CMMP 11

Investigation of pulsed D.C magnetron sputtering for the component layers of $CuInSe_2$ based solar cells

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Introduction

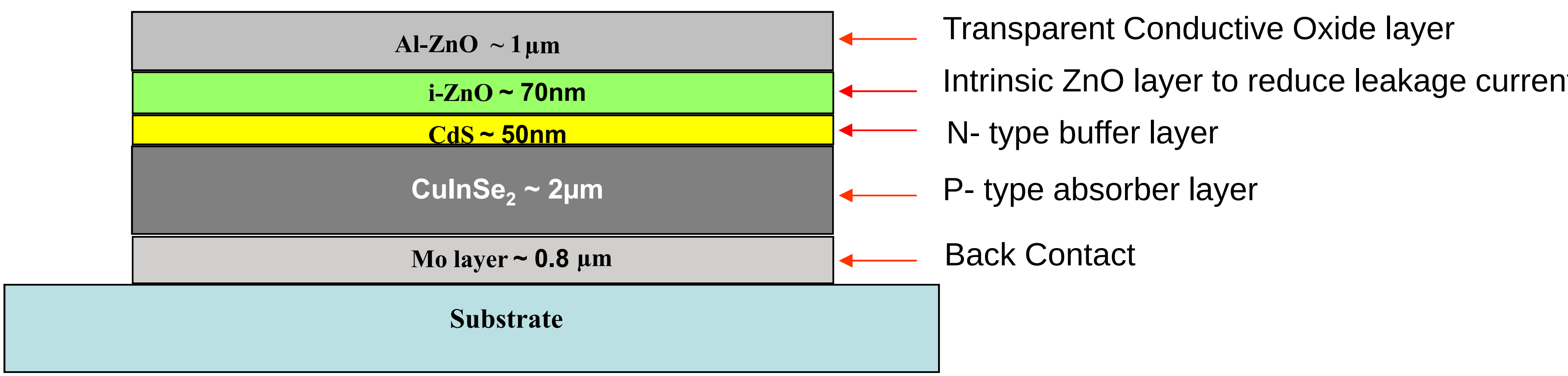
CIS/CIGS thin film based solar cells are the most promising renewable energy source because of their relatively high solar efficiency and stability.

Single crystal Si cells need more material to absorb light due to its indirect band gap.

In CIS the defect mechanisms makes it a direct semiconducting materials and no doping is needed.

Presently CIGS cells have achieved a maximum efficiency of 20.3% [1].

A typical cell CIS/CIGS structure is in the form of a heterojunction.



A typical CIGS solar cell

References

[1] P. Jackson et. al Progress in Photovoltaics: Research and Applications, (2011) EU PVSEC WCPEC-5, Valencia, Spain, 2010.

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Introduction

The first published report of a $CuInSe_2$ thin film was by the R.D Tomlinson group at the University of Salford in 1974 [2].

Films of CIS are generally made by multi-step processes

My work has been focussed on a SINGLE STEP process which can deposit films with.

- ✓ **Nearly stoichiometric ratio.**
- ✓ **p-type characteristics.**
- ✓ **No secondary phases.**
- ✓ **No additional substrate heating for crystallisation.**
- ✓ **Less material wastage.**
- ✓ **No carbon, oxygen, chlorine etc. contamination.**

This work reports such a single step deposition process for nearly stoichiometric p-type CIS layers and also for the other component layers of a cell using Pulsed D.C Magnetron Sputtering (PDMS) from powder targets.

References

[2] E. Elliott, R.D. Tomlinson, J. Parkes, M.J. Hampshire, Thin Solid Films, 20 (1974) S25-S26.

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Materials Deposited

1. **Molybdenum (back contact)**
2. **Copper indium diselenide (absorber layer)**
3. **Indium sulphide (buffer layer)**
4. **Indium oxide (Transparent Conductive Oxide layer)**

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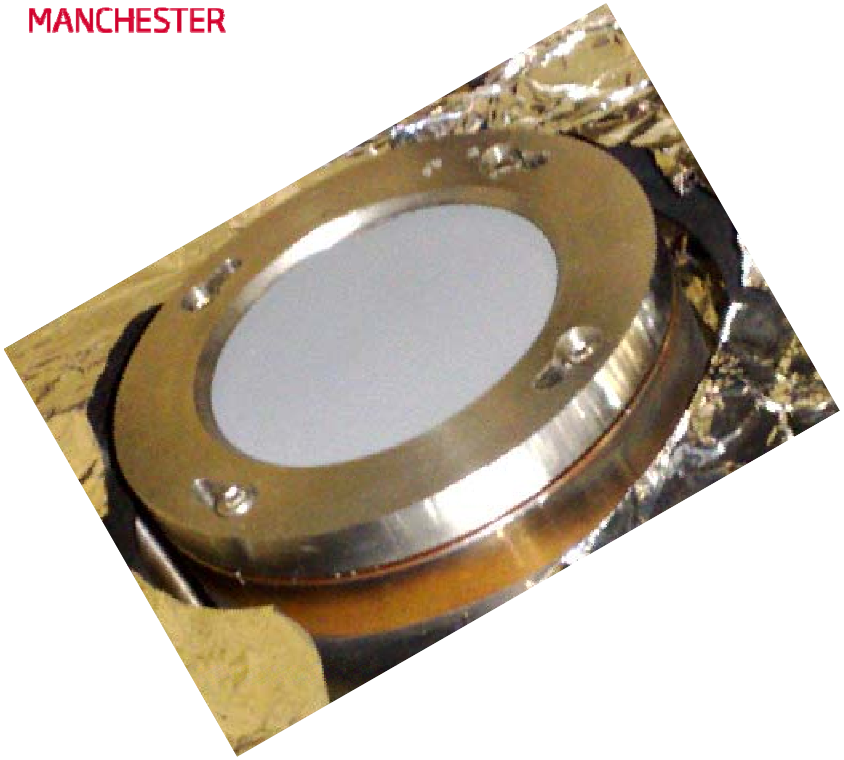
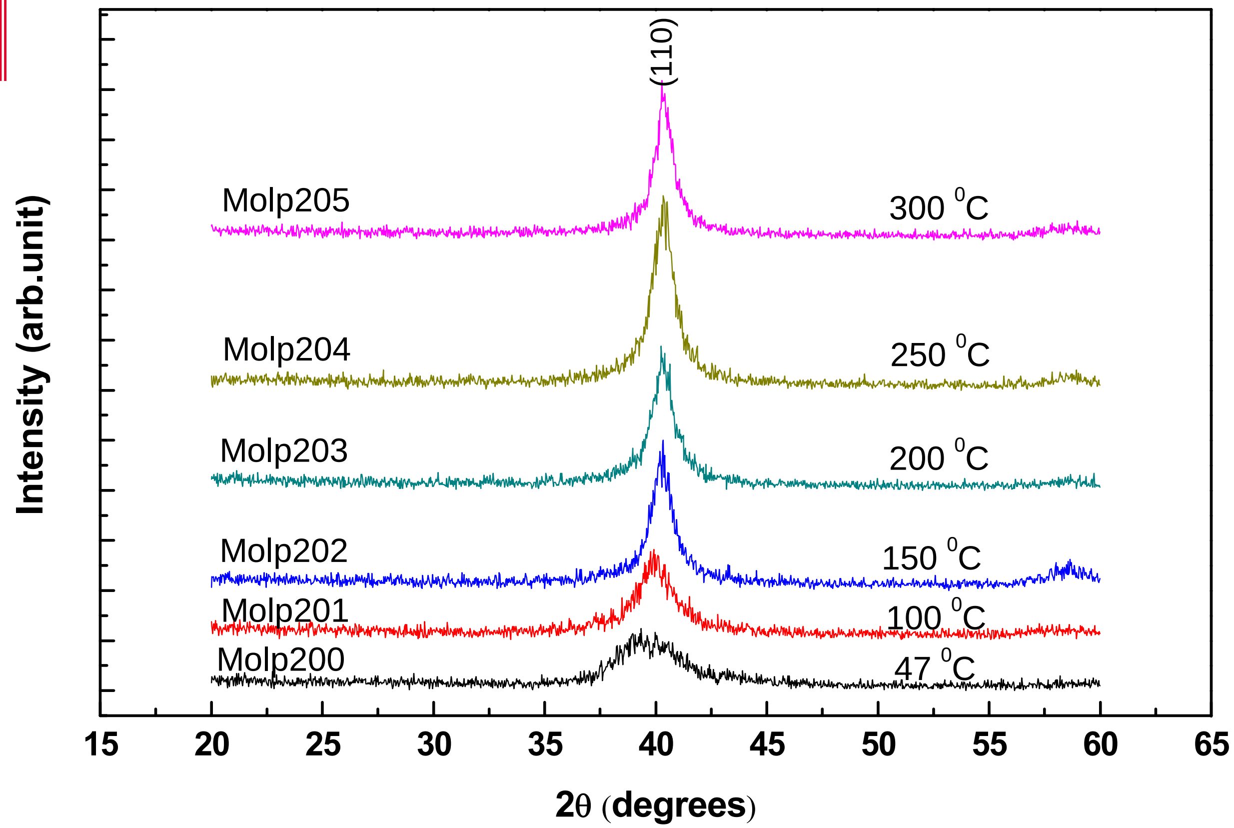


Sputtered in argon atmosphere from commercial Mo powder.

