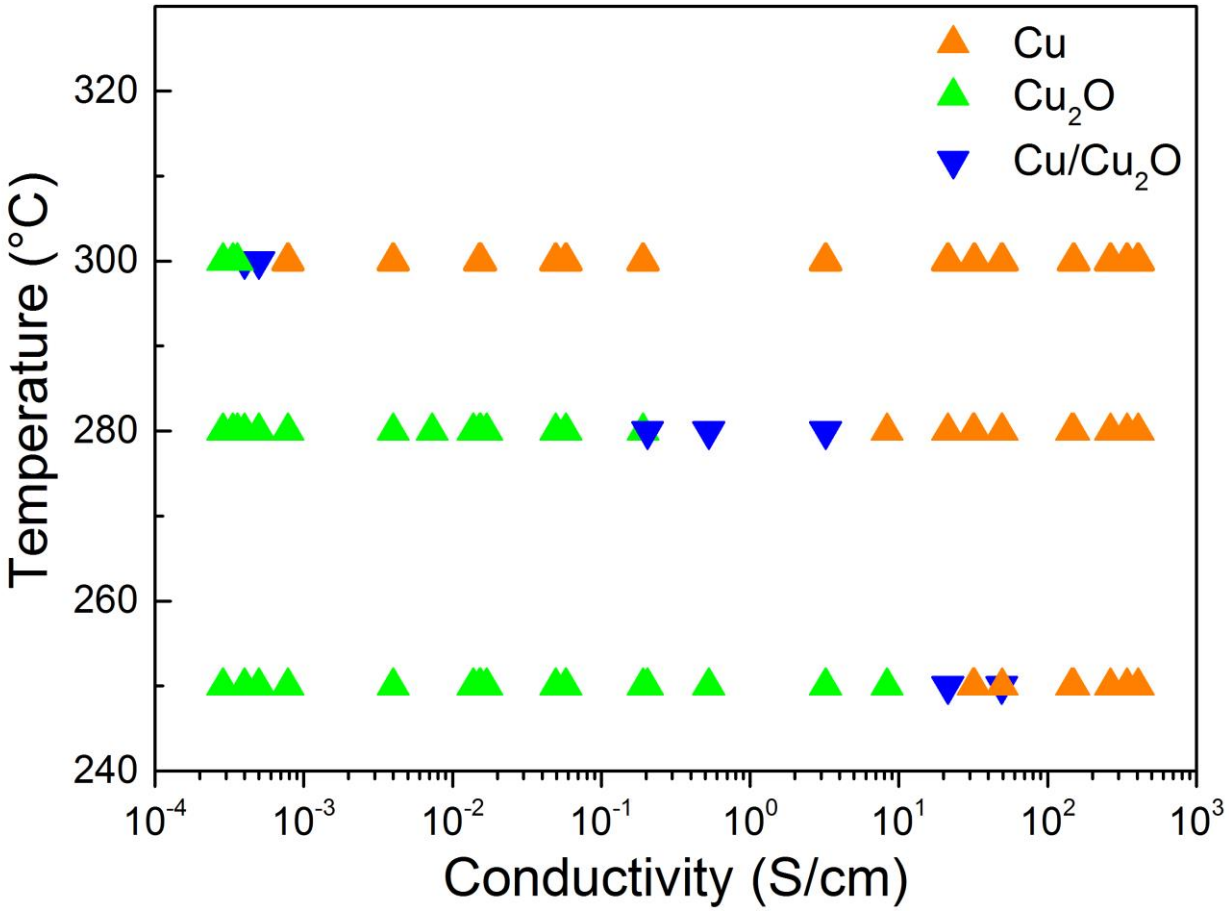
High density of donor defects



Low density of donor defects



Selective deposition driven by temperature



$Cu^{2+} \rightarrow Cu^{0}$

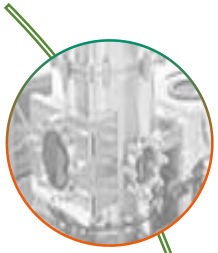
Higher temperature → Favors metallic Cu deposition

$Cu^{2+} \rightarrow Cu^{1+}$

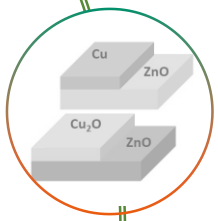
Lower temperature → Favors Cu_2O deposition

Higher deposition temperature favors the growth of metallic Cu → providing the extra energy necessary to further reduce $Cu^{+1} \rightarrow Cu^{0}$.

Outline



Experimental techniques



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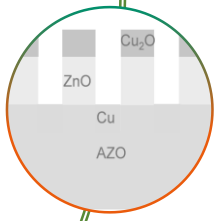
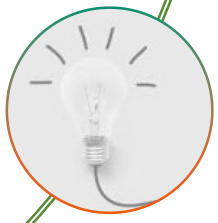


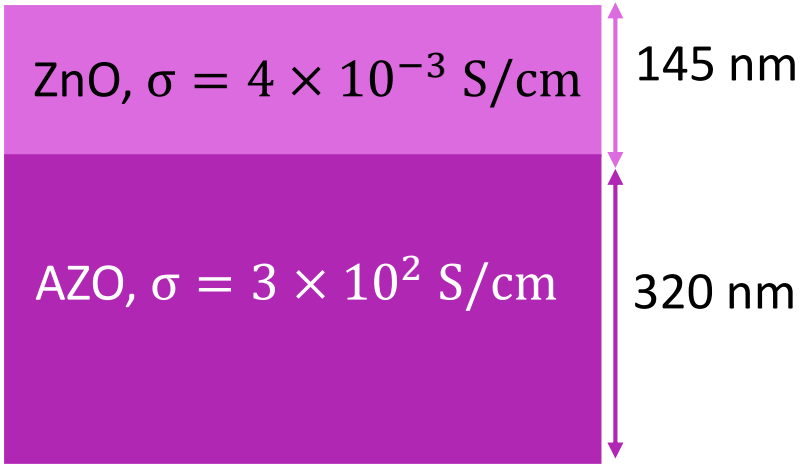
Fabrication of Cu_2O/ZnO/AZO/Cu-back electrode segmented microjunctions



