

Functional P-type and N-type Semiconductor thin films for the use in P-N Junction Diodes grown by Closed Field Magnetron Sputtering

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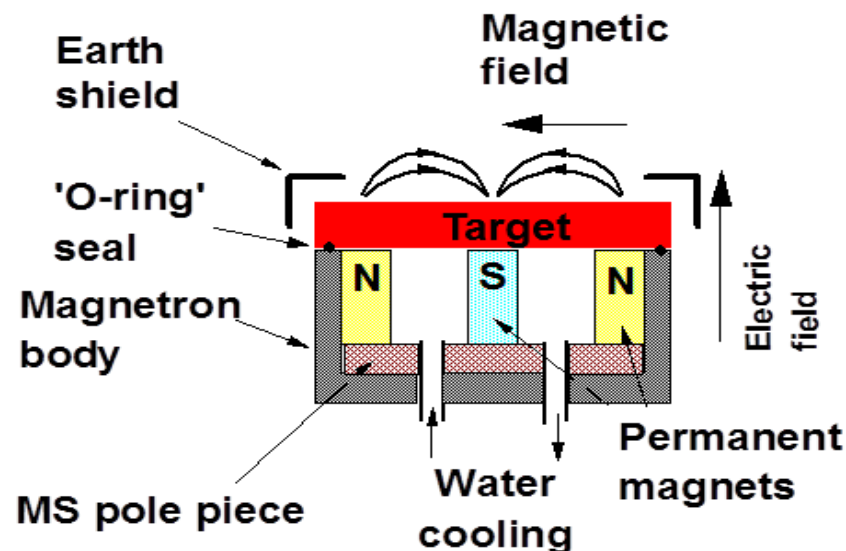
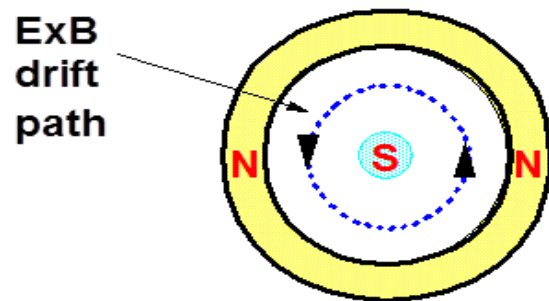
Objectives

Develop low cost p-n junction diode using $\text{SnF}_2\text{:SnO}_2$ and CuAlO_2 semiconductor thin films

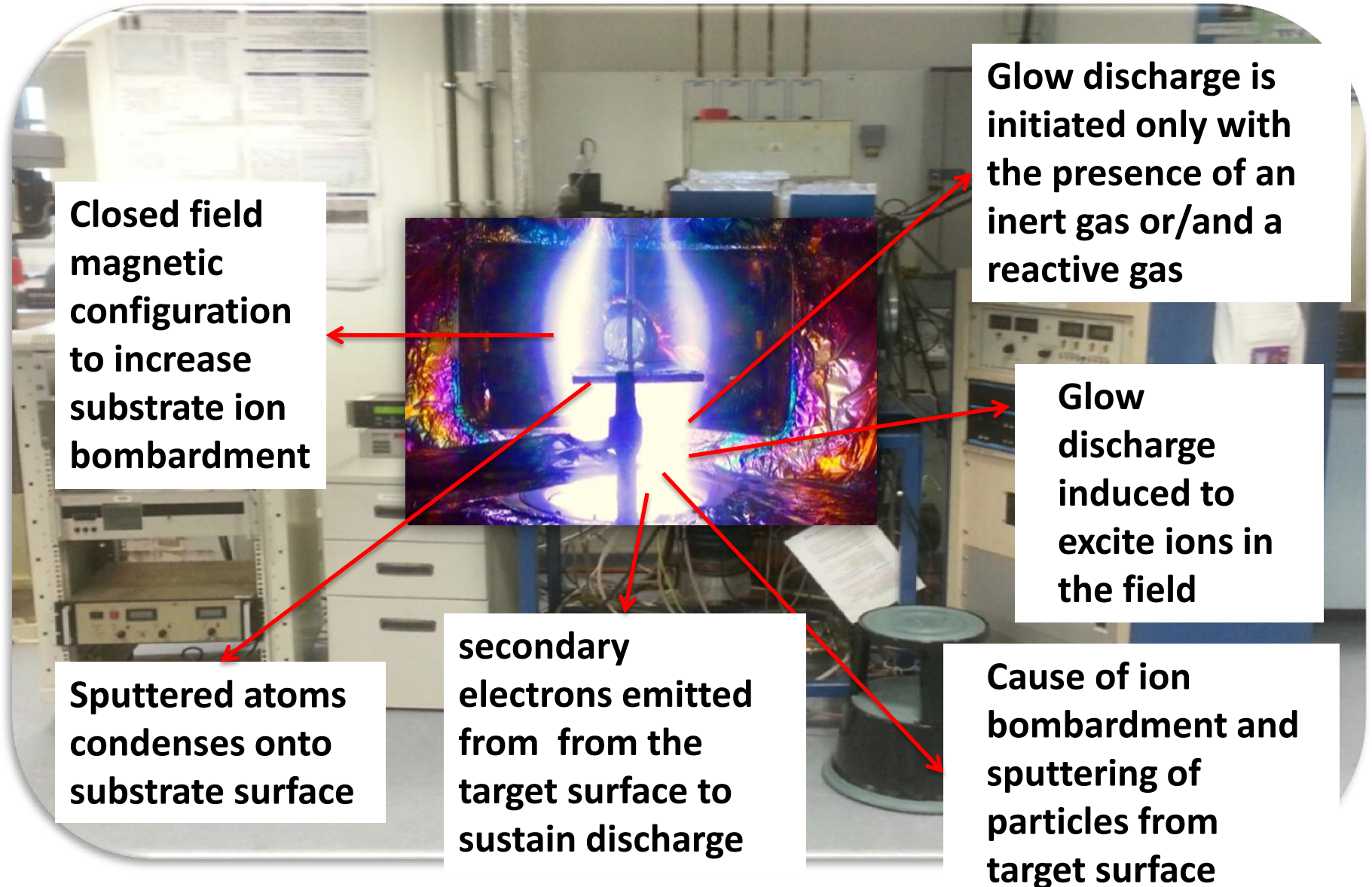
- Mid-frequency pulsed DC closed field unbalanced magnetron sputtering technique
- Loosely packed un-sintered blended powder targets
- Optimised operating conditions
- As-deposited n-type and p-type functional thin films