Films sputtered at different substrate temperatures

Molybdenum Films

XRD of Mo Films



Deposition Parameters

Pressure : $7.0x10^{-3}$ mbar
Mode : Constant Power (50W)
Frequency : 75 kHz
Pulse off Time : 0.5 µs
Distance : 10 cm

Body-centred cubic phase

With increase in substrate temperature

A shift in 2θ towards higher angles was noticed.

Reference

S. Karthikeyan *et al*, *Nano-structured features of pulsed d.c magnetron sputtered Mo films for photovoltaic application* Thin Solid Films, 2011, accepted for publication.

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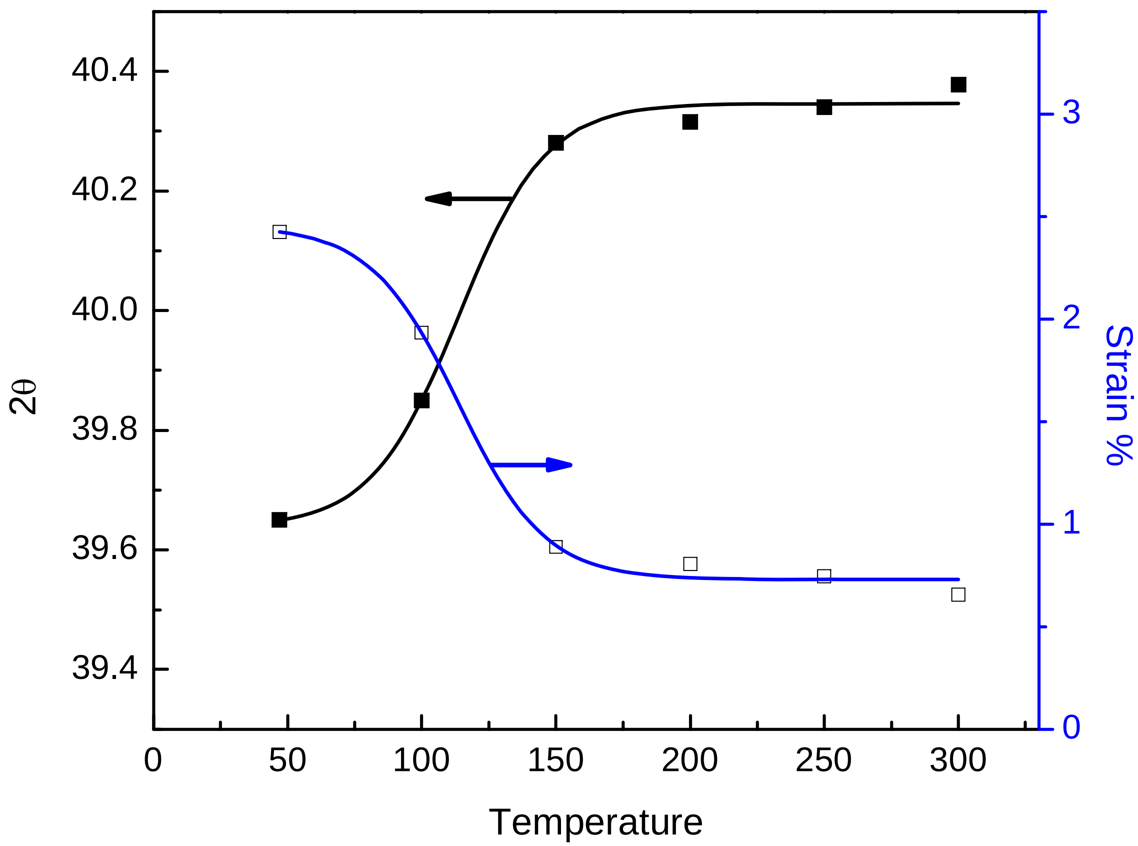
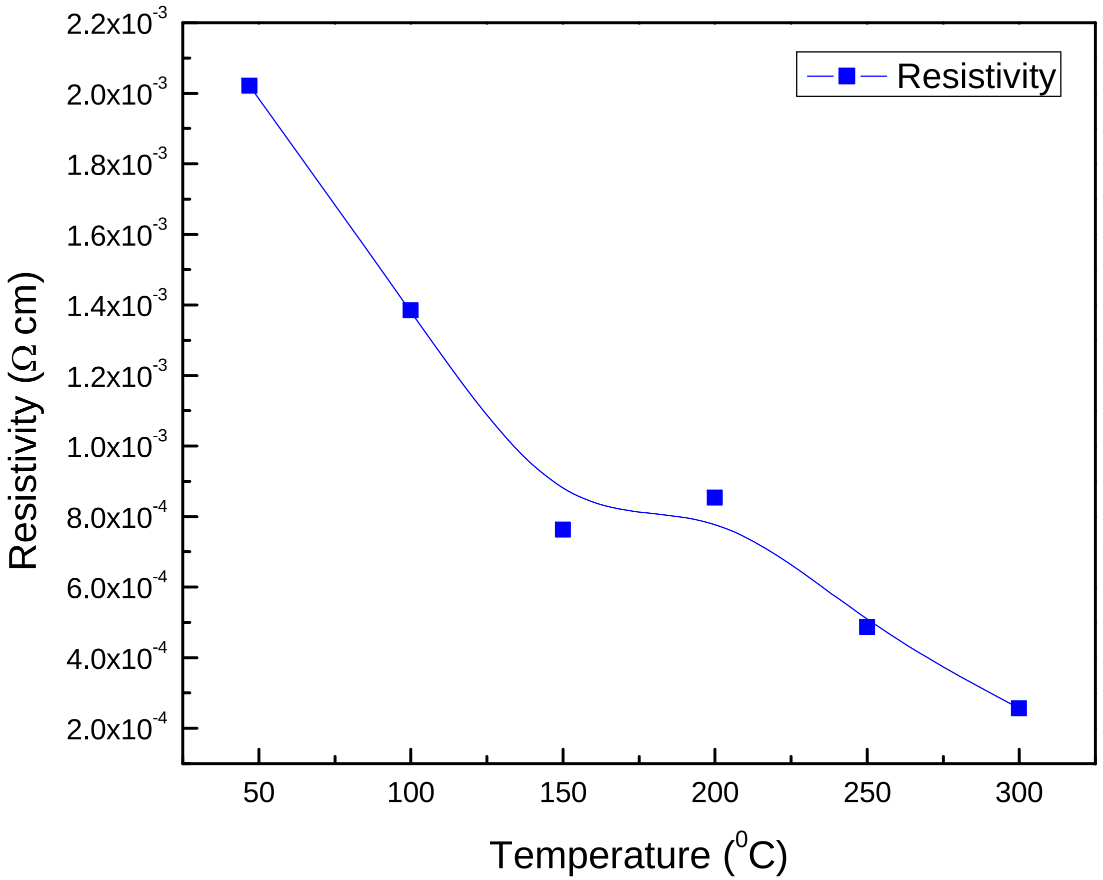
Strain Analysis of Mo Films