Conclusions

Area-selective ALD on a patterned bi-layer

Bi-layer structure



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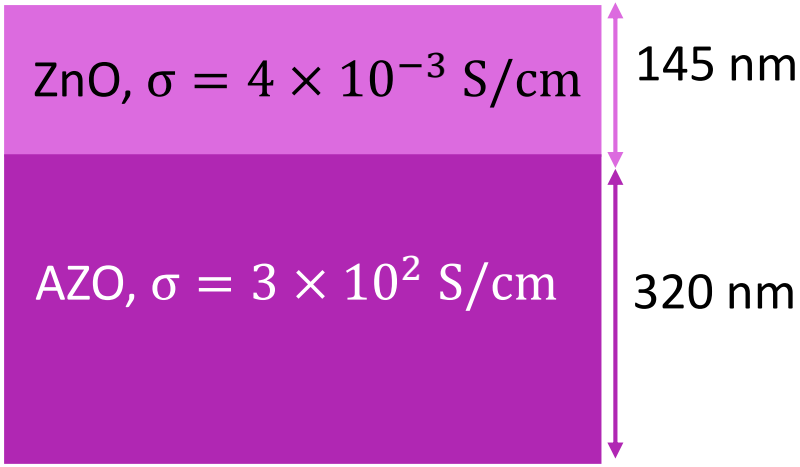
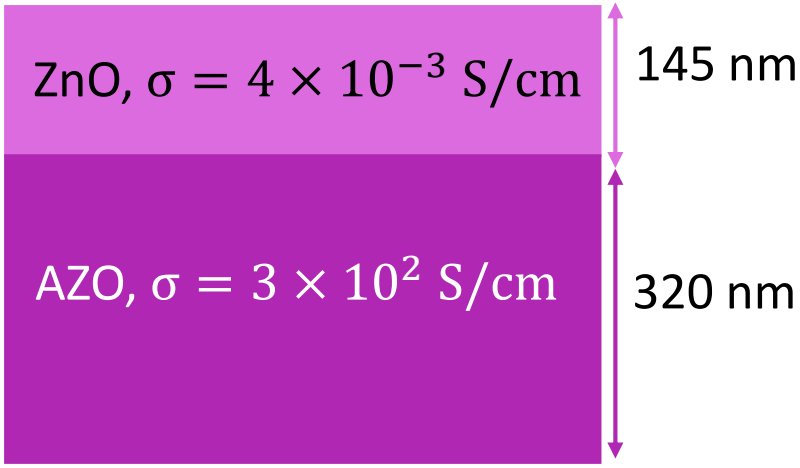
Bi-layer structure



Electron Beam Lithography (PMMA resist)
Ion beam etching

Area-selective ALD on a patterned bi-layer

Bi-layer structure



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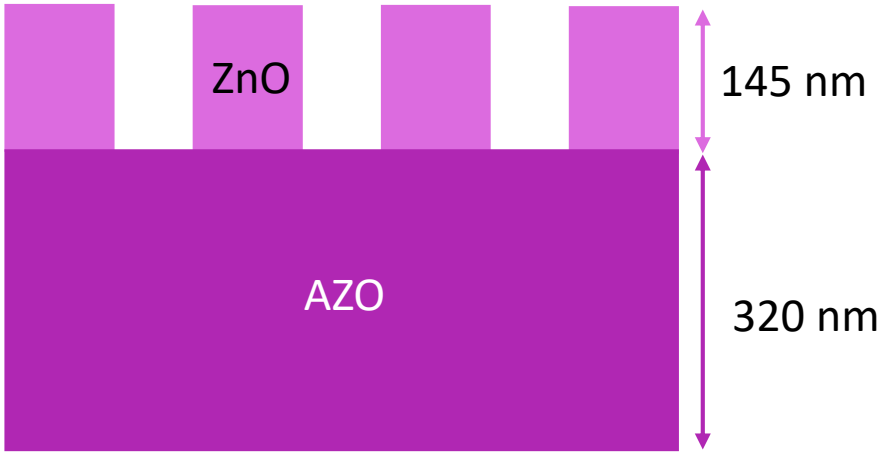
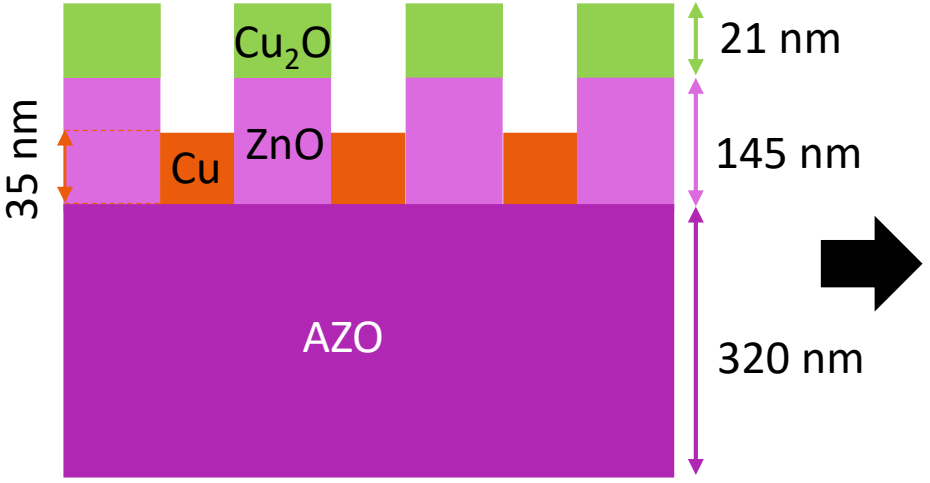
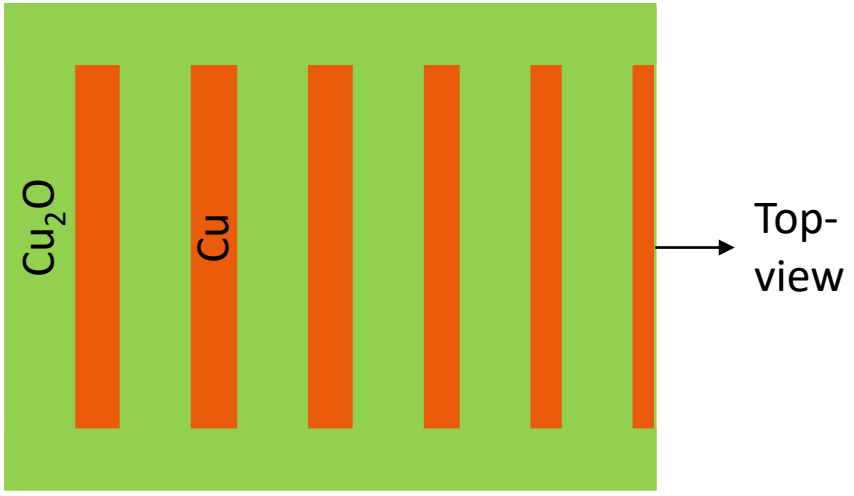
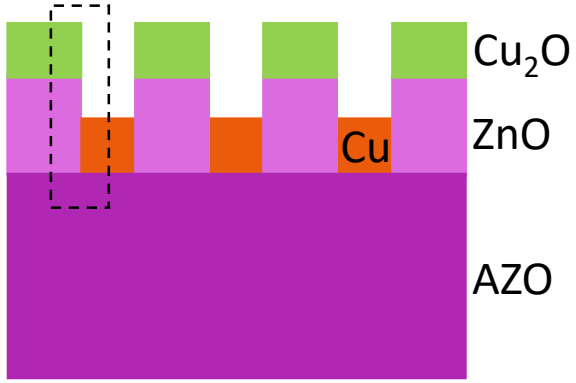




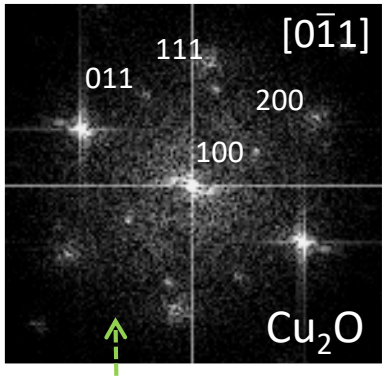


Area-selective ALD on a patterned bi-layer

T = 280°C
5 000 ALD cycles



Area-selective ALD on a patterned bi-layer



T = 280°C
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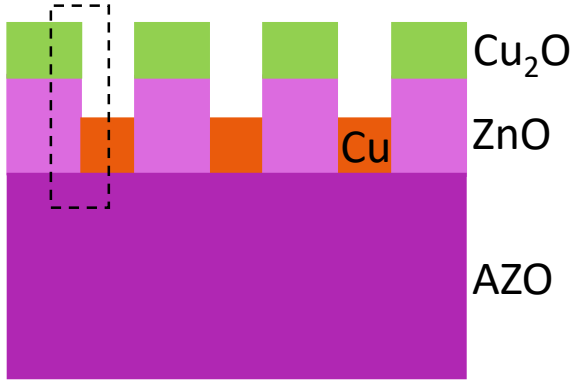