Sputter Deposition

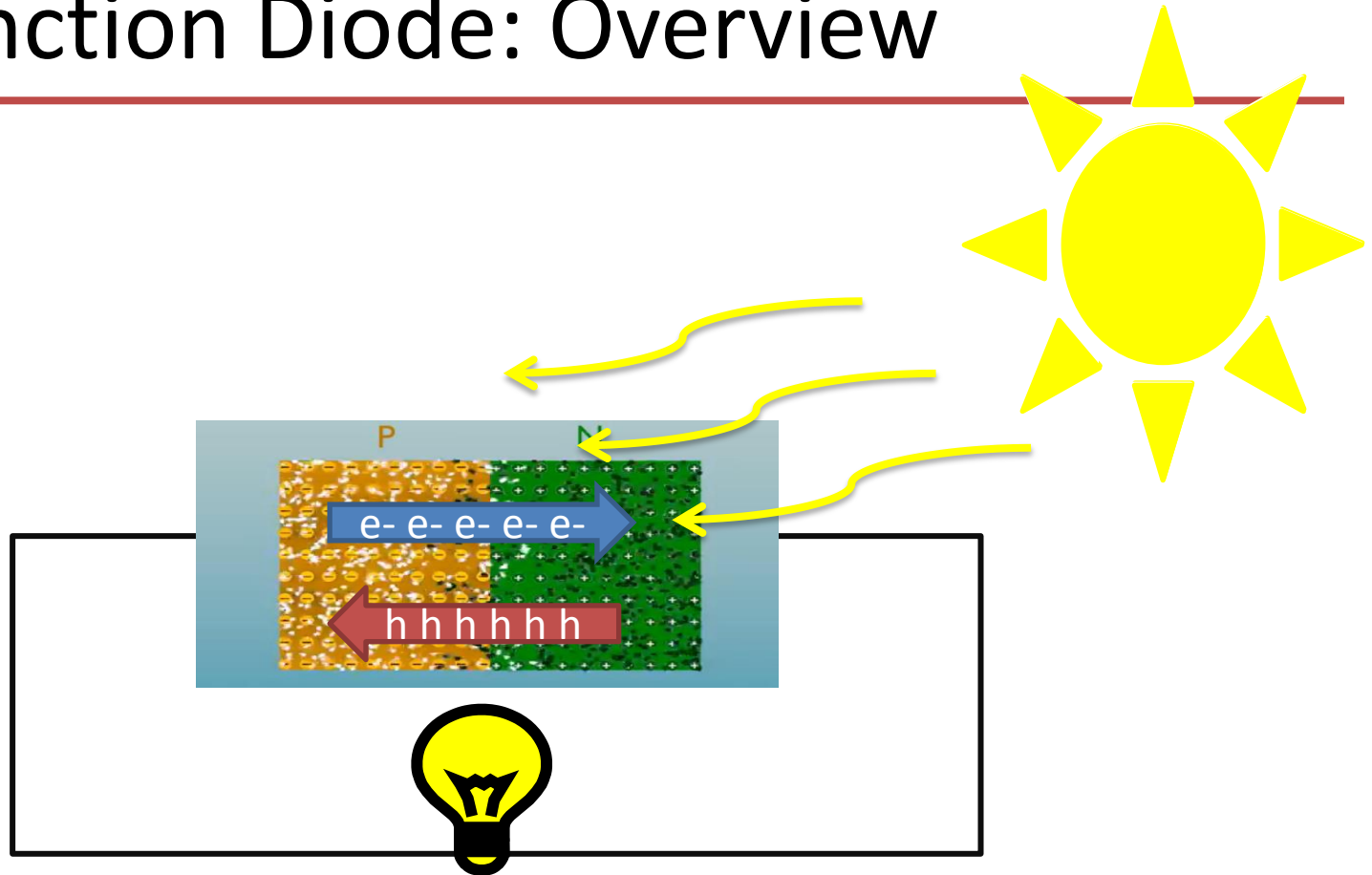
- Non-thermal evaporation technique
- Removal of atoms from target surface via momentum transfer of energetic ions of gaseous material
- Magnetic field used to improve the efficiency of the process and deposition rate



Pulsed DC magnetron sputtering technique

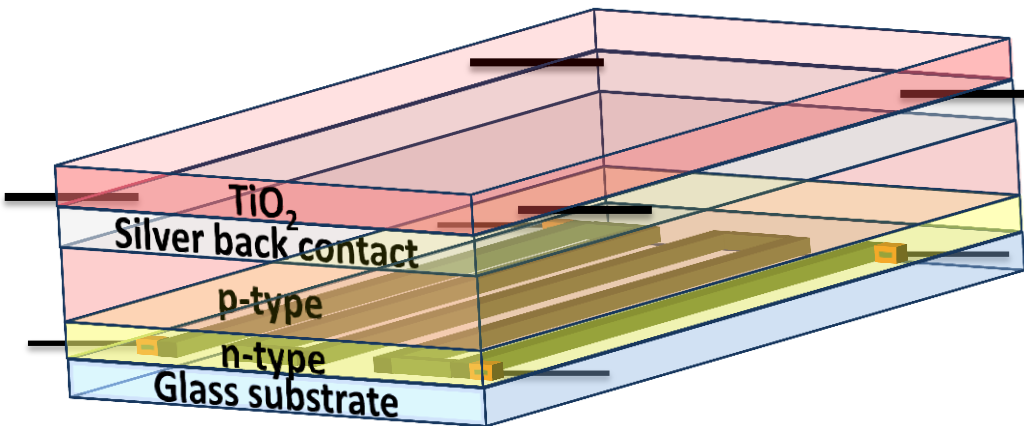


P-N Junction Diode: Overview



Connecting to a load, allows for electrons and holes to travel and recombine to the diode

Development process of p-n junction



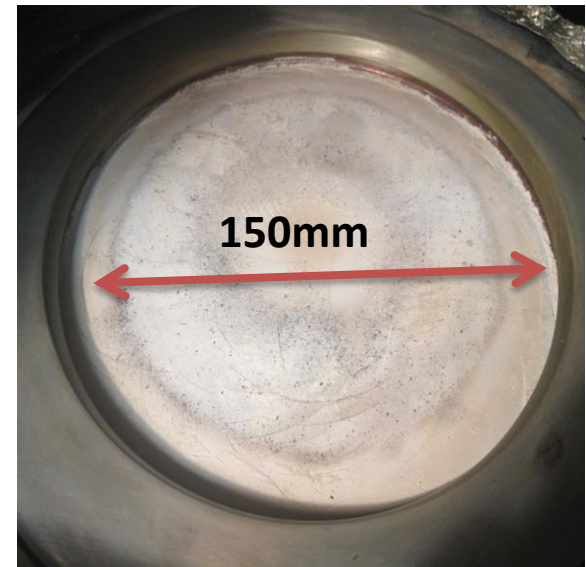
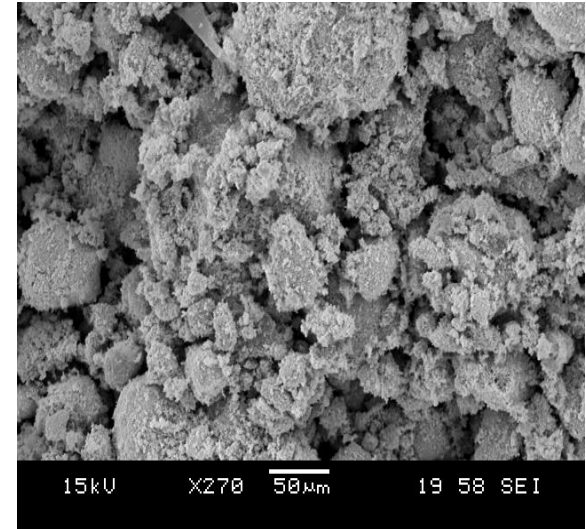
- **Titanium oxide:** 1um m thick film
Synthesised by sputtering Titanium powder target
- **Silver back contact:** 2um thick film
synthesised by sputtering silver powder target
- **p-type:** 600 nm synthesised by
reactively sputtering a mixed Cu:Al
powder target
- **n-type:** 400nm thick film
Synthesised by sputtering a
mixed SnF₂:SnO₂ powder target
- **Copper contacts:** 20um front contact
enabling connection to external DC
load deposited through a mask
- **Substrate:** 4 in² float glass substrate
Cleaned using IPA and RF plasma
treated at 200W for 10 mins