Strain % reduced with increase in temperature

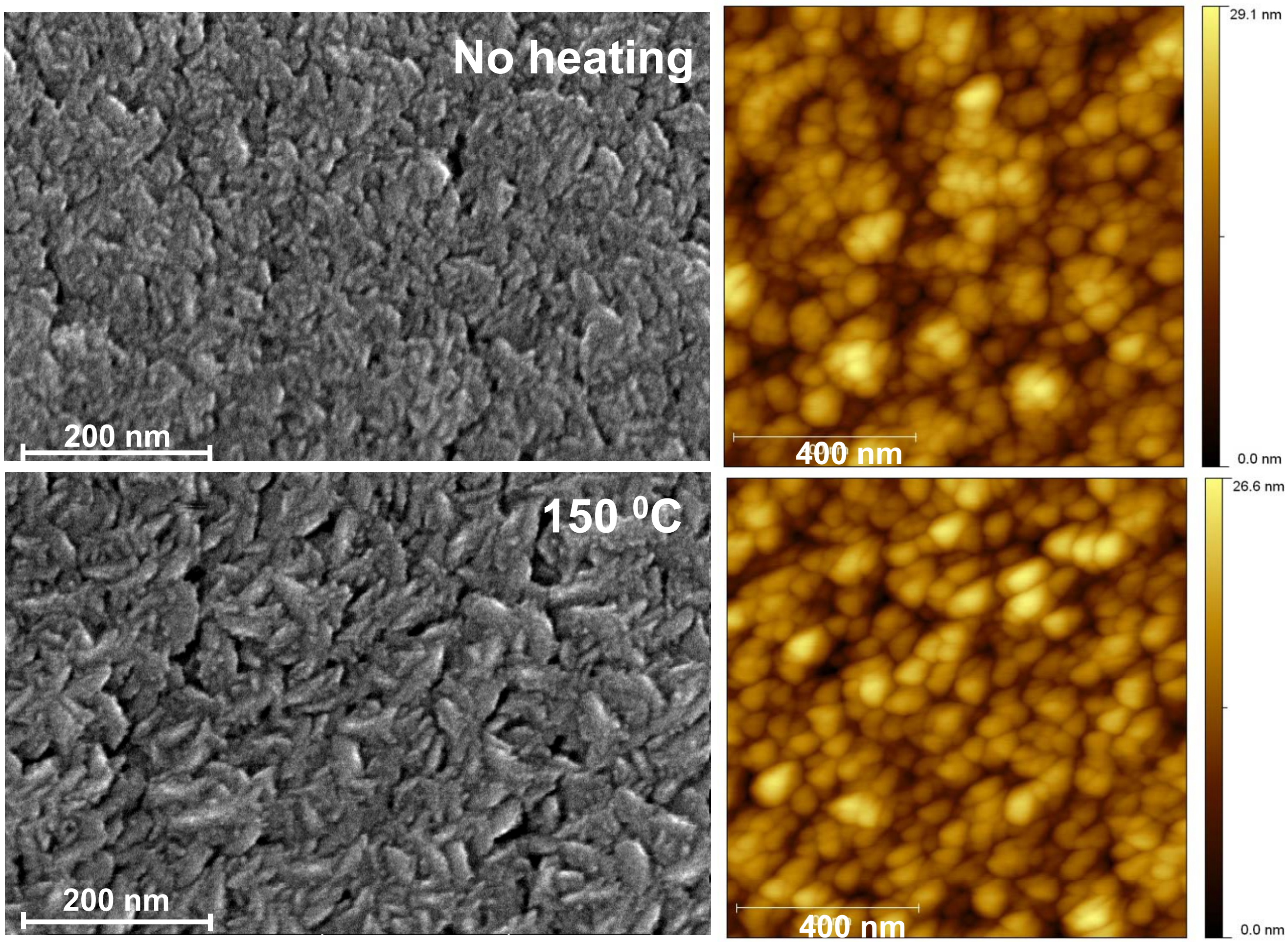
Resistivity Analysis of Mo Films



Resistivity reduced with increase in temperature

SEM and AFM Studies of Mo Films

SEM **AFM**



Morphological change from a cluster of small grains to a fibrous, columnar needle-like structure for films grown at 150 ^{0}C

References

Al-Thani, H.A *et al*, 2002,*Twenty-Ninth IEEE Photovoltaic Specialist Conference,* pp 720-3 .

Sputtered in argon atmosphere from our $CuInSe_2$ powder.

Films sputtered from CIS powder with different compositions

Copper Indium Diselenide Films

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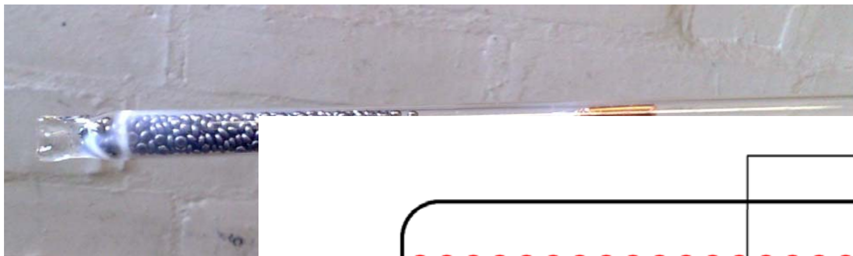
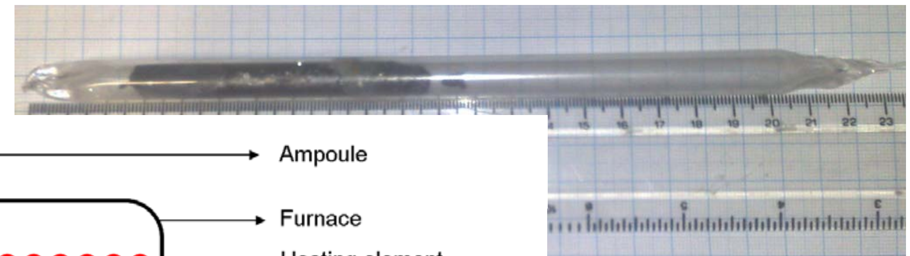
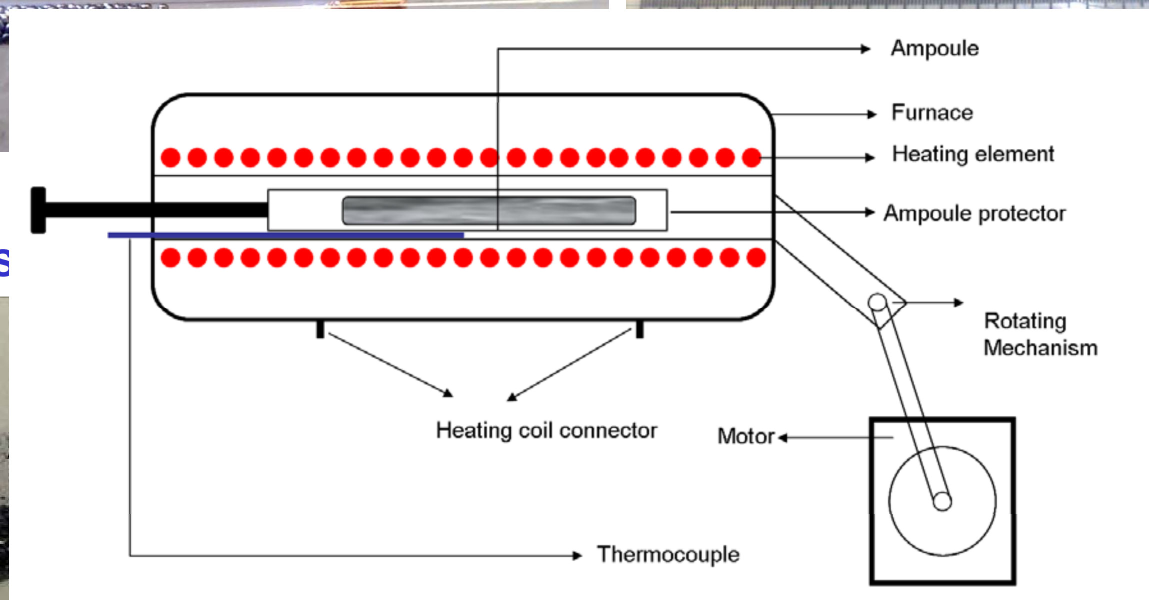
$CuInSe_2$ Crystal Growth