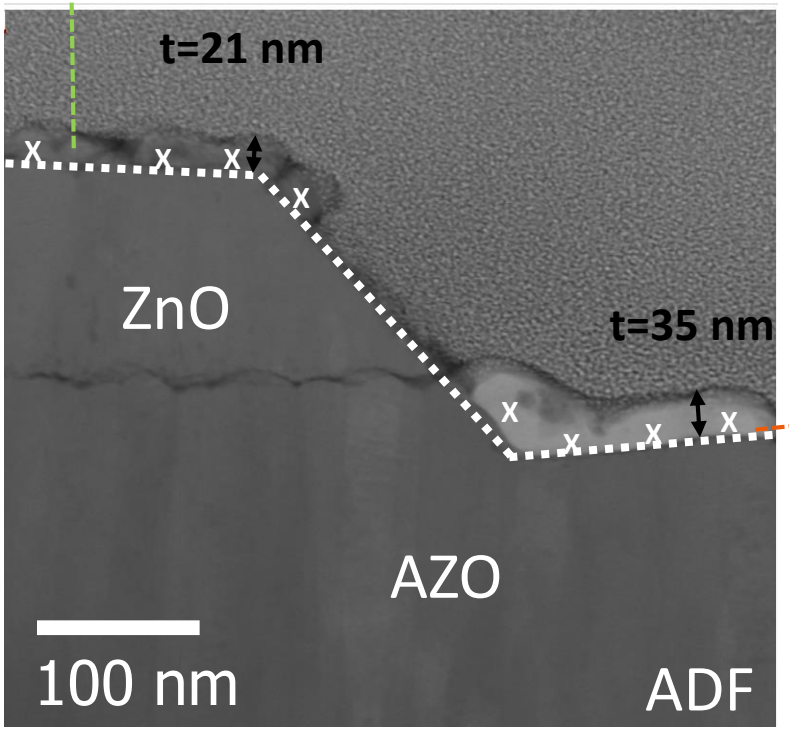

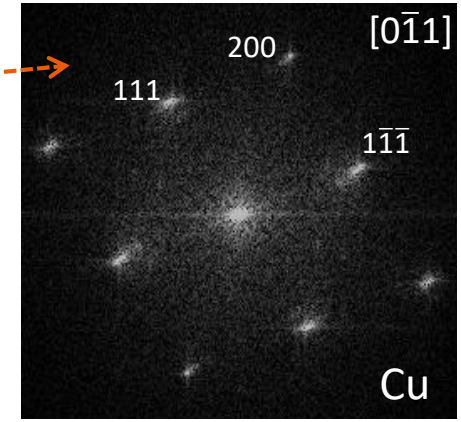

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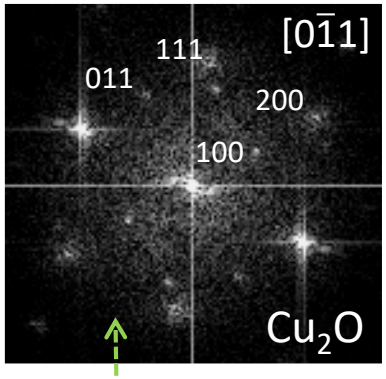

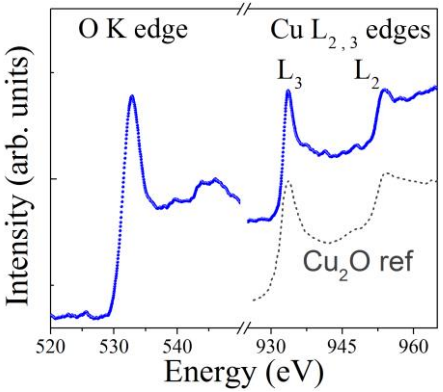

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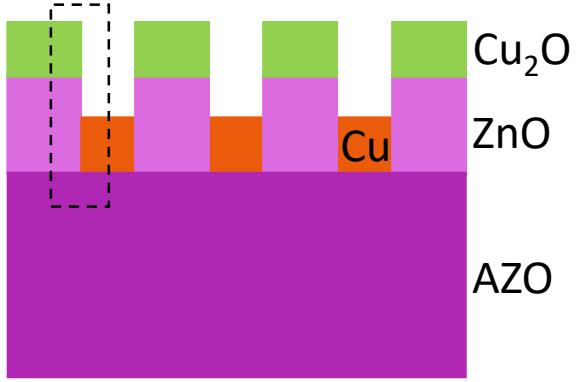
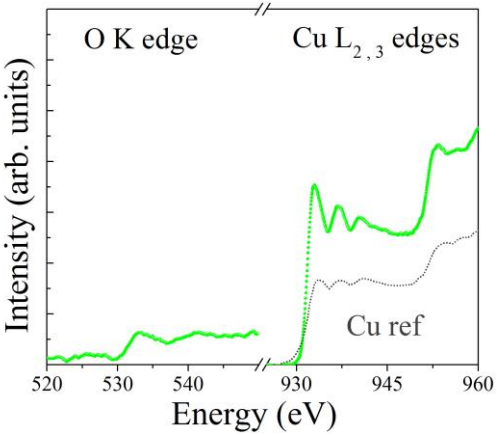
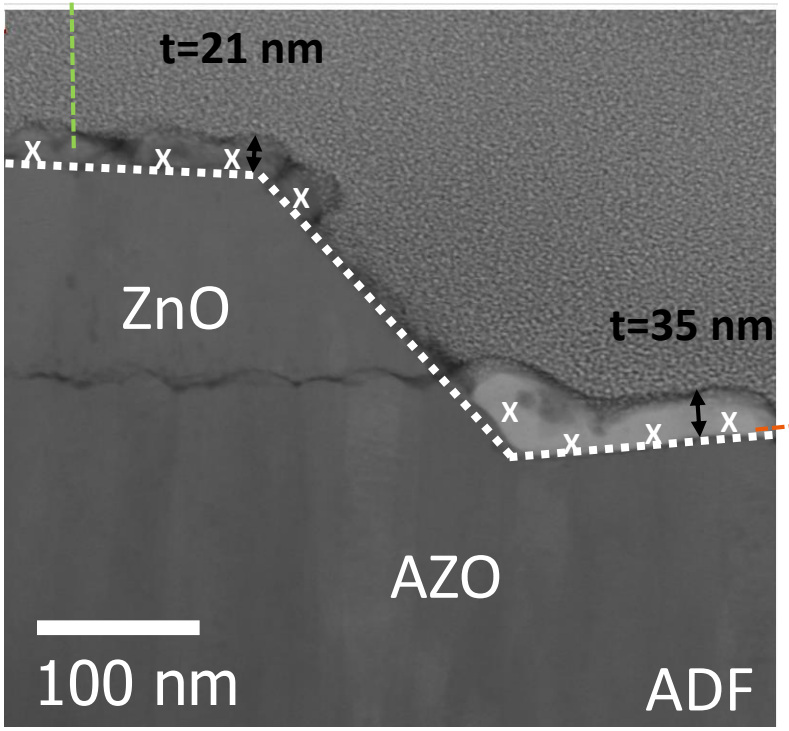
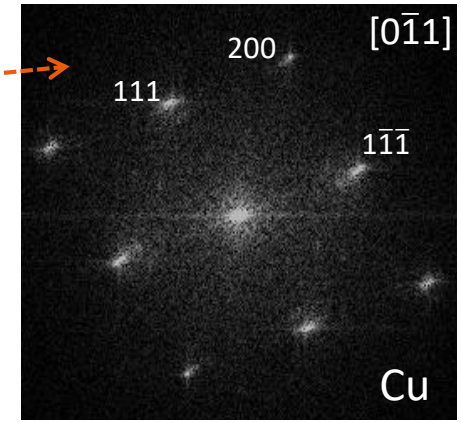