Powder Targets

- Particle size: 44 to 105 μm
- Mass of powder target: 60g
- Target thickness: 1.5mm

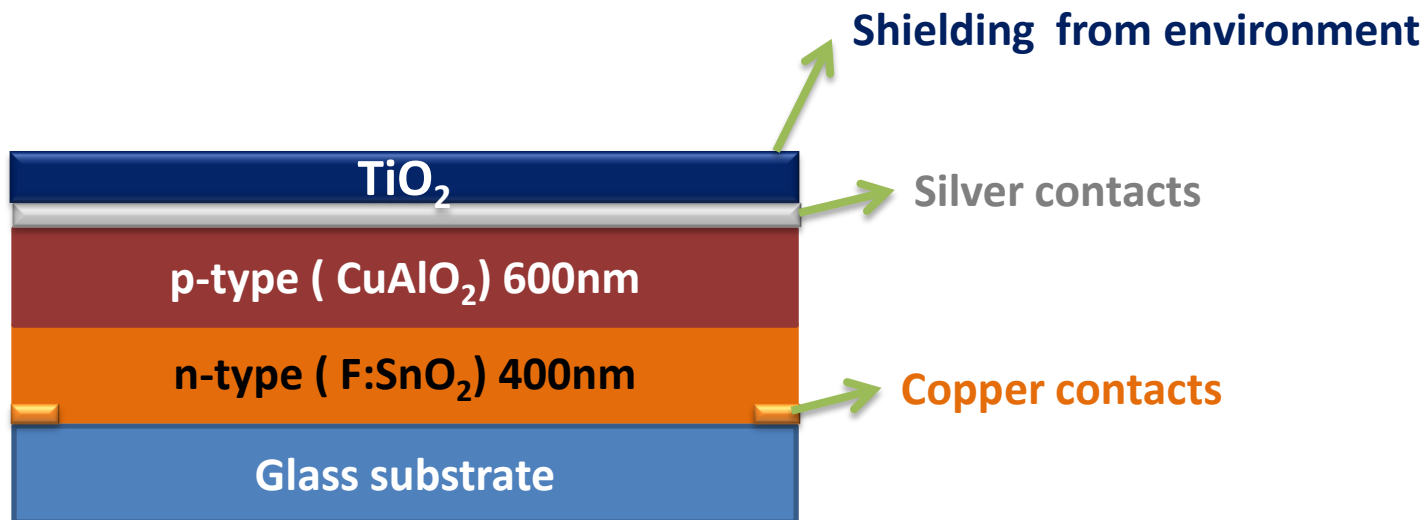
Target Mass Ratio

n-type		p-type	
SnO_2 (g)	SnF_2 (g)	Cu (g)	Al (g)
51	9	43.2	6.2



Electrical Contacts

- Front and back electric contacts were sputtered using copper and silver planar metal targets
- **Copper** Metal Target is used to sputter 20 um thick copper film onto the glass substrate
 - **Silver** Metal Target is used to sputter 2 um thick Silver film onto the CuAlO_2 layer



Experimental parameters

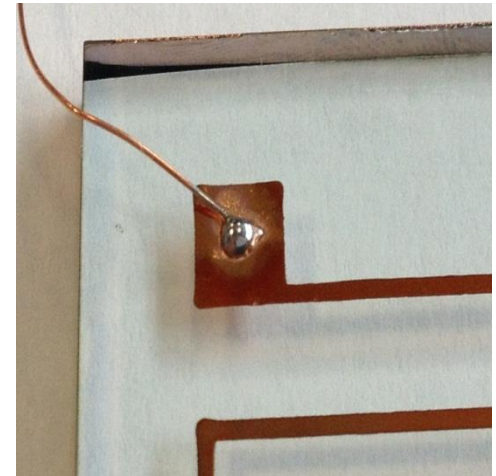
- N-type: Fluorine doping effect on the structure and opto-electrical property of tin oxide thin film
- P-type: Pulsing frequency and sputtering power effect on the structure and opto-electrical properties of the thin film using powder composition target ratio of 75at.%Cu (43.2g) and 25%at.Al (6.2g)
- TiO₂ used as a protective layer against environment conditions

Experimental Parameters	F:SnO ₂	Cu:Al	TiO ₂
Base Pressure (Pa)	2.1×10 ⁻⁴	2.1×10 ⁻⁴	2.1×10 ⁻⁴
Ar/O ₂ working pressure (Pa)	0.54	0.65	0.65
Deposition rate (nm/min)	27	8	8.25
Temperature during deposition (°C)	170	170	170
Film thickness (nm)	400	600	1000
Sputtering power (W)	400	350	400
Pulsing frequency (kHz)	200	100	100
Pulse duty cycle (%)	90	50	90
Deposition time (mins)	15	150	120

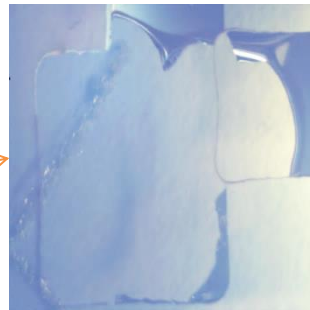
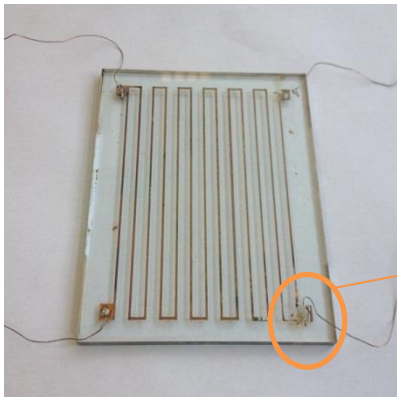
Results: Electric contacts

- Good adhesion was achieved by growing thicker contacts
- Optimised contact design to increase carrier extraction
- Coating of 20um thick was used to withstand excess heat from soldering iron