Selenium, Indium and Copper inside quartz tube before sealing

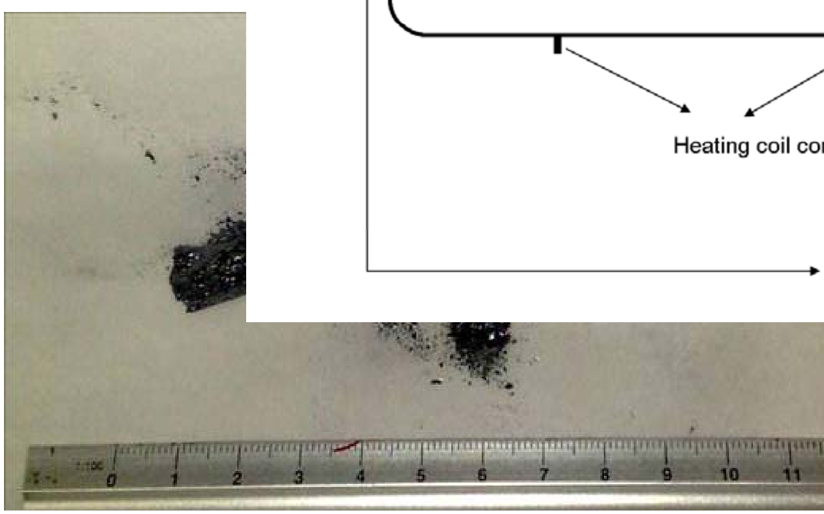


$CuInSe_2$ inside ampoule after direct fusion





CuInS



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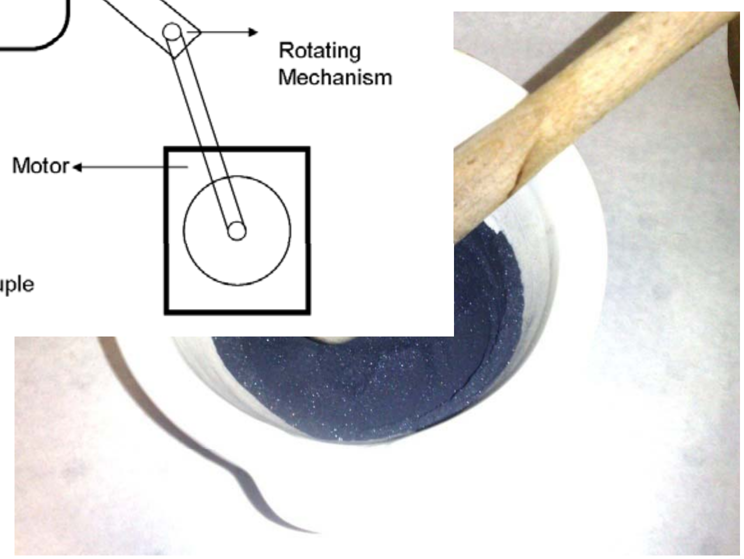
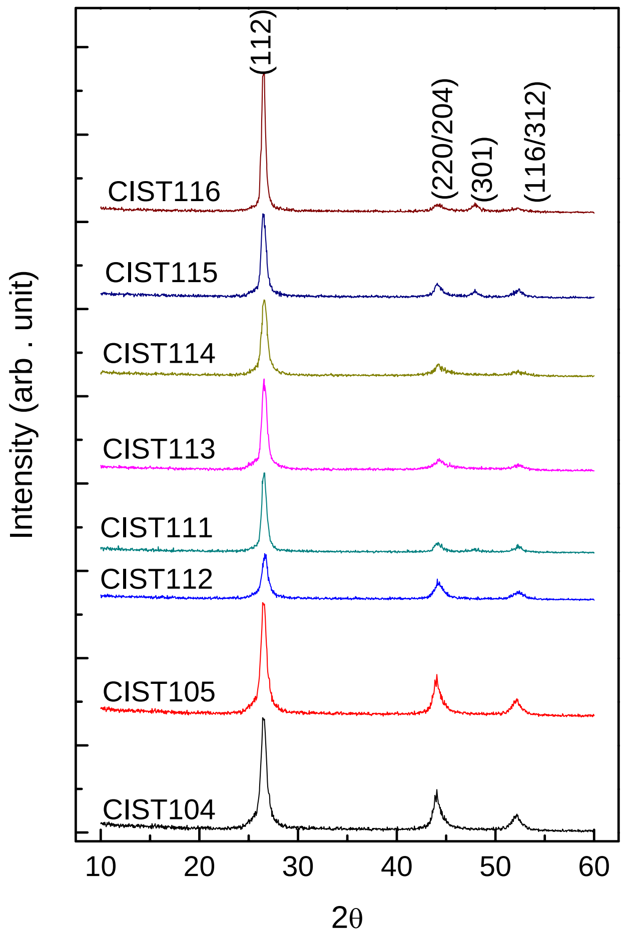


References

S.Karthikeyan *et al*, Thin Solid Films, 2011, 519; pp.3107 -3112

XRD of $CuInSe_2$ Films

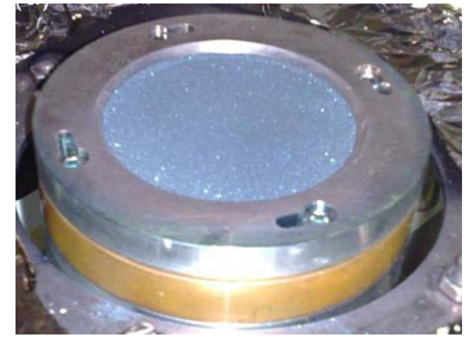


5 % extra In (20.53:27.97:51.50)

5 % extra Se (21.54:24.29:54.17)

Nearly stoichiometric powder (23.03:23.32:53.66)

In rich powder (19.95 : 34 .10 : 45.95)



Deposition Parameters

Pressure : $7.5x10^{-3}$ mbar
Mode : Constant Current (0.12A
Frequency : 130 kHz
Pulse off Time : 1.0 µs
Distance : 10 cm

Preferred (112) orientation

Single Phase

No heating !!

Reference

S.Karthikeyan *et al*, Thin Solid Films, 2011, 519; pp.3107 -3112

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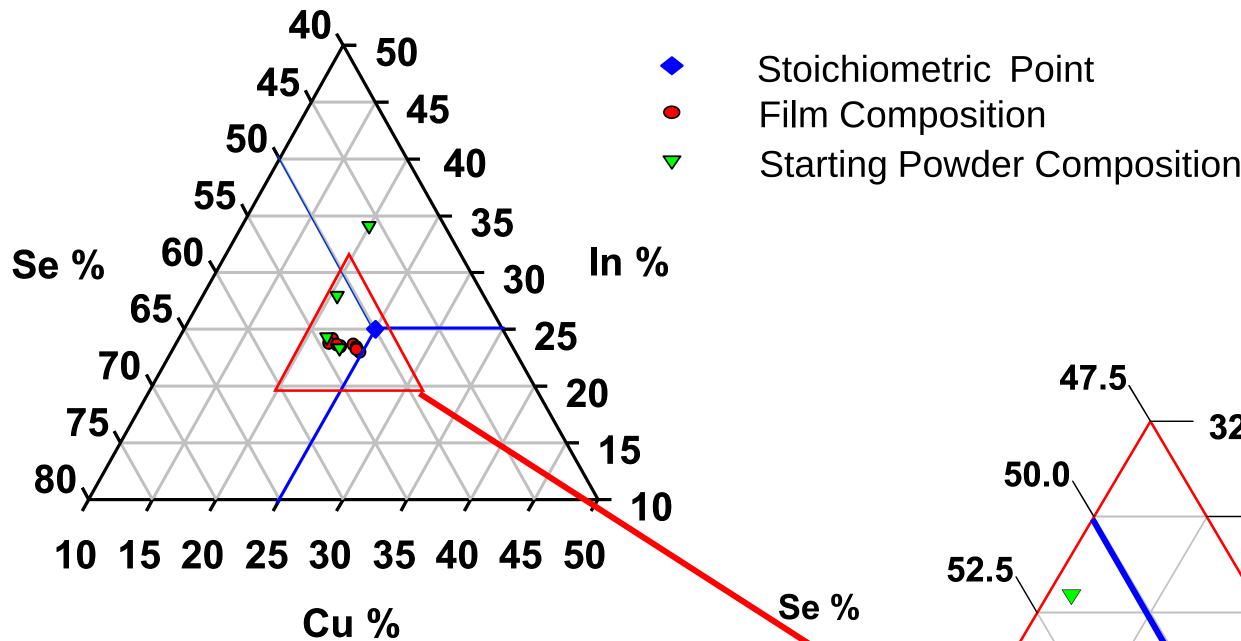
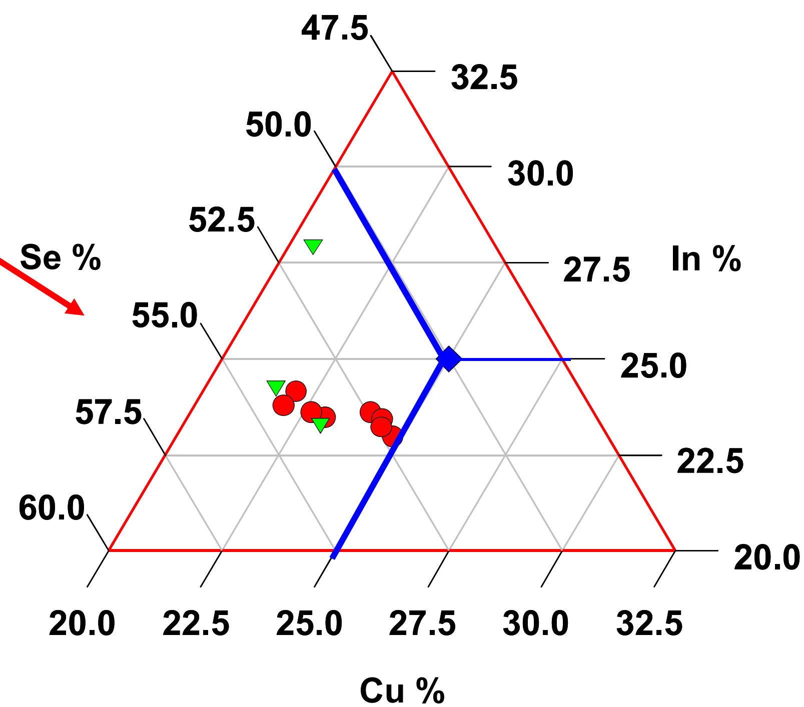
Ternary Diagram of $CuInSe_2$ Films and Powder