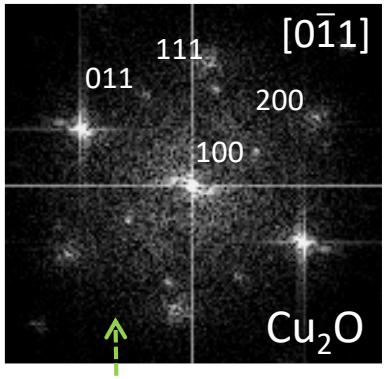


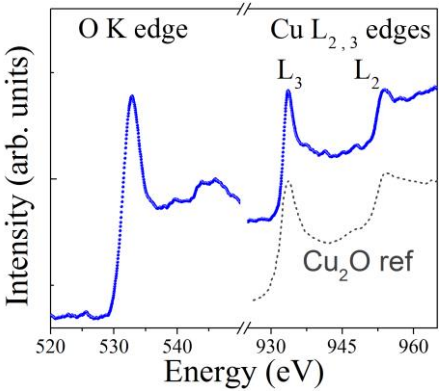




EELS Data Base, 2007

Area-selective ALD on a patterned bi-layer





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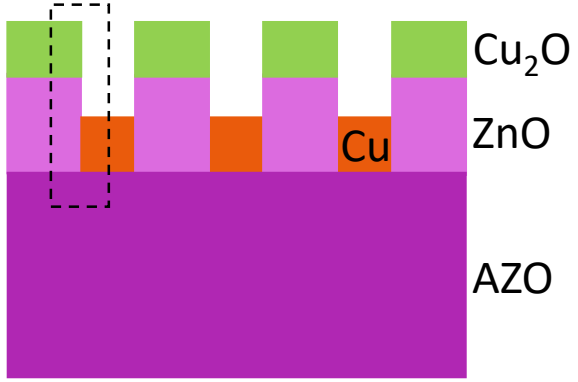
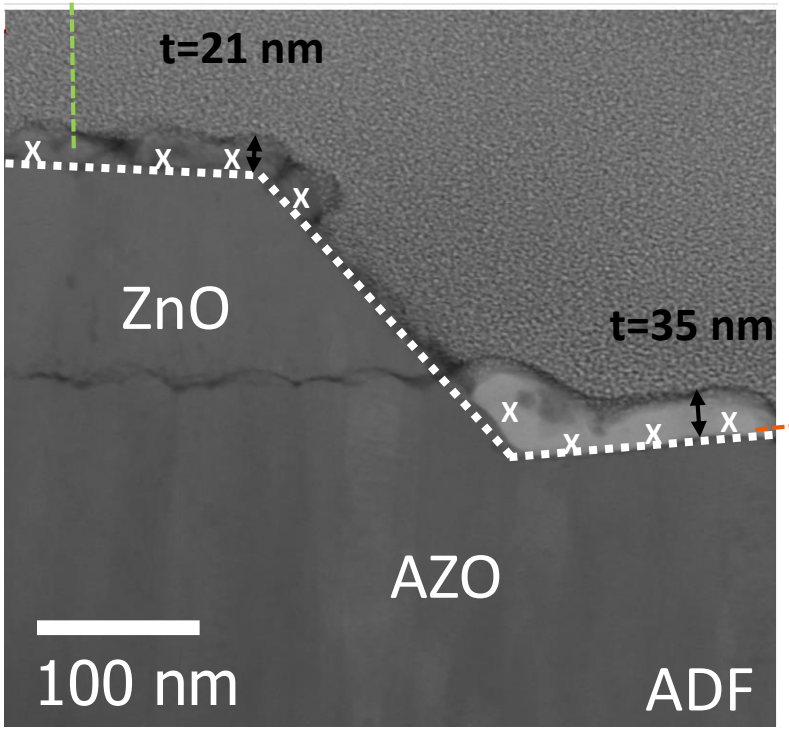
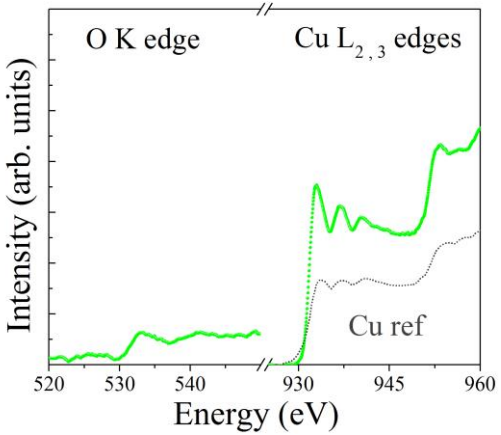
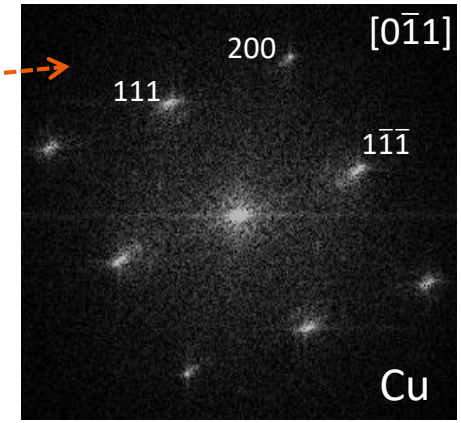
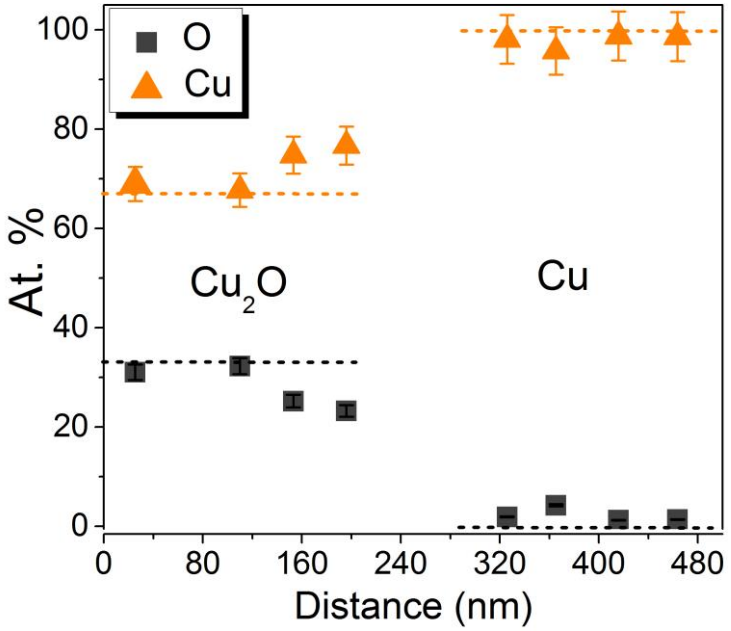




