Elaboration and characterization of ZnO films

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- TCO process optimization and characterization
  - Electrical Properties
  - Optical Properties of TCO’s

- Conclusions
Applications of TCO

- Varistor (variable resistor)
- Light Emitting Diodes (LED)
- Sun cream
- Solar cells
- Filter
- Gas sensor

Efectele dopajului și ale dimensionalității asupra proprietăților magnetice, structurale și morfologice și dinamicii de spin în micro și nanostructuri oxidice feromagnetice
TCO film for CIGS solar cells

Main target properties:
- Controlled thickness (50 nm – 700 nm)
- Low resistivity (below $5 \times 10^{-3} \Omega \text{cm}$)
- High transmission (higher 70%)
  - Figure of merit $= -\frac{1}{\rho \cdot \ln(T)}$

![Diagram of TCO film structure for CIGS solar cells](image)
Efectele dopajului si ale dimensionalitatii asupra proprietatilor magnetice, structurale si morfologice si dinamicii de spin in micro si nanostructuri oxidice feromagnetice

TCO thin Films

THIN FILM DEPOSITION

CHEMICAL PROCESS

CHEMICAL SOLUTION DEPOSITION

ELECTROCHEMICAL DEPOSITION

PHYSICAL PROCESS

EVAPORATION

SPUTTERING
Efectele dopajului si ale dimensionalitatii asupra proprietatilor magnetice, structurale si morfologice si dinamicii de spin in micro si nanostructuri oxidice feromagnetice

Outline
(Chemical )

Precursor powders:
* TG-DTA-MS analyses
* FT-IR spectroscopy

Precursor solution:
• Synthesis
  • FT-IR spectroscopy

Nanopowders
* FT-IR spectroscopy
* UV-VIS
* SEM

Thin films
* Optical properties
* X-ray diffraction
* AFM
* SEM
Physical deposition

- Deposition: ZnO thin films via r.f. magnetron sputtering
  AZO & ITO thin films via pulsed d.c magnetron sputtering
  Sputtering system equipped with 3 8” diameter targets
    - ZnO (99.95%)
    - AZO (ZnO/Al2O3)(98:2 wt%)
    - ITO (In2O3/SnO2)(90/10 wt%)

- Substrates: 9×9 cm, glass

- Optimized parameter: thickness, sputtering pressure, pulsed frequency, temperature, substrate distance

- Parameter optimization for bi-layer thin film deposition
ZnO thin films via r.f. sputtering

Optimal deposition parameters:
- **Sputtering target**: ZnO 99.99%
- **Sputtering pressure**: $6.00 \times 10^{-3}$ mBar
- **R.F. sputtering power**: 400W
- **Temperature**: room temperature
- **Atmosphere**: Ar+O$_2$

- Thickness: 85 nm
- Thickness dispersion: ±3%
- Average transmission: 89%
- $E_g$ = 3.22 eV

Optical properties

![Optical properties graph]

Profilometry

![Profilometry graph]
AZO vs. ITO thin films via d.c. sputtering

*Thickness effect*

Deposition parameters: AZO power: 867W, frequency: 2kHz, pressure: 2×10⁻³ mBar

ITO power: 635W, frequency: 2kHz, pressure: 2×10⁻³ mBar

- **AZO**
  - Resistivity (Ω·cm)
  - Average transmission 400-800 nm (%)
  - Figure of merit

- **ITO**
  - Resistivity (Ω·cm)
  - Average transmission 400-800 nm (%)
  - Figure of merit

\[ \rho = 1.8 \times 10^{-3} \, \Omega \cdot \text{cm} \]

\[ \rho = 5.0 \times 10^{-4} \, \Omega \cdot \text{cm} \]
AZO vs. ITO thin films via d.c. sputtering

**Pressure effect**

Deposition parameters:
- AZO power: 867W, frequency: 2kHz, deposition time: 600sec, thickness: 850nm
- ITO power: 610W, frequency: 2kHz, deposition time: 200sec, thickness: 250nm, temp.: room temp & 150°C

- **AZO**
  - Resistivity: \( \rho = 9.7 \times 10^{-4} \ \Omega \text{cm} \)

- **ITO**
  - Resistivity: \( \rho = 2.7 \times 10^{-4} \ \Omega \text{cm} \)
AZO vs. ITO thin films via pulsed d.c. sputtering

**Frequency effect**

Deposition parameters: AZO power: 860W, pressure: $2 \times 10^{-3}$ mBar, deposition time: 200 sec

ITO power: 610W, pressure: $2 \times 10^{-3}$ mBar, deposition time: 200 sec, thickness: 260 nm

- **AZO**

\[ \rho = 1.9 \times 10^{-3} \, \Omega \text{cm} \]

- **ITO**

\[ \rho = 5.4 \times 10^{-3} \, \Omega \text{cm} \]
AZO/i-ZnO thin films - Characterization

- Effect of i-ZnO thickness.

- Effect of AZO thickness.

- Effect of temperature, AZO's thickness and the distance between substrate and target

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Deposition time (sec)</th>
<th>Ar pressure (mbar)</th>
<th>Temperature (°C)</th>
<th>Thickness (nm)</th>
<th>Rmed (sheet resistance) (Ω/□)</th>
<th>Resistivity (Ohm cm)</th>
<th>Average transmission 400-800 nm (%)</th>
<th>Figure of merit (Ω⁻¹cm¹)</th>
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<tbody>
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</table>
ITO/i-ZnO thin films - Characterization

- **Effect of ITO thickness.**
  - average resistivity in the range of $3.5 \times 10^{-3} \ \Omega \text{cm}$ to $6.0 \times 10^{-3} \ \Omega \text{cm}$.
  - inserting a thin ZnO as a buffer deteriorate the resistivity of the ITO.
  - resistivity of ITO/glass $7.5 \times 10^{-4} \ \Omega \text{cm}$ increase to $4.9 \times 10^{-3} \ \Omega \text{cm}$ for the ITO/i-ZnO.
  - optical transmittance in the range of 85% - 88%.

- **Effects of pulsed frequency and the substrate temperature.**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Freq (kHz)</th>
<th>Deposition time (sec)</th>
<th>Ar pressure (mbar)</th>
<th>Temp. (°C)</th>
<th>Thickness (nm)</th>
<th>Rmed (sheet resistance) (Ω/□)</th>
<th>Resistivity (Ω cm)</th>
<th>Average transmission 400-800 nm (%)</th>
<th>Figure of merit (Ω⁻¹ cm⁻¹)</th>
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</table>
Conclusions

- Transparent conductive oxide thin films were obtained by r.f. and d.c. sputtering on 9x9 cm glass substrates.

- The influence of the deposition parameters like thickness, pressure, frequency, temperature and the distance between the substrate and the target was investigated.

- The lowest resistivity obtained in ours sputtering system was $9.7 \times 10^{-4} \Omega \text{cm}$ for a 891 nm AZO thin film and $2.7 \times 10^{-4} \Omega \text{cm}$ for a 231 nm ITO thin film.

- The bi-layer thin films optimization.

- We observed that insertion of a thin layer of i-ZnO under the AZO or ITO deteriorates electrical properties of the TCO’s.
Thank you for the attention!