Ternary Diagram



All films were p-type

References

S.Karthikeyan *et al*, Thin Solid Films, 2011, 519; pp.3107 -3112

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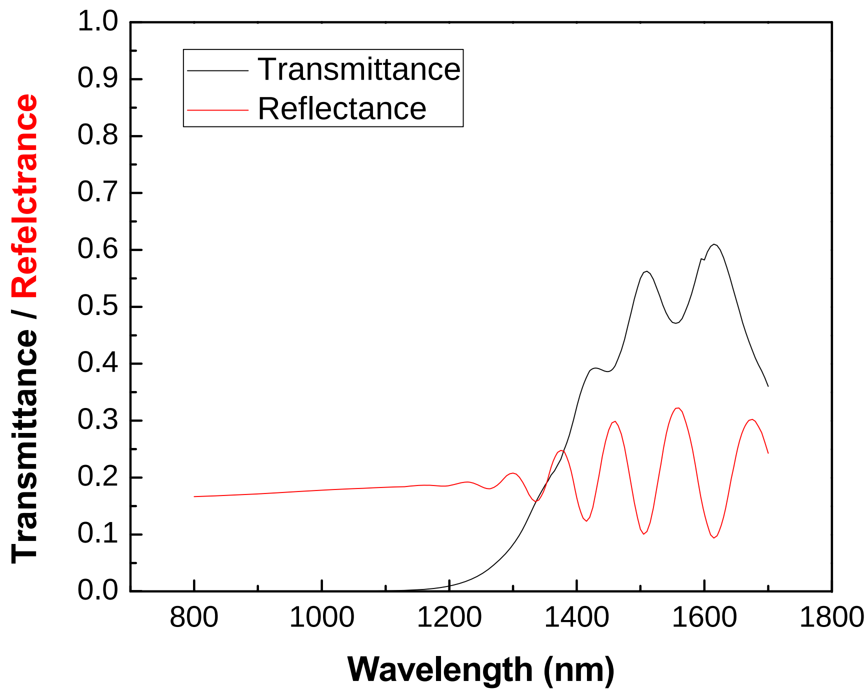
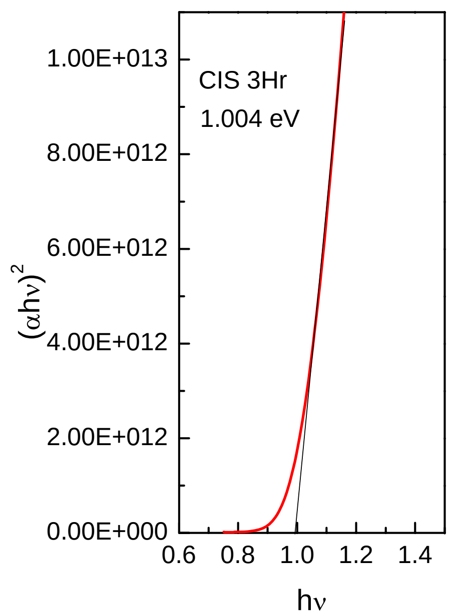
Optical Studies of $CuInSe_2$ Films

$$\alpha = -\frac{1}{d}.\ln\left(\frac{(1-R)^2}{2.T} + \sqrt{\frac{((1-R^4))}{4.T^2} + R^2}\right)$$





Band gap is very close to the reported value of 1.02 eV

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Sputtered in argon atmosphere from commercial In_2S_3 powder.

Films sputtered at different substrate temperatures

Indium Sulphide Films

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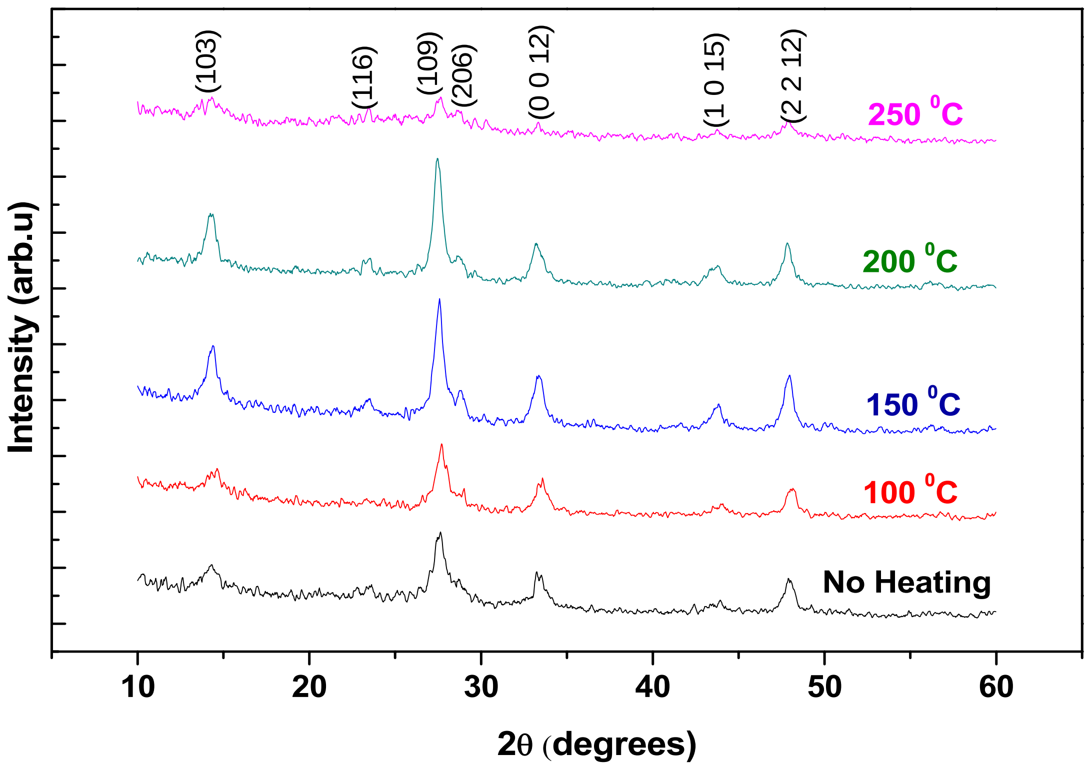
XRD of In_2S_3 Films



Deposition Parameters

Pressure : $7.3x10^{-3}$ mbar
Mode : Constant Power (25 W)
Frequency : 100 kHz
Pulse off Time : 0.5 µs
Distance : 8 cm

Preferred (109) orientation

Tetragonal – β In_2S_3 formed with

No heating !!

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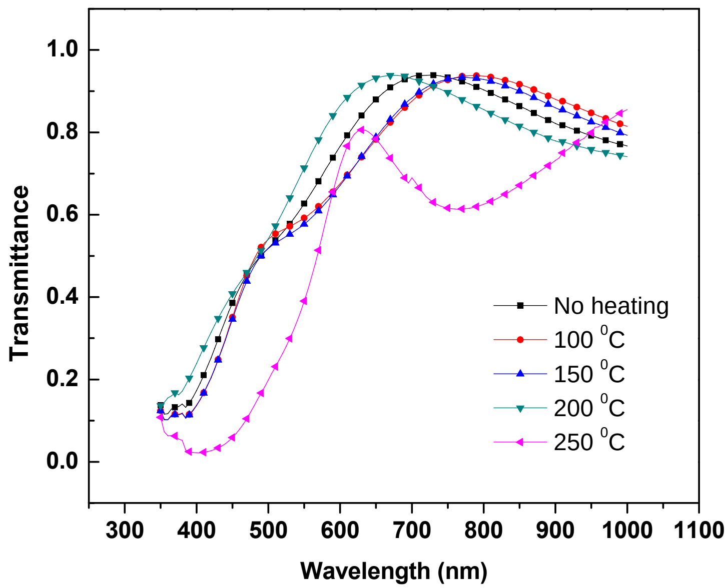
Optical and AFM studies of In_2S_3 Films



Band gap decreased with decrease in sulphur content

Deposition Temperature	% In	%S	$\frac{[\%S]}{[\%In]}$	Band Gap eV
Non heated	41.26	58.74	1.42	2.768
100 ^{0}C	41.84	58.16	1.39	2.735
150 ^{0}C	42.86	57.14	1.33	2.708
200 ^{0}C	43.5	56.5	1.29	2.667
250 ^{0}C	48.51	51.49	1.20	2.526

Reactive sputtered in oxygen and argon atmosphere from commercial In_2O_3 powder.