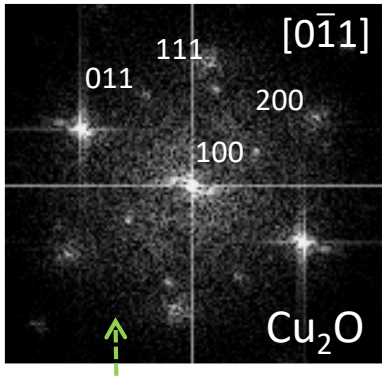


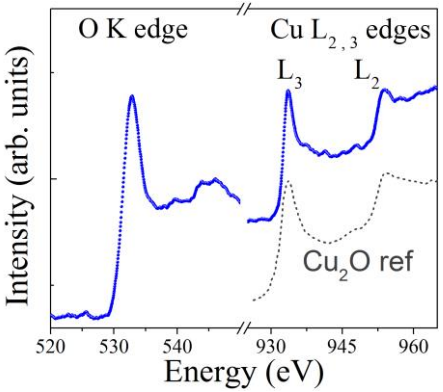




EELS Data Base, 2007

Area-selective ALD on a patterned bi-layer





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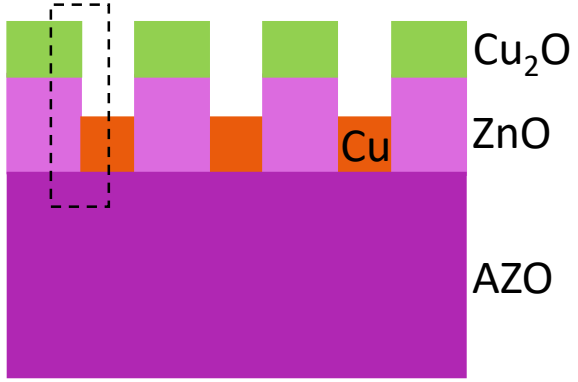
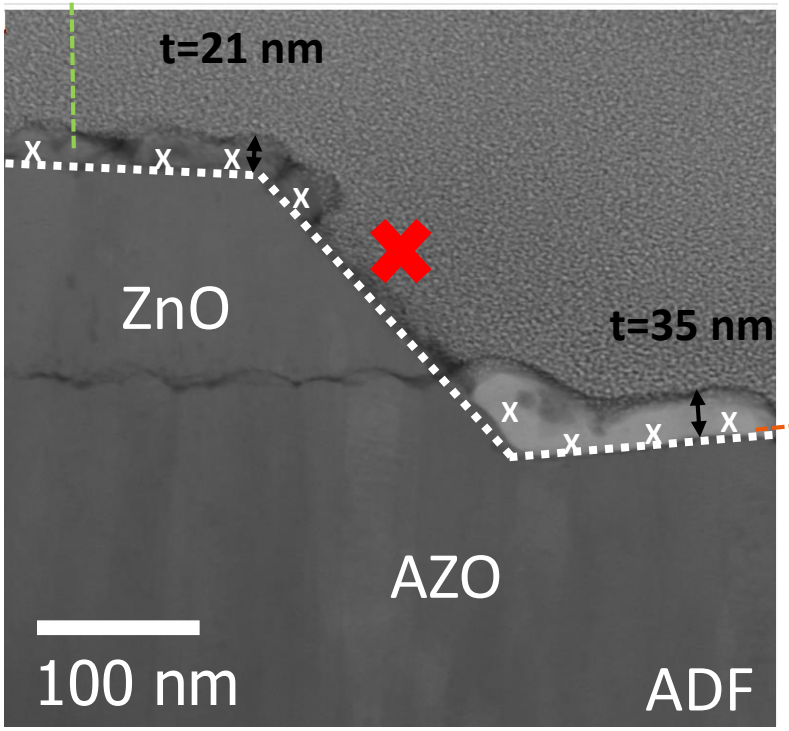
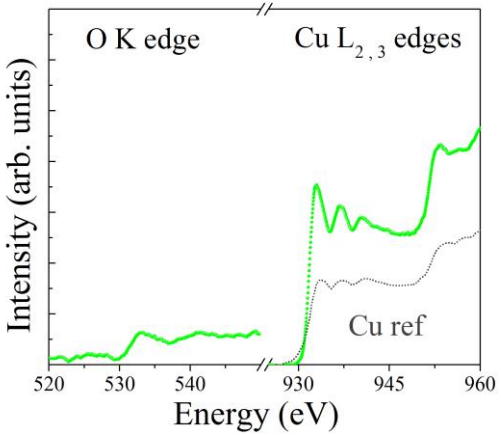
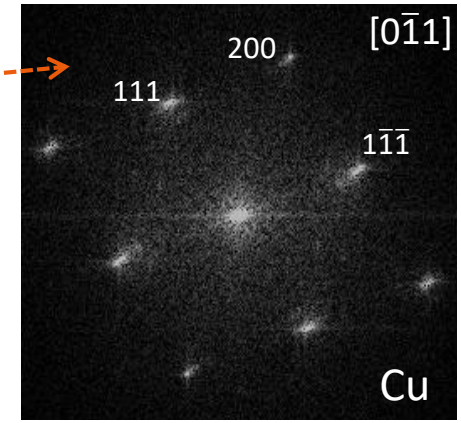
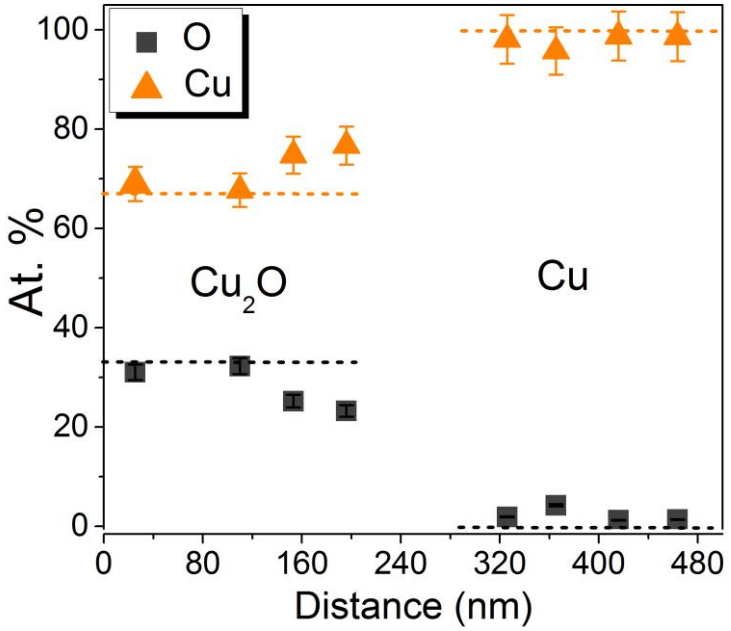