Electrical parameter	Copper	Silver
Conductivity	1.19E+05	3.47E+04



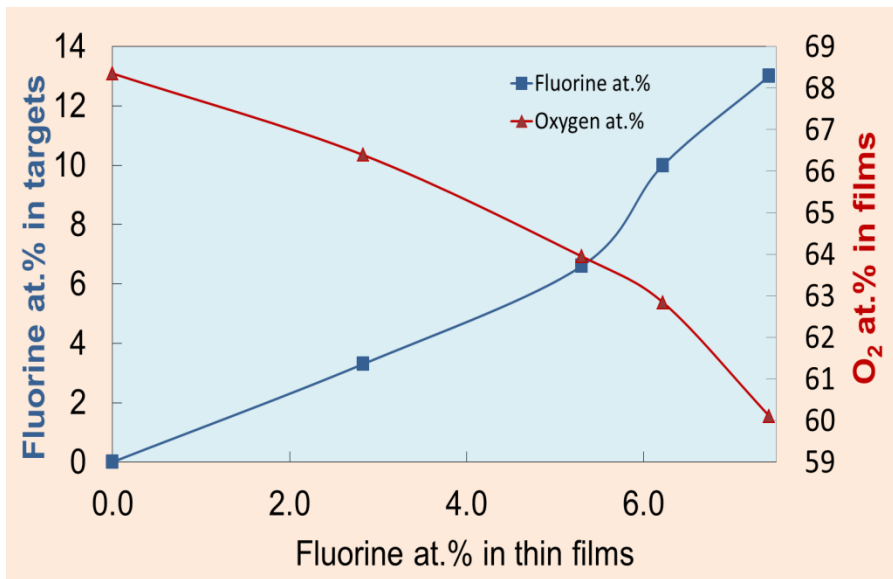
**Successful
soldering onto
copper contact
pads**



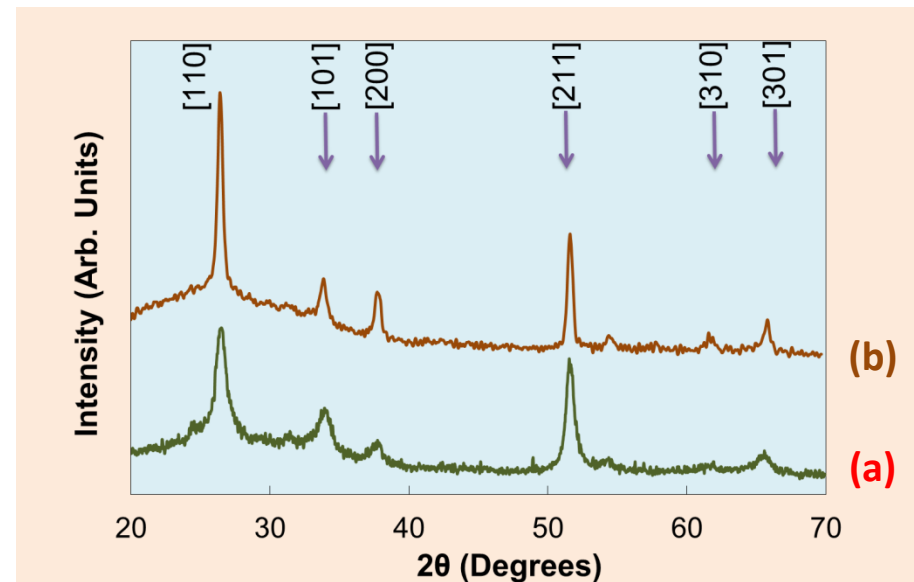
**Delamination
of contacts pads
With thickness
<1um**

F:SnO₂ Composition and structure

- Stoichiometric un-doped SnO₂ achieved
- Successful incorporation of fluorine into the SnO₂ lattice
- 6.22 at.% of fluorine in the lattice is the optimum composition, of those tested, for grain growth.



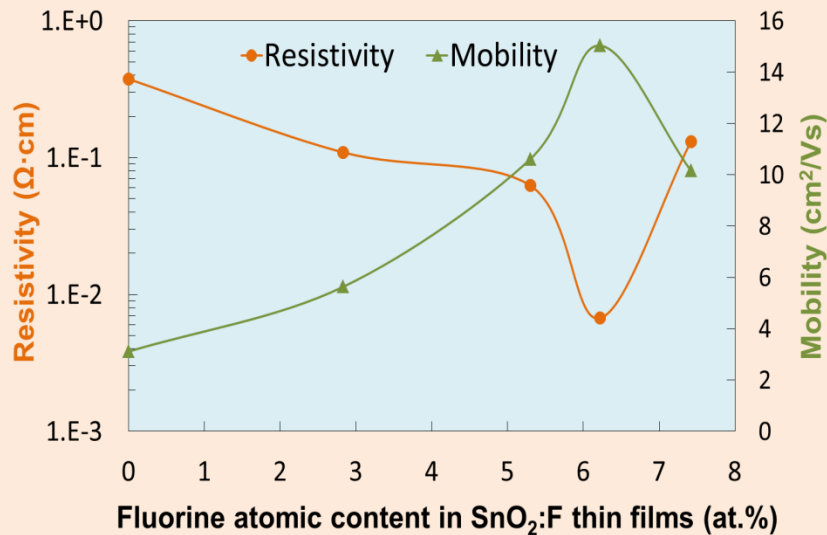
EDS analysis of F:SnO₂



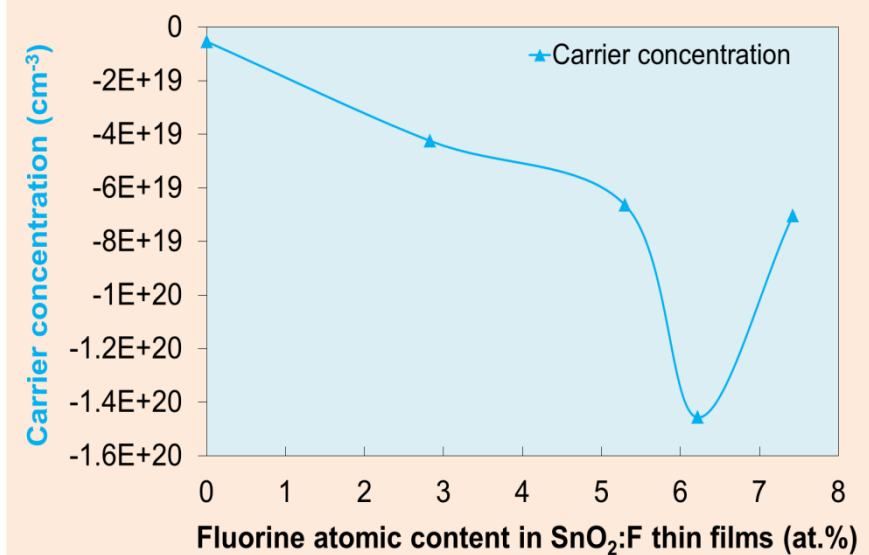
XRD structure: (a) SnO₂ (b) F:SnO₂

F:SnO₂ :Electrical properties

- **SnO₂** :Resistivity and mobility of $3.71 \times 10^{-1} \Omega \cdot \text{cm}$ and $3.1 \text{ cm}^2/\text{Vs}$ and a corresponding carrier concentration of $-5.5 \times 10^{18} \text{ cm}^{-3}$
- **F:SnO₂** : Best electrical properties are achieved at **fluorine** content **6.22 at.%**, corresponding to a resistivity of $6.71 \times 10^{-3} \Omega \cdot \text{cm}$, mobility of $15.1 \text{ cm}^2/\text{Vs}$ and a carrier concentration of $-1.46 \times 10^{20} \text{ cm}^{-3}$ for the as-deposited films.