Films sputtered at different oxygen flow rates with no additional heating

Indium Oxide Films

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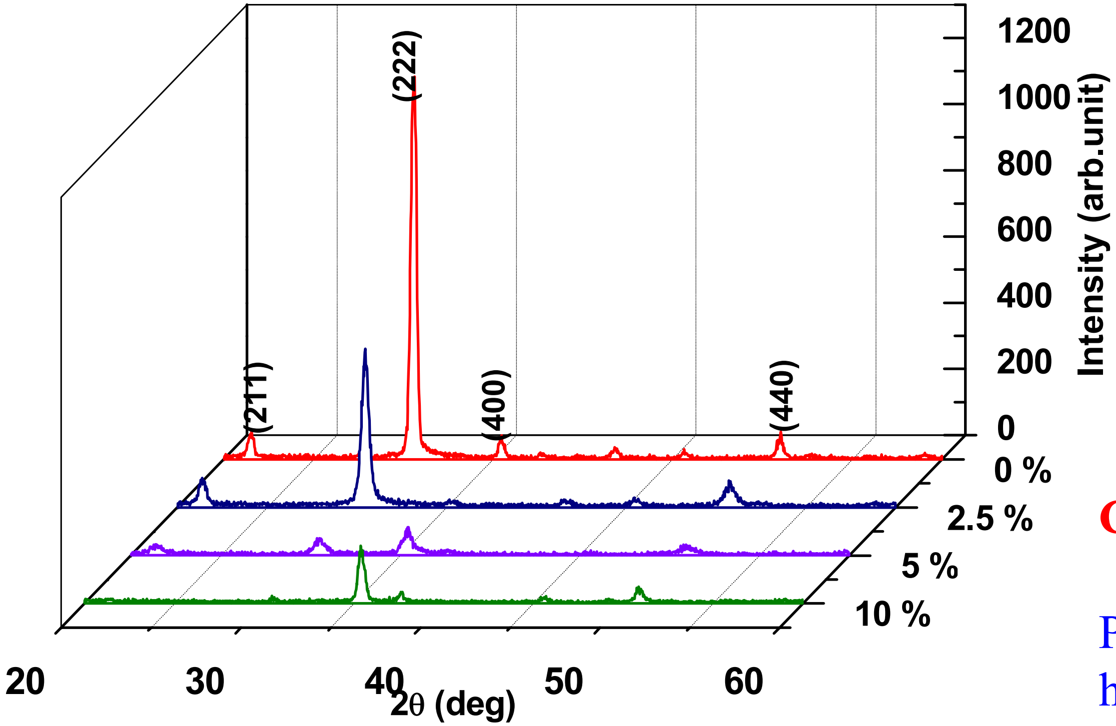
In_2O_3 Films

Deposition Parameters

Pressure : 4.0x10^{-3} Pa
Mode : Constant Power (60W)
Frequency : 60 kHz
Pulse off Time : 0.5 µs
Distance : 9 cm
MFC : F_{Ar} + F_{Oxygen} = 20sccm
Thickness ~ 500 nm

X-ray diffraction spectra



Cubic bixbyite In_2O_3 phase.

Preferred (400) (440) orientation at higher O_2 concentration

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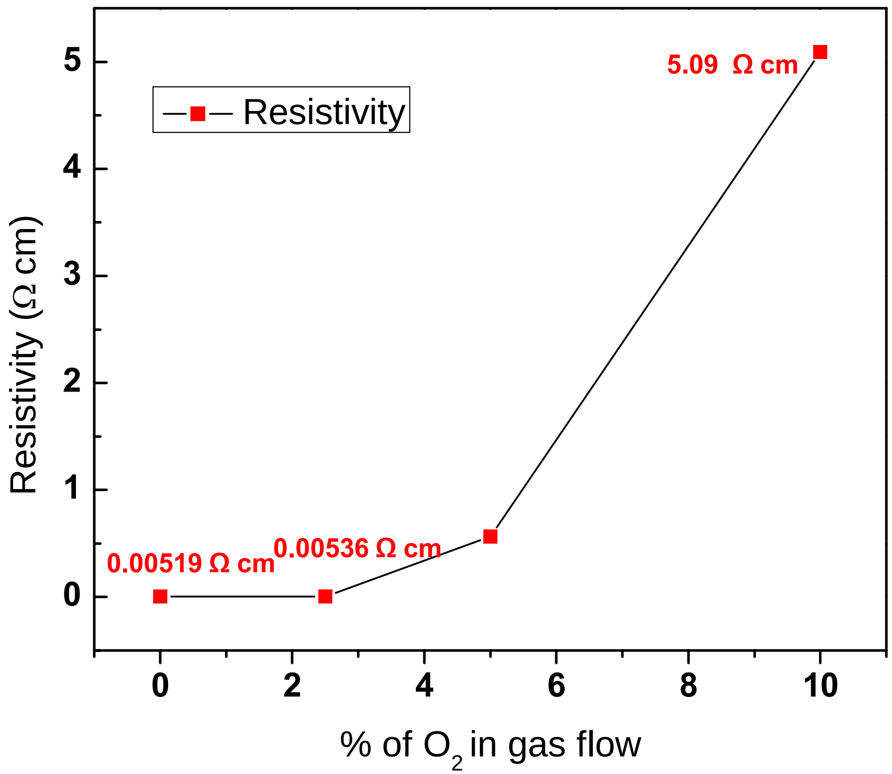
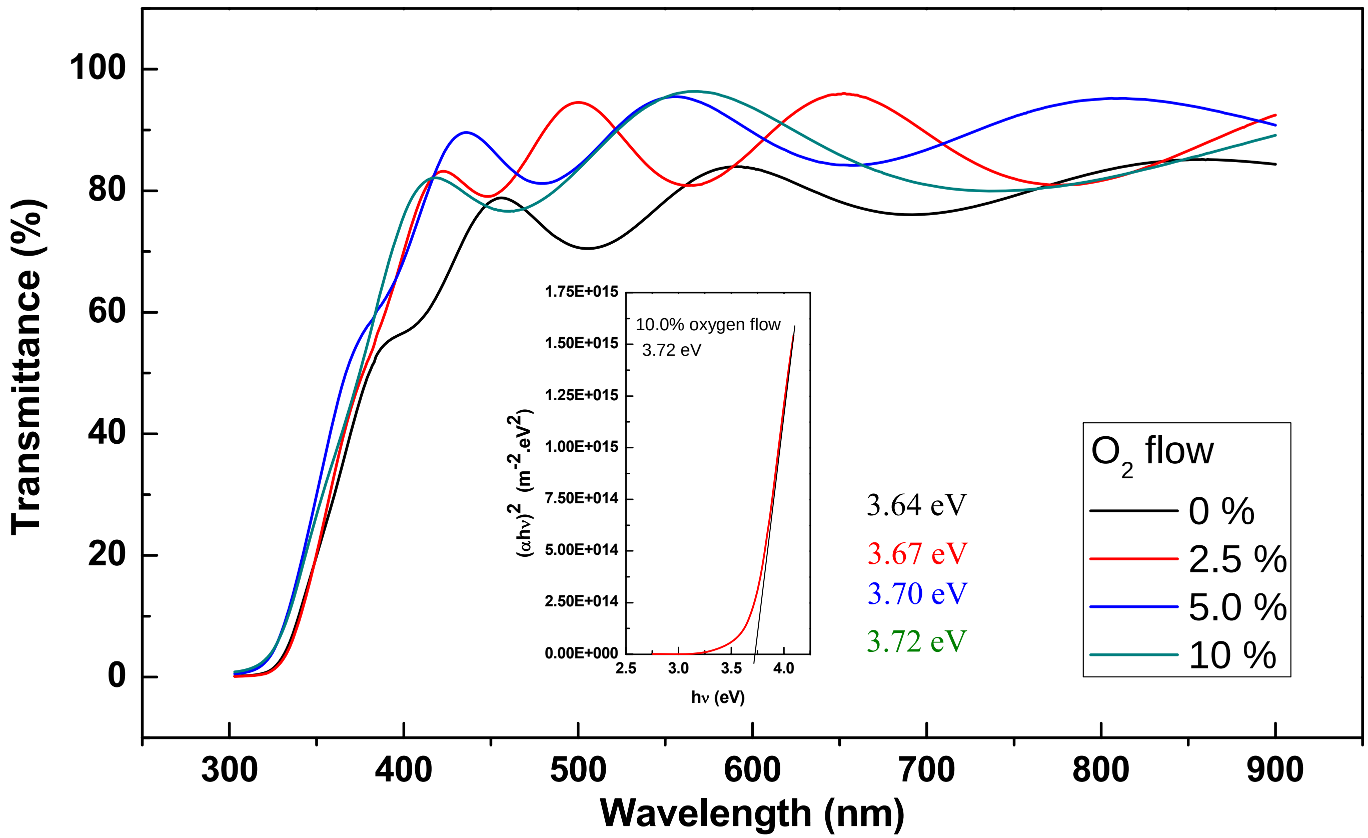
Resistivity of In_2O_3 Films