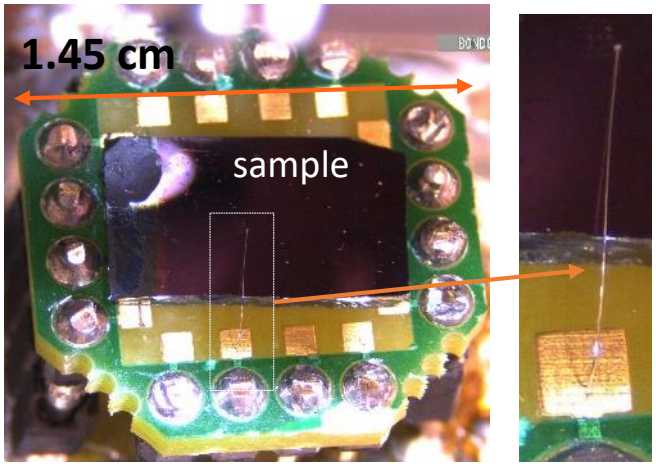


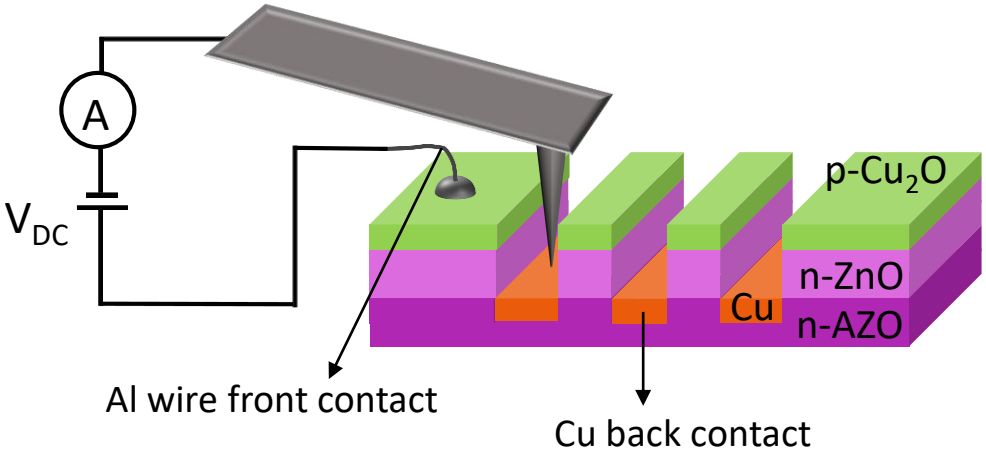




EELS Data Base, 2007

Electrical characterization of the micro-junctions





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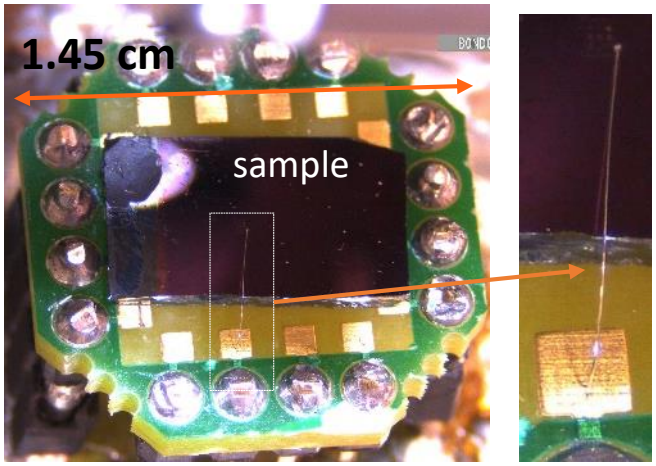
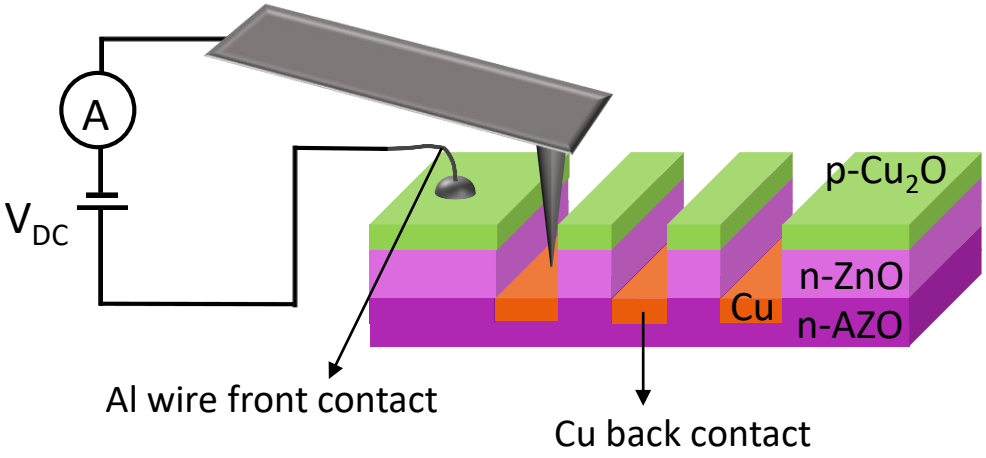
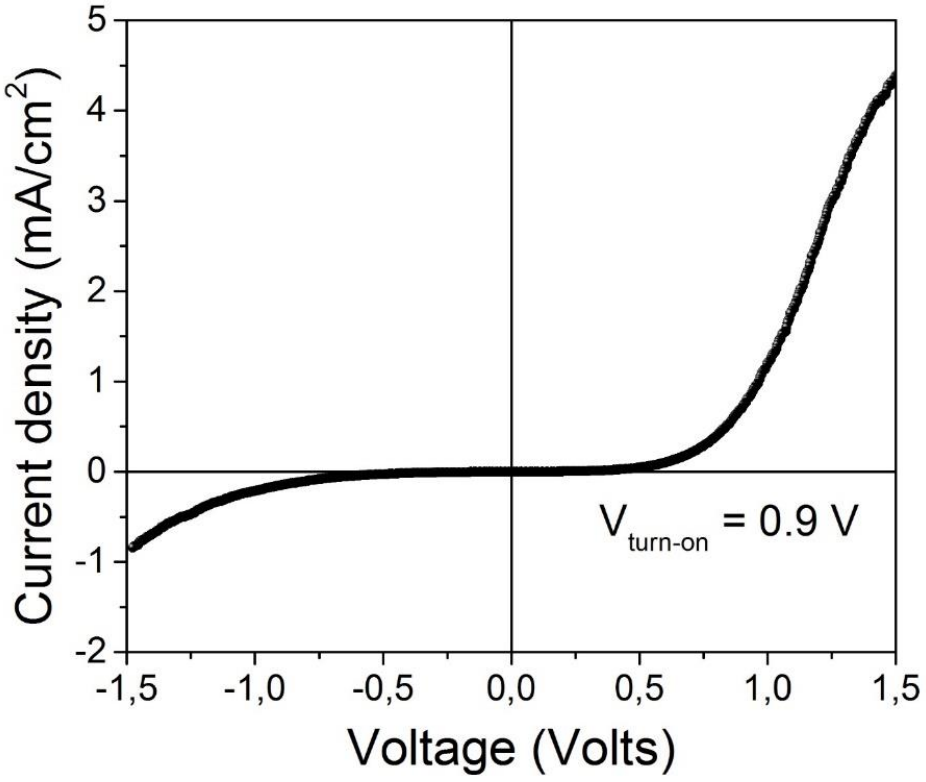
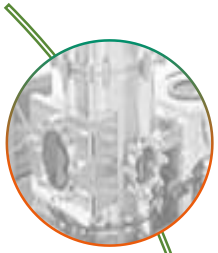






C. de Melo et al., ACS Appl. Mater. Interfaces **10,** 37671 (2018).

Outline



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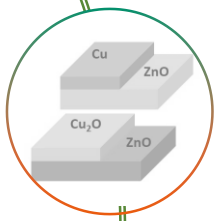

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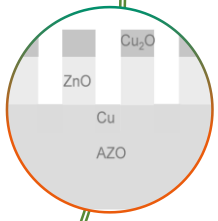

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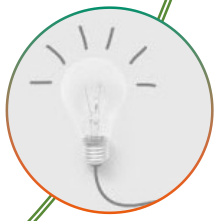

Conclusions

Conclusions

- Area selective atomic layer deposition of Cu_2O and metallic Cu was achieved based on the inherent selectivity of the $Cu(hfac)_2$ precursor toward different ZnO surfaces with different conductivity/density of donor defects.