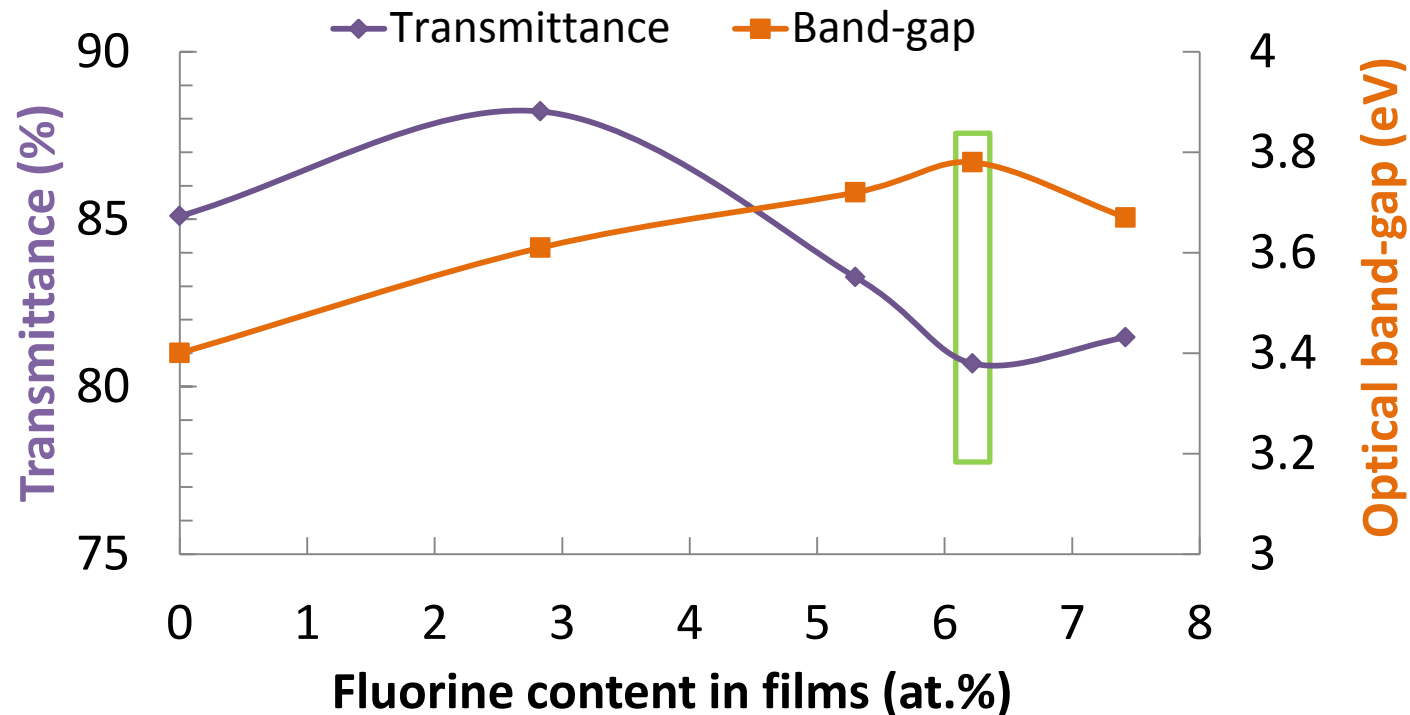
Resistivity and mobility at different fluorine concentration in FTO films.



Carrier concentration and conductivity at different fluorine concentration in FTO films.

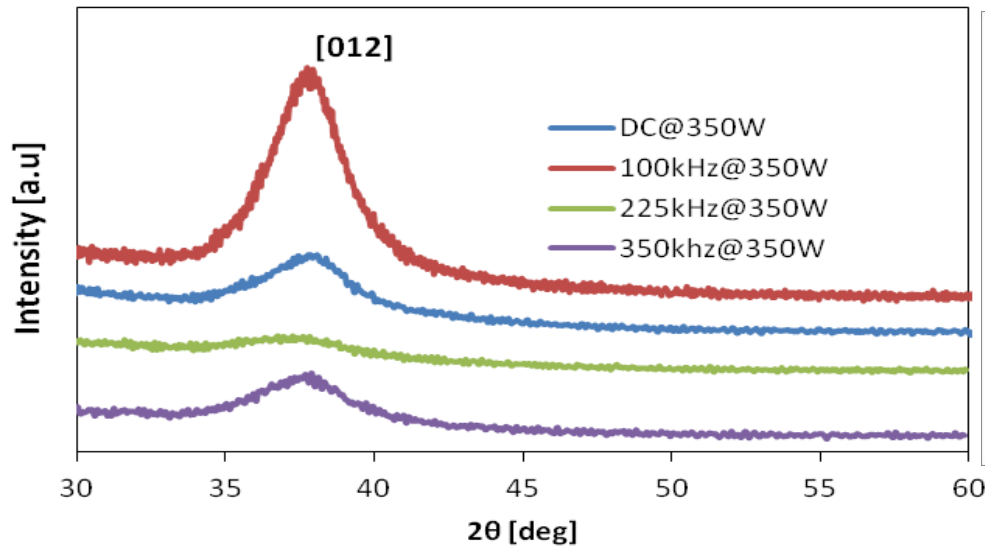
F:SnO₂ : *Optical properties*

- Transmittance decrease due to the extra electron concentration
- The shift in the band-gap can be attributed to the Burstein-Moss (B-M) shift
- Fluorine content higher than 6.2at.% in the film resulted in the decrease in E_g due to the decline in carrier concentration