Strongly n-type 0 - 2.5% O_2

Weakly n-type 5 – 10% O_2

Optical Properties of In_2O_3 Films



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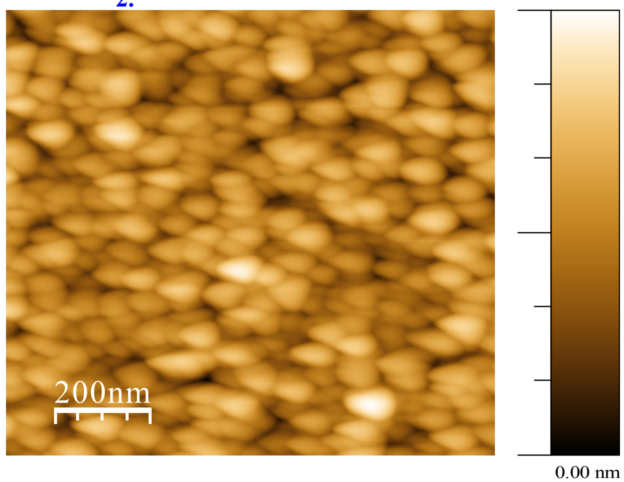
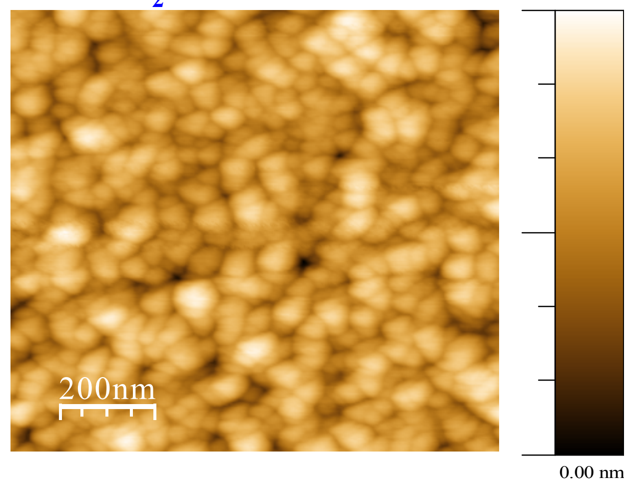
AFM of In_2O_3 Films

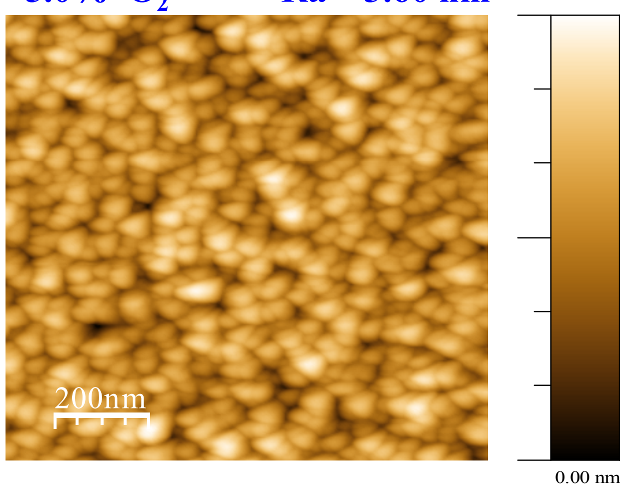
0% O_2. **Ra – 2.63nm**



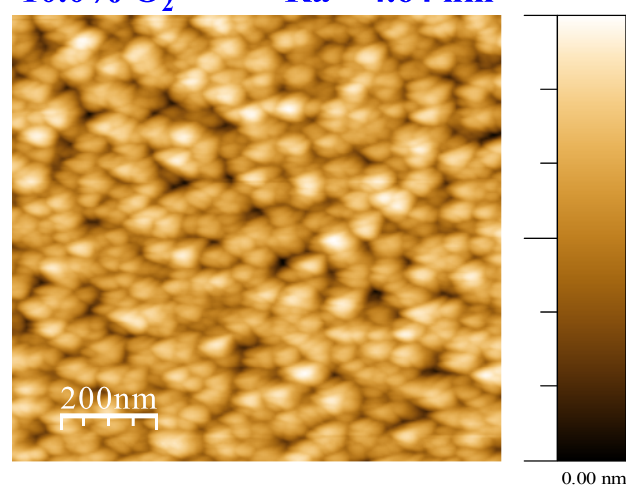
2.5% O_2 **Ra – 3.06nm**



5.0% O_2 **Ra – 3.60 nm**



10.0% O_2 **Ra – 4.64 nm**



References

Y.C Liang *et al*, Appl Phys A, 2009, 97; pp.249-255.

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Conclusion

- The possibilities of pulsed d.c magnetron sputtering for the deposition of Mo, $CuInSe_2$ In_2S_3 and In_2O_3 films from powdered targets were studied.
- The analysis showed that these PDMS grown films can be used for solar cell applications.
- The most surprising outcome is the nearly stoichometric nature of the CIS films largely irrespective of the starting composition of the material
- Single phase CIS and In_2S_3 films were produced using PDMS technique without the aid of additional substrate heating.
- Films grown from this single step process can cut down the cost and also the dangerous selenisation processes that have previously been associated with the production of high efficiency CIS solar cells.

