Reaktives Magnetron Sputtern von CuInS$_2$-Schichten: Untersuchung des Schichtwachstums

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Reaktives Magnetronsputtern von CuInS₂-Schichten: Untersuchung des Schichtwachstums

Introduction: Thin film solar cells based on CuInS₂

0.6 µm front contact (TCO)
0.1 µm buffer layer CdS
2.5 µm absorber layer CuInS₂

Molybdenum

float glass

sequential process

laser scribing

dc-magnetron-sputtering

Mg-Target

Cu-Target

In-target

magnetron-sputtering

400°-500°C sulfurization

Heater

KCN etching step

chemical bath deposition

ZnO-Target

RF/DC magnetron-sputtering

mechanical scribing

mechanical scribing

reactive magnetron sputtering

sunlight
Why reactive magnetron sputtering of CuInS$_2$ absorber layers?

- large area deposition technique
- lower substrate temperature
- completely sputtered solar cell
- avoiding of KCN etching
Prospects

- Solar cell parameters (at AM1.5)
- Efficiency ($\eta$) and open circuit voltage ($V_{oc}$) are independent of the deposition method.

- In principle, reactive sputtering is suited to prepare high quality CuInS$_2$ layers.

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XVI. Erfahrungsaustausch “Oberflächentechnologie mit Plasma-und Ionenstrahlprozessen” 10. – 12. März 2009 Mühlleiten
Reactive sputtering of CuInS$_2$ Films: Prospects and Problems

System parameters:
- target dimension: $104 \times 54 \times 10 \text{ mm}^3$
- base pressure: $p < 10^{-4} \text{ Pa}$
- gas flow:
  - H$_2$S 17 sccm
  - Ar 34 sccm
- deposition area: $50 \times 50 \text{ mm}^2$
- target-to-substrate distance: 180 mm
- heater: boron nitrid encapsulated graphit meander up to 700°C
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Reproducibility

macroscopic defects
- scratches
- flakes from copper target
- dust particles

material defects
- crystal structure (CuAu-ordering)
- intrinsic material quality

microscopic defects
- pin holes
- morphology (change of Cu/In ratio)

1 mm

1 nm

1 µm
cause for microscopic defects

microscopic defects depend on the copper-to-indium ratio
Microscopic defects: SEM and IR-Thermography

Solar Cell Efficiency: 10%

Solar Cell Efficiency: 1%

good intrinsic material quality but solar cells are shunted due to microscopic defects
Aim:
Preparation of CuInS₂ films with a compact morphology

(1). ion assistance: applying a negative substrate bias

• rf-plasma excitation (27.12 MHz)
  - lower discharge voltage compared to dc-excitation
  - charge built-up is avoided (sulfidic target surface)
  - higher ionization probability (low H₂S/Ar ratio (5%))
  - target-to-substrate distance 9 cm

• variation of the substrate bias
  - floating potential (+10 V) up to a substrate voltage of -150 V
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schematic potential distribution

1. **neutrals**
   - Cu$^0$, In$^0$
   - (\(<10\ \text{eV}\))

2. **negative ions**
   - S$^-$, InS$^-$, InS$_2$$^-$
   - (up to 450 eV)

3. **positive ions**
   - S$^+$, Cu$^+$, In$^+$, In$_2$$^+$
   - InS$^+$, InS$_2$$^+$
   - (15-20 eV)

V$_t$ = 450 V
V$_{pl}$ = +20 V
V$_{fl}$ = -20 V
Substrate bias: film composition and morphology

RBS-Spectrometry (Rutherford Backscattering)

- Cu/In ratio
- Sulphur
- Indium
- Copper

\[ \text{Cu/In ratio} \]

\[ \text{atomic concentration (atoms/cm}^2) \]

\[ \times 10^{17} \]

\[ -V_{\text{sub}} (V) \]

\[ \begin{array}{c|c|c}
\text{Vs} = -15 \text{ V} & \text{Vs} = -25 \text{ V} & \text{Vs} = -50 \text{ V} \\
\end{array} \]

Cu: 120W, In: 180W, p=1Pa, T=450°C, H\textsubscript{2}S:Ar=5%

high substrate bias (more than -50 V) leads to:
- loss of sulfur
- loss of indium
- Cu/In ratio increases

- up to Vs =-50 V mainly CuInS\textsubscript{2} phase (XRD)
- size of the crystallites increases
Motivation: Preparation of CuInS$_2$ films with a compact morphology

(2). Cu/In ratio: \textit{in situ} control of the deposition rate
- deposition monitor
- optical methods
- EDXRD (energy dispersive X-ray diffraction)
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**In situ energy dispersive X-ray diffraction (EDXRD)** [1,2]


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**in situ energy dispersive X-ray diffraction (EDXRD)**

- fluorescence signal $(\text{InK}_{\alpha\beta} \text{CuK}_{\alpha\beta})$
- diffraction pattern

![Graph showing counts vs. deposition time and photon energy](image)

**Time resolution**: 5 s
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reactive sputtering of indium sulfide: temperature variation

deposition rate depends on the substrate temperature
reactive sputtering of copper sulfide: temperature variation

- deposition rate depends not on the substrate temperature
- at a temperature of about 375°C
- X-ray amorph (liquid)
summary

• reactive Magnetron Sputtering is suitable to prepare thin film solar cells based on CuInS$_2$ absorber layers

• to establish a stable CuInS$_2$ deposition process an in situ-control of the Cu/In ratio and the film morphology seems to be mandatory

• ion assistance with ion energies up to 50 eV during the films growth effects the film composition
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Thank you for your attention!