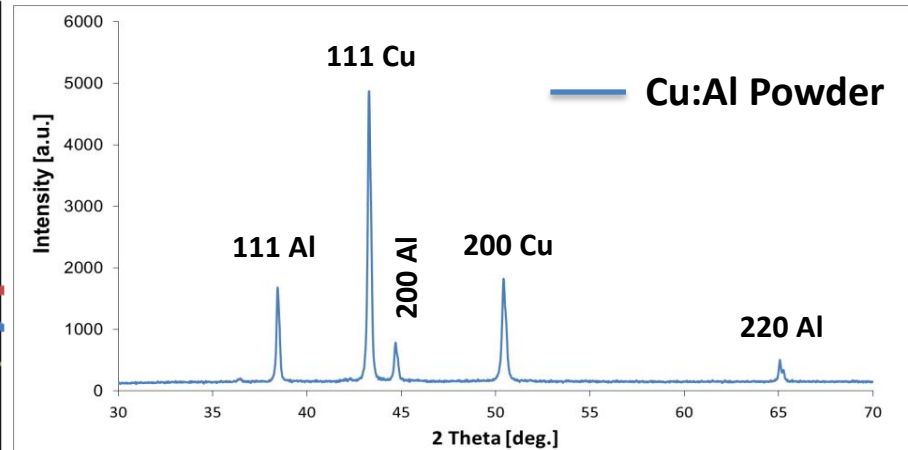


CuAlO_2 :Composition and structure

Frequency (kHz)	Power (w)	Cu (at.%)	Al (at.%)	O ₂ (at.%)
100	350	38.3	10.0	51.8



XRD analysis of CuAlO_2 films

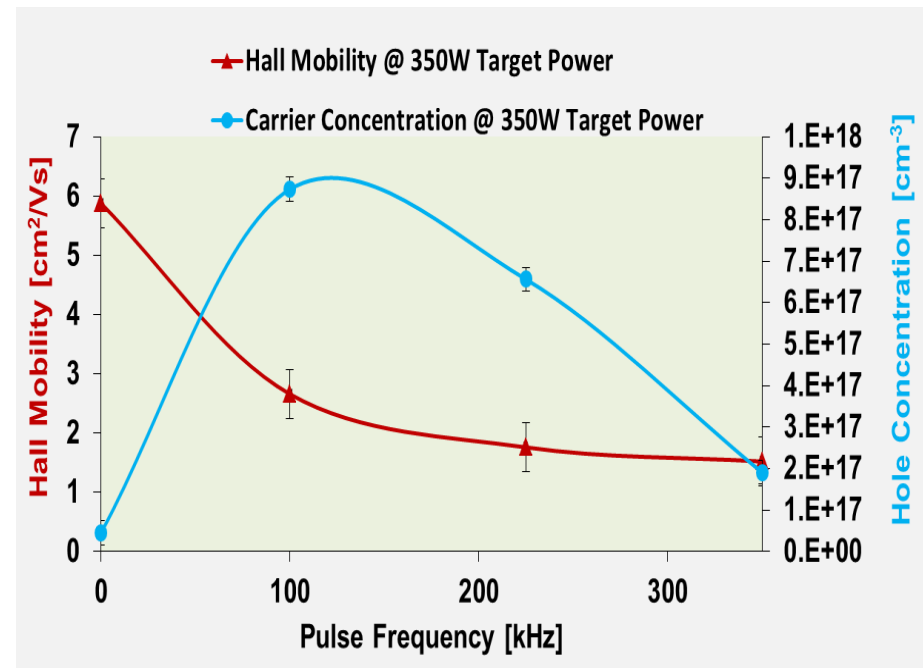
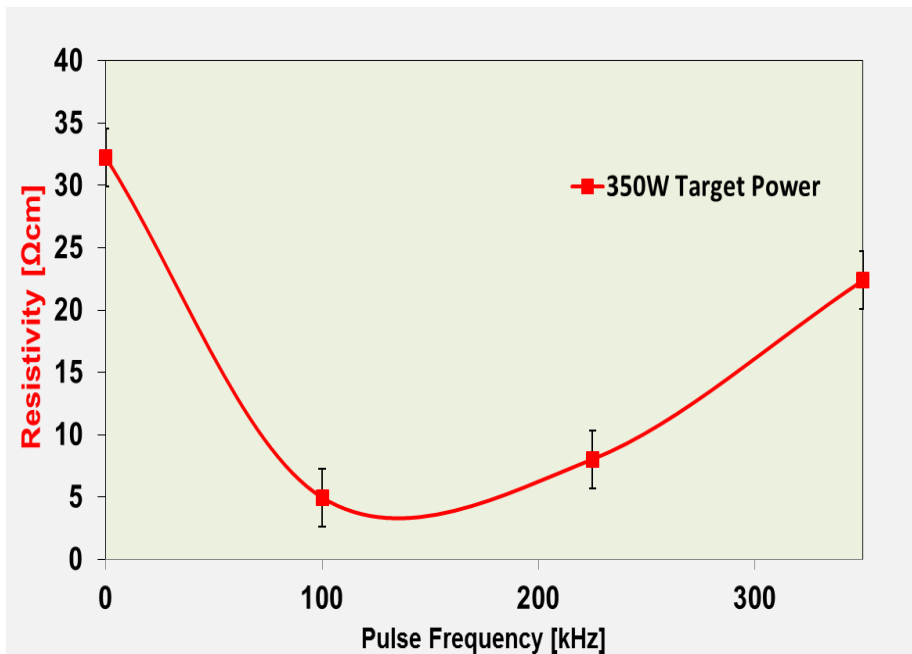


XRD analysis of Cu:Al powder target

Target power [W]	Pulse frequency [kHz]	Average grain size [nm]
350	100	4

CuAlO_2 : *Electrical properties*

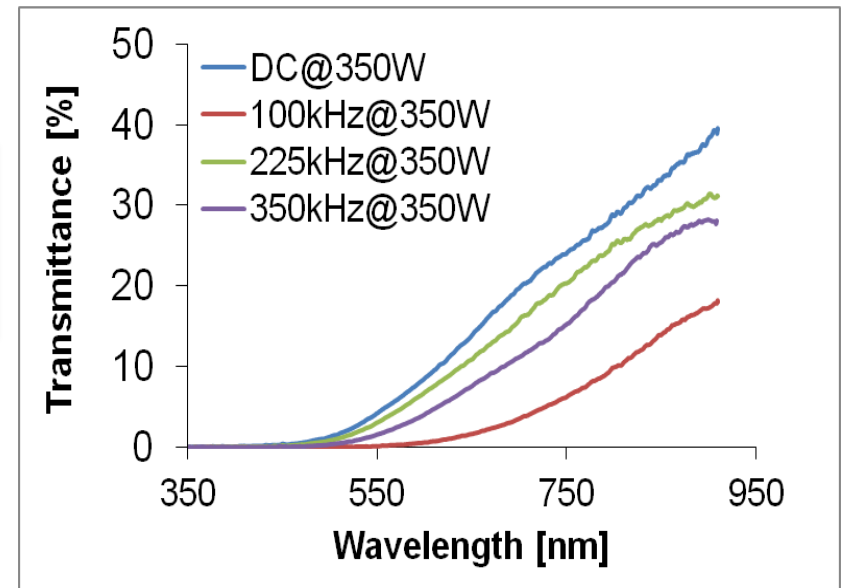
- Resistivity and mobility values to $5 \Omega\cdot\text{cm}$ and $3.1 \text{ cm}^2/\text{Vs}$ and a corresponding hole concentration of $8.7 \times 10^{17} \text{ cm}^{-3}$
- The low mobility is primarily due to the grain boundary defects in the film.