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joule CENTRE

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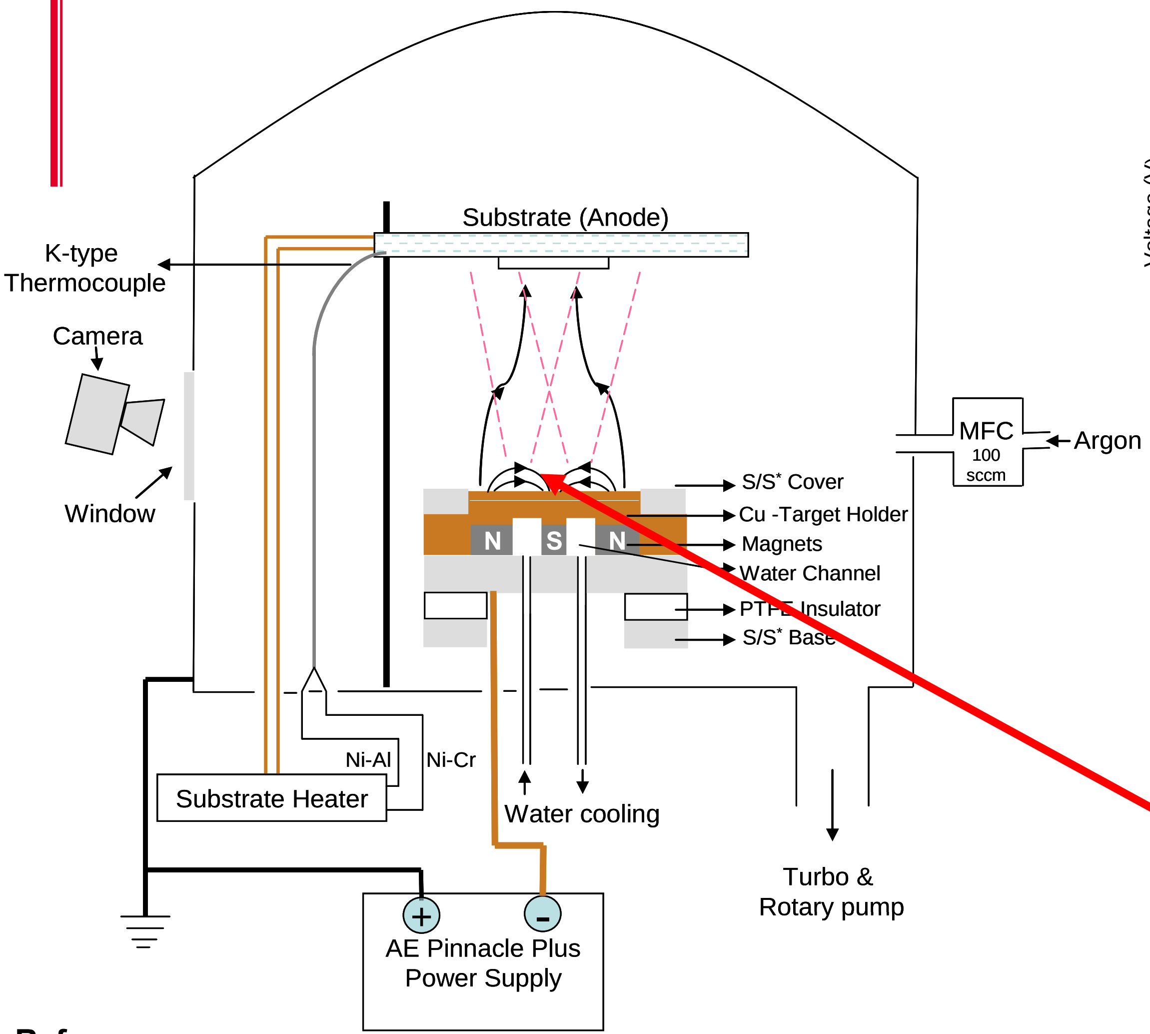
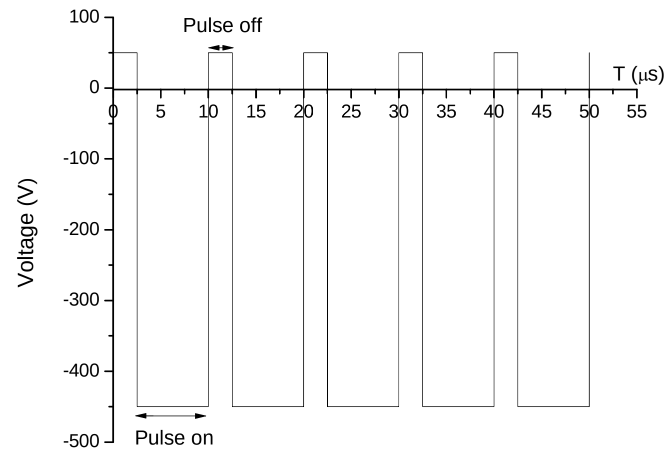
THANK FOR YOUR ATTENTION

Questions ?

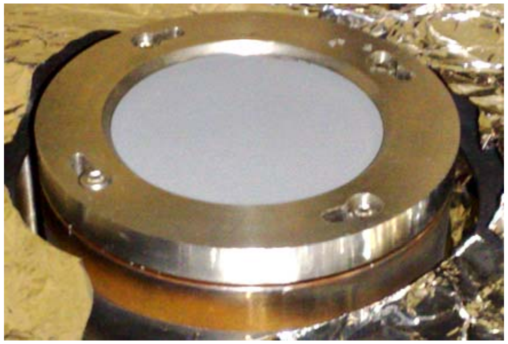
email : s.karthikeyan@edu.salford.ac.uk

Pulsed D.C. Magnetron Sputtering System





Ideal pulsed d.c signal for 100kHz



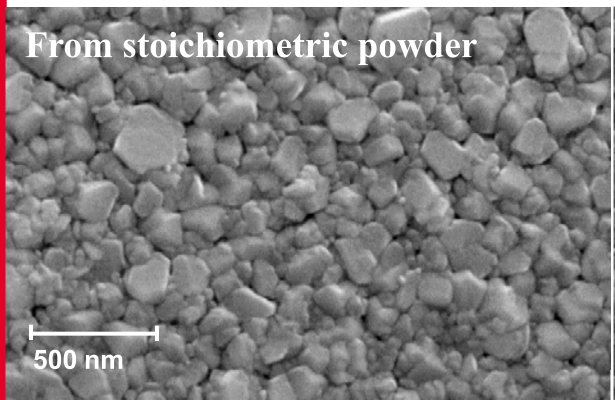
Mo powder target

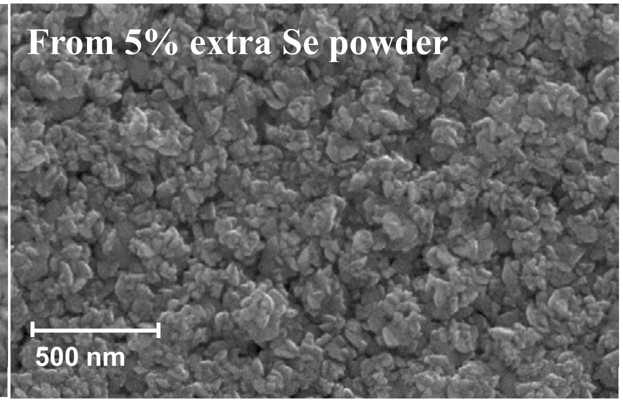
Reference

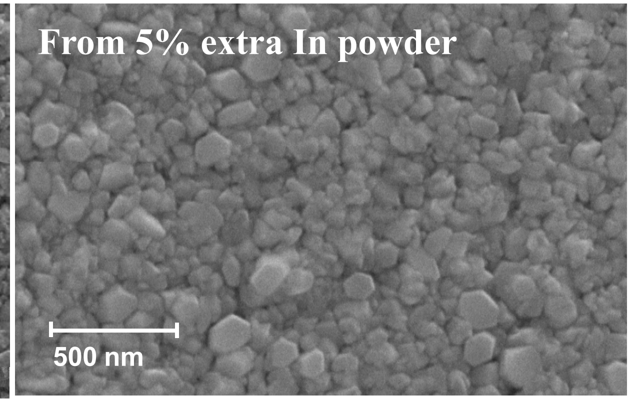
S. Karthikeyan *et al*, Vacuum, 2010, 85; pp.634-638.

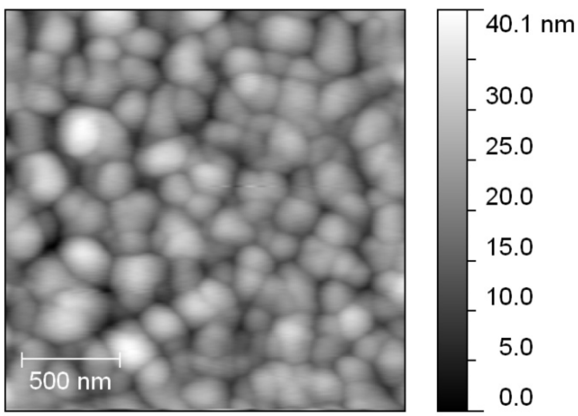
SEM and AFM $CuInSe_2$ Films

~180-210 nm particle size

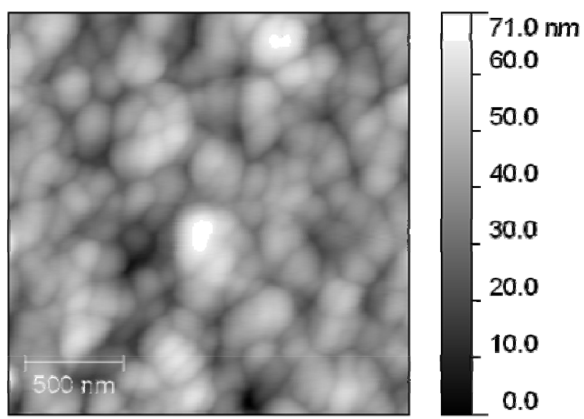




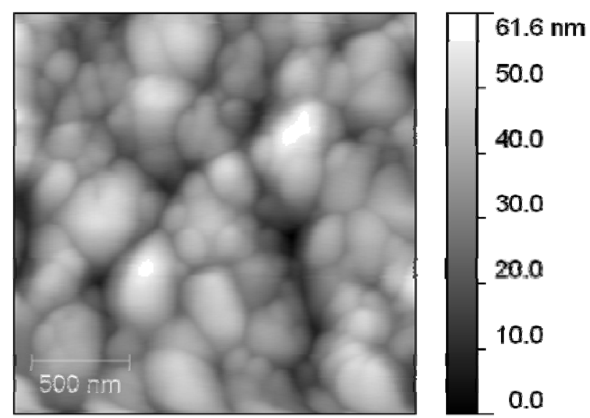




Ra – 4.42 nm



Ra – 7.83 nm



Ra – 7.63 nm