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.

References

A typical CIGS solar cell

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

1. Molybdenum (back contact)
2. Copper indium diselenide (absorber layer)
3. Indium sulphide (buffer layer)
4. Indium oxide (Transparent Conductive Oxide layer)
Sputtered in argon atmosphere from commercial Mo powder.

Films sputtered at different substrate temperatures

Molybdenum Films
## XRD of Mo Films

### Deposition Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>$7.0 \times 10^{-3}$ mbar</td>
</tr>
<tr>
<td>Mode</td>
<td>Constant Power (50W)</td>
</tr>
<tr>
<td>Frequency</td>
<td>75 kHz</td>
</tr>
<tr>
<td>Pulse off Time</td>
<td>0.5 µs</td>
</tr>
<tr>
<td>Distance</td>
<td>10 cm</td>
</tr>
</tbody>
</table>

### Body-centred cubic phase

With increase in substrate temperature, a shift in $2\theta$ towards higher angles was noticed.

### Reference

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

Morphological change from a cluster of small grains to a fibrous, columnar needle-like structure for films grown at 150 °C.

References
Copper Indium Diselenide Films

Sputtered in argon atmosphere from our CuInSe$_2$ powder.

Films sputtered from CIS powder with different compositions.
CuInSe$_2$ Crystal Growth

Selenium, Indium and Copper inside quartz tube before sealing

CuInSe$_2$ inside ampoule after direct fusion

References
XRD of CuInSe₂ Films

Deposition Parameters

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

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)

Preferred (112) orientation
Single Phase
No heating !!

Reference
Ternary Diagram of CuInSe$_2$ Films and Powder

All films were p-type

References
Optical Studies of CuInSe₂ Films

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

Band gap is very close to the reported value of 1.02 eV
Sputtered in argon atmosphere from commercial In$_2$S$_3$ powder.

Films sputtered at different substrate temperatures

Indium Sulphide Films
XRD of In$_2$S$_3$ 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$_2$S$_3$ formed with No heating !!
Optical and AFM studies of In$_2$S$_3$ Films

Band gap decreased with decrease in sulphur content

![Graph showing transmittance vs. wavelength for different temperatures.](image)

<table>
<thead>
<tr>
<th>Deposition Temperature</th>
<th>% In</th>
<th>%S</th>
<th>[%S] / [%In]</th>
<th>Band Gap eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non heated</td>
<td>41.26</td>
<td>58.74</td>
<td>1.42</td>
<td>2.768</td>
</tr>
<tr>
<td>100 °C</td>
<td>41.84</td>
<td>58.16</td>
<td>1.39</td>
<td>2.735</td>
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<tr>
<td>150 °C</td>
<td>42.86</td>
<td>57.14</td>
<td>1.33</td>
<td>2.708</td>
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<tr>
<td>200 °C</td>
<td>43.5</td>
<td>56.5</td>
<td>1.29</td>
<td>2.667</td>
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<td>250 °C</td>
<td>48.51</td>
<td>51.49</td>
<td>1.20</td>
<td>2.526</td>
</tr>
</tbody>
</table>
Reactive sputtered in oxygen and argon atmosphere from commercial In$_2$O$_3$ powder.

Films sputtered at different oxygen flow rates with no additional heating

Indium Oxide Films
In$_2$O$_3$ Films

X-ray diffraction spectra

Cubic bixbyite In$_2$O$_3$ phase.

Preferred (400) (440) orientation at higher O$_2$ concentration

Deposition Parameters
Pressure : $4.0 \times 10^{-3}$ 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
Resistivity of In$_2$O$_3$ Films

Strongly n-type 0 - 2.5% O$_2$

Weakly n-type 5 – 10% O$_2$
Optical Properties of In$_2$O$_3$ Films

![Graph showing transmittance vs. wavelength with different O$_2$ flows (0%, 2.5%, 5.0%, 10%) and corresponding energy levels (3.64 eV, 3.67 eV, 3.70 eV, 3.72 eV).]
AFM of In$_2$O$_3$ Films

- **0% O$_2$**: Ra – 2.63nm
- **2.5% O$_2$**: Ra – 3.06nm
- **5.0% O$_2$**: Ra – 3.60nm
- **10.0% O$_2$**: Ra – 4.64nm

References
Conclusion

- The possibilities of pulsed d.c magnetron sputtering for the deposition of Mo, CuInSe₂, In₂S₃ and In₂O₃ 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 stoichiometric nature of the CIS films largely irrespective of the starting composition of the material.
- Single phase CIS and In₂S₃ 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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THANK FOR YOUR ATTENTION
Questions?

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Pulsed D.C. Magnetron Sputtering System

Reference
SEM and AFM CuInSe₂ Films

~180-210 nm particle size

From stoichiometric powder
From 5% extra Se powder
From 5% extra In powder

Ra – 4.42 nm
Ra – 7.83 nm
Ra – 7.63 nm