CuAlO₂: *Optical properties*

- Low transmission is found at shorter wavelength, due to the excitation of charge carriers across the optical E_g
- The optical E_g is estimated to be lower than the reported values of 2.9-3.5 eV in other studies
 - This maybe due to the nanostructure of the developed CuAlO₂ which is scattering the light due to grain boundaries

Target Power [W]	Pulsing frequency [kHz]	Average transmittance [%] 400-900nm	Eg-direct optical [eV]
350	100	7.9	1.8



Transmittance data for as-deposited
CuAlO₂

Summary and Future work

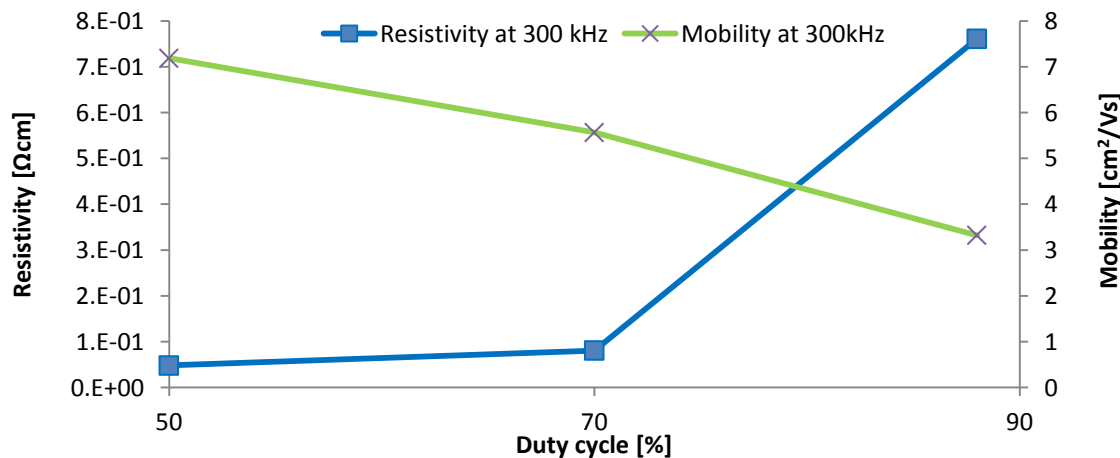
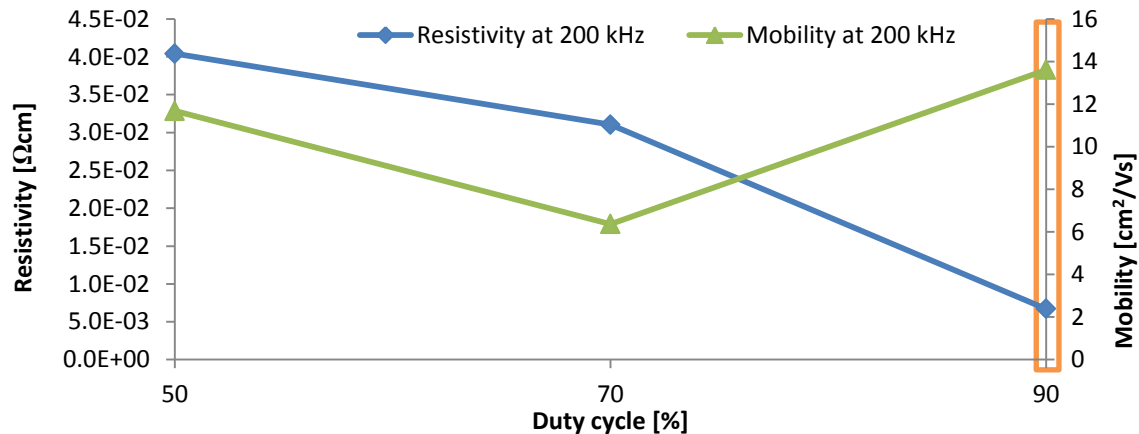
- ✓ N-type $\text{SnF}_2:\text{SnO}_2$ polycrystalline transparent conductive oxide thin films was successfully deposited onto glass substrate using pulsed DC magnetron sputtering technique from un-sintered powder targets
- ✓ P-type CuAlO_2 single phase nano crystalline conductive oxide thin film have been successfully deposited onto glass substrate using pulsed DC magnetron sputtering technique from un-sintered powder targets
- ✓ Successful deposition of the copper, silver metal contacts and the titanium dioxide protective layer
- ❖ Complete fabrication of the p-n junction diode
- ❖ Electrically quantify the device
- ❖ Test against weather conditions

Thank You

n-type (F:SnO₂)

cont..

- ➔ The pulsing frequency and the duty cycle were investigated to study its effect on the electrical properties



Duty Cycle (%)	Pulsing Frequency (kHz)	
	200	300
50	✓	✓
70	✓	✓
90	✓	✓

EDS of FTO

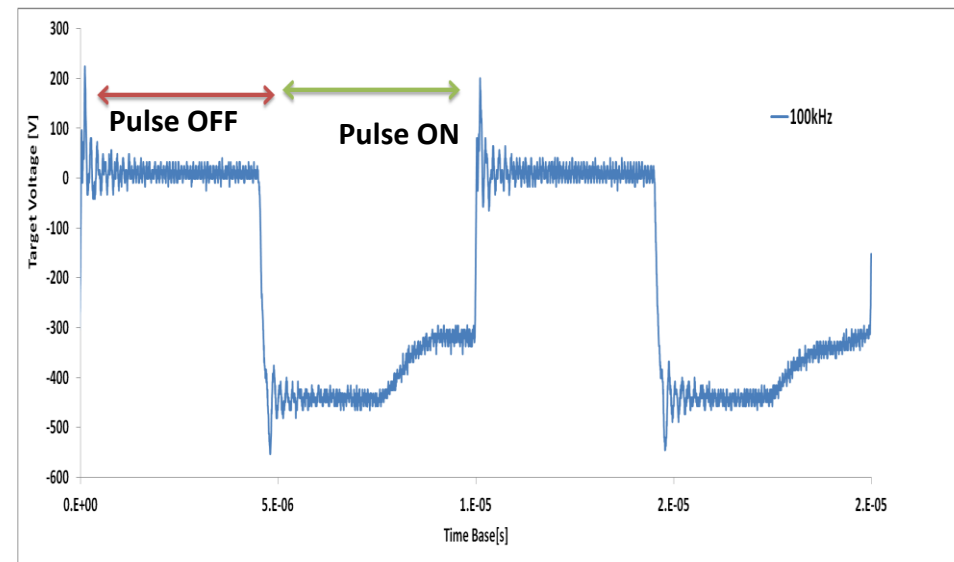
Sample ID	Element at.% in films			Element at.% in targets		
	O	F	Sn	O	F	Sn
SnO ₂	68.4	0.0	31.7	66.7	0.0	33.4
SnO ₂ :F1	66.4	2.8	30.8	63.3	3.3	33.3
SnO ₂ :F2	64.0	5.3	30.7	60.0	6.6	33.3
SnO ₂ :F3	62.8	6.2	30.9	56.7	10.0	33.2
SnO ₂ :F4	60.1	7.4	32.5	53.4	13.0	33.3

Elemental analysis: p-type (CuAlO_2)

- EDS analysis used to determine the variation of the copper, aluminium and oxygen content in thin films
- Varying the sputtering power did not vary the Cu:Al ratio in the thin films, however more oxygen content is found when sputtering at 250W
 - Higher content of Cu:Al ratio in thin films achieved with pulsing at 100kHz using 350W of sputtering power
 - ✓ Less frequent positive overshoot, indicating less intense plasma, therefore greater mean free-path.