- The selective growth of these materials allows the fabrication of p-Cu_2O/n-ZnO micro-junctions with the Cu film deposited on top of the Al-doped ZnO layer working as electrical contact. The micro-junctions show a non-linear rectifying behavior typical of a p-n junction, as confirmed by conductive atomic force microscopy.

- This configuration is a first approach of the many different ones than could be achieved. Defining otherwise the conductivity zones one would create different interfaces, allowing the formation of different architectures. These results are very promising for low-cost all-oxide transparent microelectronics.

Acknowledgements

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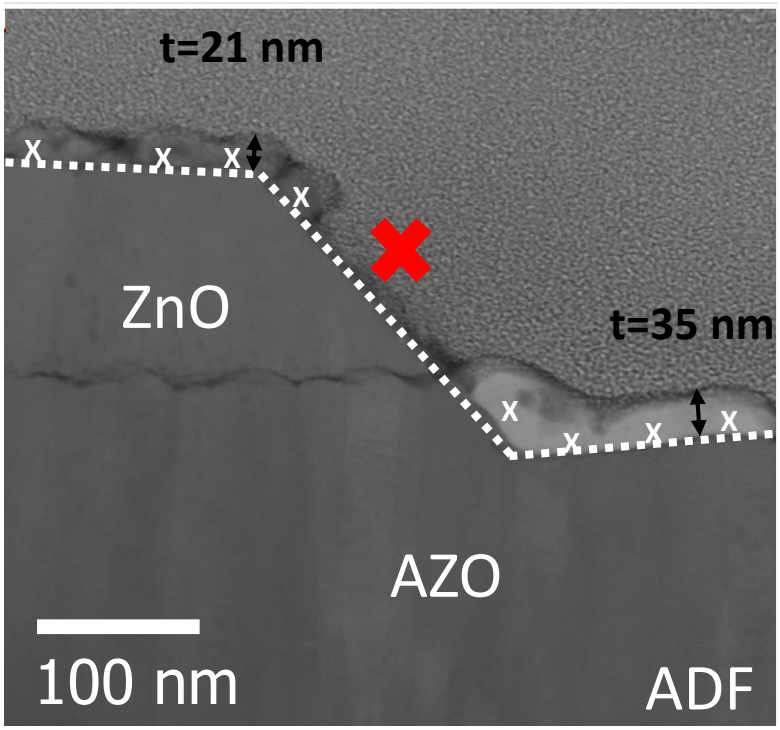
Université franco-allemande Deutsch-Französische Hochschule

CC-DAUM

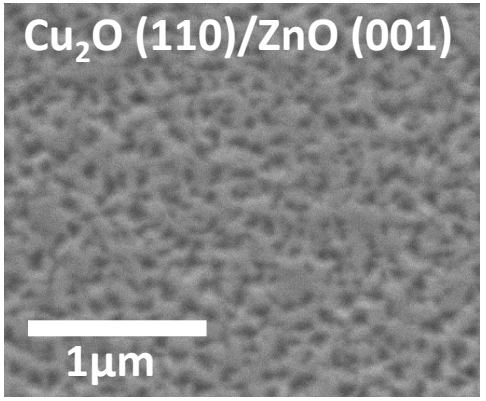
Education and Culture

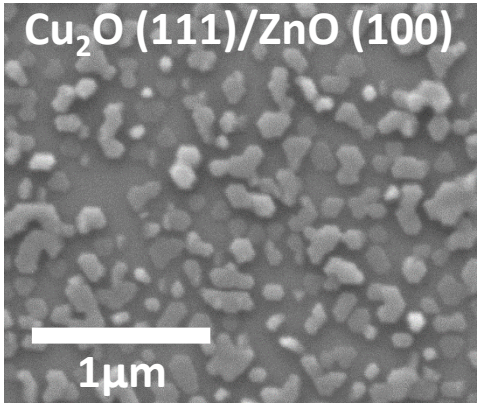
Erasmus Mundus

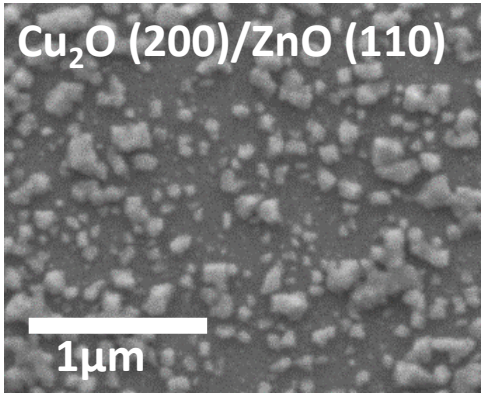
Area-selective ALD on a patterned bi-layer



Cu_2O growth on monocrystalline ZnO substrates







Surface chemistry and structure of the underlying substrates strongly impact the growth of the Cu_2O films

Selective growth mechanism

↓ Cu(II)-$(hfac)_2$

Donor defects

V_O

Zn_i

$Cu^{+2} + Zn_i{}^{0} \Rightarrow Cu^{+1} + Zn_i{}^{+1}$

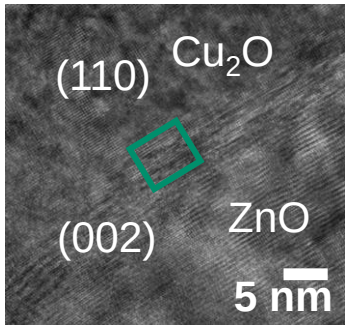
$Cu^{+2}(hfac)_2$ (g) ⇒ Cu^{+1} (hfac) (ad) + hfac (ad)

↓ H_2O

+2hfac-H ↑
or related volatile products

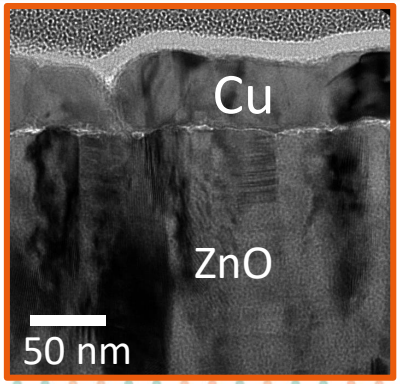
S.L. Cohen et al., Appl. Phys. Lett. **60**, 50 (1992).

epitaxy

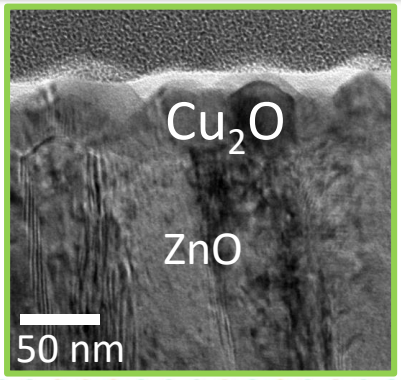


$Cu^{+1} + Zn_i{}^{+1} \Rightarrow Cu^{0} + Zn_i{}^{+2}$

High density of donor defects



Low density of donor defects



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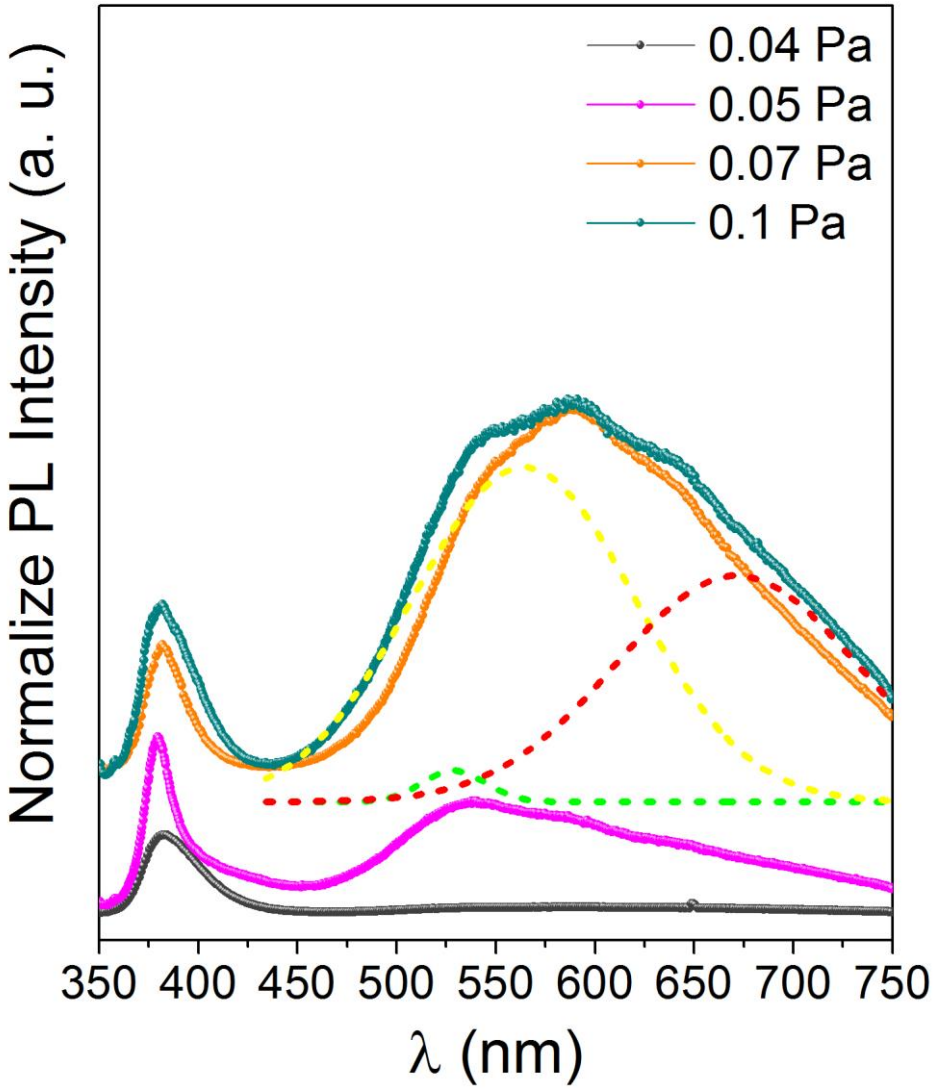
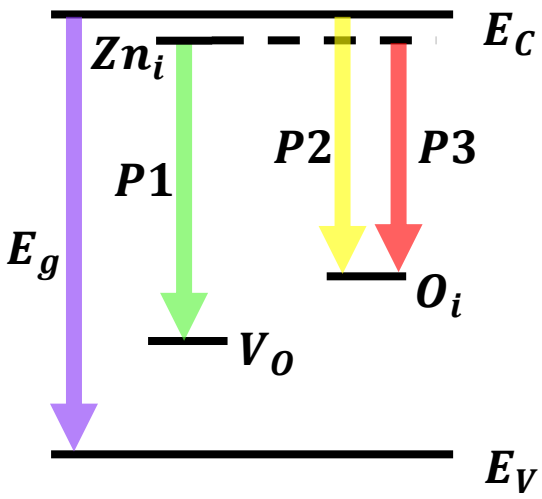
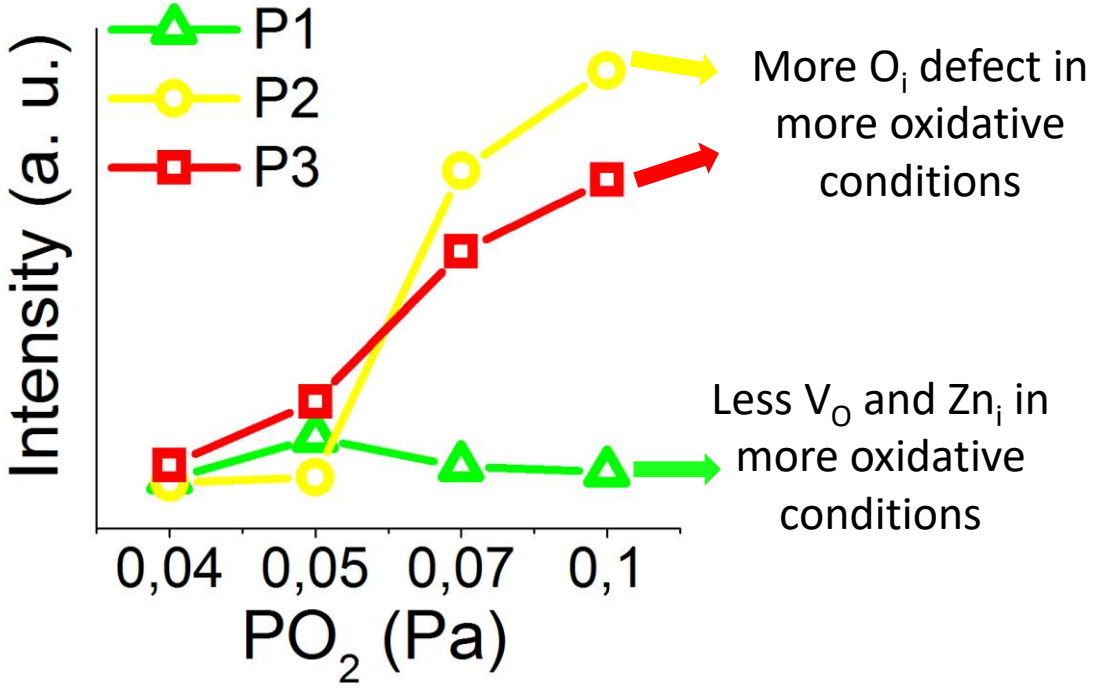
Photoluminescence







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