EDS analysis of thin films

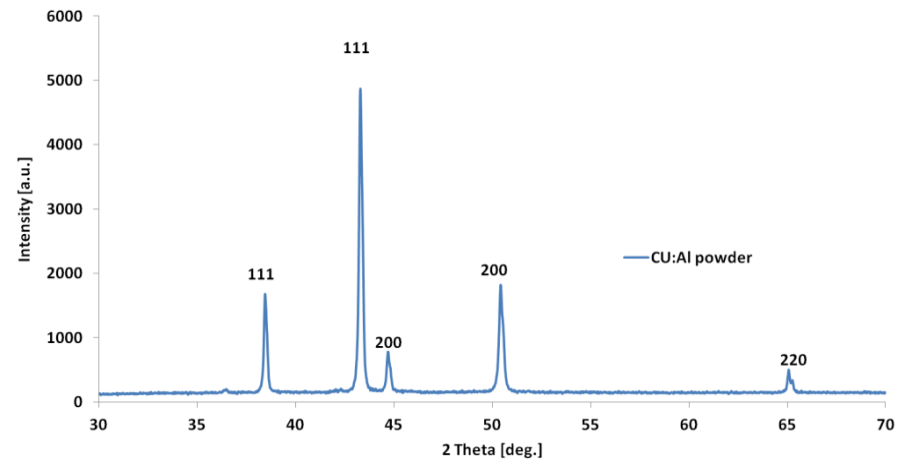
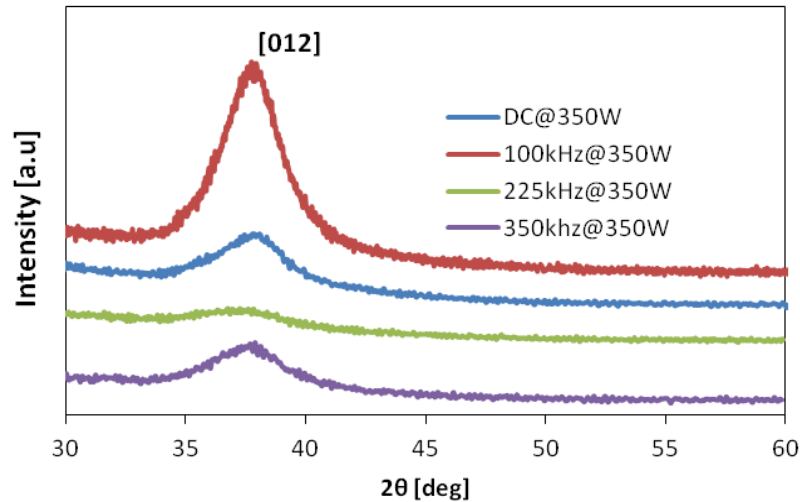
Frequency (kHz)	Power (w)	Cu (at.%)	Al (at.%)	O ₂ (at.%)	Cu/Al
350	350	34.5	12.4	50.1	2.8
225	350	33.5	15.2	51.3	2.2
100	350	38.3	10.0	51.8	3.8
0	350	33.5	14.7	51.7	2.3
350	250	31.2	14.5	54.3	2.1
225	250	32.0	14.9	53.1	2.1
100	250	34.1	8.1	57.8	4.2
0	250	29.0	9.0	62.0	3.2



Target voltage during pulsed sputtering at 100kHz and 50% duty

Structural properties: p-type (CuAl_2)

→ XRD analysis was used to determine the crystal structure of the thin films



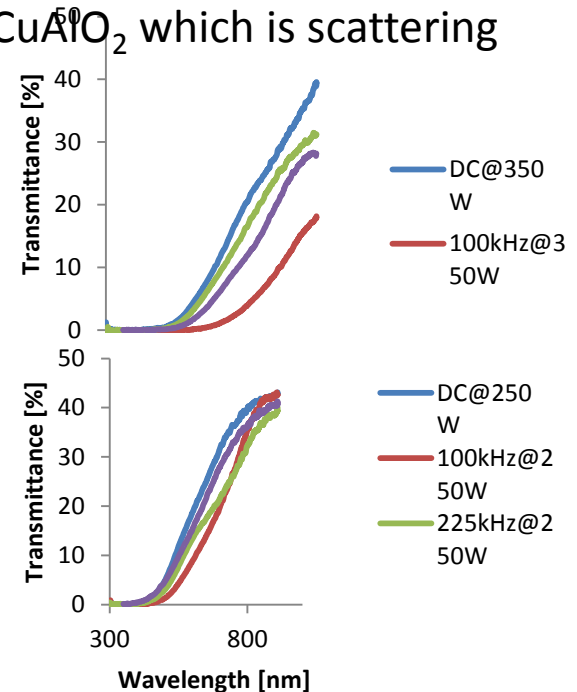
XRD analysis of Cu:Al powder

Target power [W]	Pulse frequency [kHz]	Average grain size [nm]
350	DC	3.4
	100	4
	225	3.1
	350	3.3
250	DC	2.8
	100	3.0
	225	2.2
	350	2.4

CuAlO₂: *Optical properties*

- Optical transmittance was measured using UV-vis spectrophotometer with $300 \leq \lambda \leq 900$ nm
- Low transmission is found at shorter wavelength, due to the excitation of charge carriers across the optical E_g
 - The Absorption coefficient is found to decrease with higher wavelength transmission
 - The optical E_g is estimated to be lower than the reported values of 2.9-3.5 eV in other studies
 - This maybe due to the nanostructure of the developed CuAlO₂ which is scattering the light due to grain boundaries

Target Power [W]	Pulsing frequency [kHz]	Average transmittance [%] 400-900nm	Eg-direct optical [eV]
350	DC	16.2	2.2
	100	7.9	1.8
	225	12.7	2.1
	350	8.9	2.0
250	DC	27.5	2.3
	100	15.9	2.1
	225	18.9	2.0
	350	24.0	2.0



Transmittance data for as-deposited CuAlO₂

Magnetron Sputtering

