Solution-processed ZnO films as an alternative to sputtered buffer layers for inorganic photovoltaics

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Solution Processed Inorganic PV @ CSIRO

Introduction

Different solution-based approaches...

Metal Nano / Microcrystals (Cu, Ag, Ni…)

Metal Chalcogenides Molecular Precursors (CdS, ZnS, CZTS, CIGS…)

Chemical Bath Deposition of Oxides / Sulphides (ZnO, ZnS, CdS…)

Metal Chalcogenide Nanocrystals (CdTe, ZnS, CZTS, CIGS…)

Metal Oxide Nanocrystals / Sol-Gel (ZnO, TiO₂, CuO…)

…one goal: solution-processed inorganic solar cells

FAST

CHEAP

LARGE SCALE PRODUCTION

FLEXIBLE SUBSTRATES
Introduction

**Substrate:** Molybdenum film sputtered on glass.

**Absorbing layer:** sputtered, evaporated or deposited from solution (molecular precursors, colloidal inks).

**Window layer:** chemical bath deposition of CdS.

**Buffer layer:** sputtered intrinsic ZnO.

**Charge transport layer:** sputtered ITO or doped-ZnO.

**Charge collection grid:** evaporated Al, Ag or Ni.

Even if the whole p-n junction can be deposited from solutions, scientists still rely on vacuum based depositions for the top layers and contacts for CTZS-CIGS devices.
Intrinsic ZnO acts as a shunt barrier between the CdS and the TCO. Improvement of the performances and the reliability of the device. ZnO film has to be continuous, dense and thin:

**NO ZnO:** the shunt resistance of the device decreases, with the consequent detrimental effect on the performances (shorting).

**THICK ZnO:** device too resistive (problem with charge collection). Also light is absorbed in the near UV (decrease in efficiency).

Sputtering of ZnO-based layers is a well established technique to prepare dense and homogeneous films. When deposited by sputtering, ZnO usually crystallizes with grains oriented along the c-axis of the hexagonal cell.

**MOTIVATION:** Is it possible to obtain the morphology and the properties of sputtered films using a solution-process approach?
Publications on ZnO by CBD usually focus on long wires and on scattering layers. There are a few examples of dense coatings, but always very thick (microns).

Even if precise control on nanowires length, density and alignment is achieved, the first few hundreds of nm are usually disordered.

Several parameters can be changed to tune the ZnO morphology and properties:

- Zinc precursor
- pH
- Time
- Concentration
- Type of base
- Temperature
- Seeds
- ...

Zn(NO₃)₂ → Zn²⁺ + 2NO₃⁻
C₆H₁₂N₄ + 6H₂O → 4NH₃ + 6HCHO
H₂O + NH₃ ↔ OH⁻ + NH₄
Zn²⁺ + 4NH₃ ↔ Zn(NH₃)₄²⁺
Zn²⁺ + 2OH⁻ → Zn(OH)₂ or Zn(NH₃)₄²⁺ + 2OH⁻ → Zn(OH)₂(NH₃)₄
Zn(OH)₂/Zn(OH)₂(NH₃)₄ → ZnO + H₂O

ZnO films from chemical bath deposition

**Seeds Deposition**

- **Substrate**
  - Sol-Gel
  - Colloids

**Chemical Bath**

- **Oriented long wires**
- **Oriented short rods:** Dense film
- **Not oriented Rods /wires**

- **High T (°C)**
  - Low [OH⁻]
  - Low [Zn²⁺]

- **Low T (°C)**
  - High [OH⁻]
  - High [Zn²⁺]
Unseeded substrates (even if crystalline) did not show any ZnO deposition.
Higher Zn concentration causes enhanced nucleation and growth leading to denser coatings. The pH affects the lateral growth, because OH$^-$ groups can absorb on (0001) planes limiting vertical growth. Moreover seeds are more stable at neutral pH.

Increasing the reaction time causes a progressive increase in thickness, fairly linear up to 2 hours (~300 nm final thickness). Lateral size increases with time as well.
ZnO films by CBD

Effect of temperature

Increasing the reaction temperature causes a progressive increase in thickness of ZnO films. ZnO growth is fairly slow below ~75°C. At higher temperatures it is much faster and harder to control.
ZnO films by CBD

Sample facing UP

Precipitates can deposit on the surface of the sample causing irregular growth.

200 nm

Sample facing DOWN

Precipitates deposit on the back of the substrate: ZnO growth is not affected.

200 nm
ZnO films by CBD

Optimized conditions:
◊ Seeds: sol-gel, 180 °C
◊ Zinc: nitrate, 75 mM
◊ Temperature: 70 °C
◊ Position: facing down
◊ Base: HMTA, 75mM
◊ pH: 7
◊ Time: 30-60 min
◊ Substrate: any

Great reproducibility confirmed after repeated syntheses, also on different substrates (properly seeded): SiO₂, Si, CdS, Mo.

These ZnO films prepared by CBD have very similar morphology and properties compared to sputtered layers!
At a set thickness, dense ZnO film has a much higher absorbance in the near UV. ZnO coatings are transparent in the visible and NIR range. Depositions with almost identical properties are obtained on glass and CdS.

Provided the use of a seeded surface, this procedure can be applied on potentially any substrate, crystalline or amorphous. Moreover, due to the low deposition temperature, and the benign (aqueous at neutral pH) environment, it is applicable to plastic substrates.
FTIR shows very little amount of organic compounds and a sharp and intense Zn-O peak, very similar to the sputtered sample.

The refractive index of ZnO films by CBD is only about 6% less than the bulk value*: very dense films (sputtered film is 2% less)

Other solution processed films (NPs, sol-gel) show much larger porosity, presence of organic contaminants and are inherently less crystalline unless annealed at high temperatures

* CRC Handbook of Chemistry and Physics, 2007, 10–248
ZnO films by CBD

Grain Alignment

Texture Coefficient

\[ P(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[ \frac{1}{n} \sum_{i=1}^{n} \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right]^{-1} \]

Alignment Factor

\[ A = \frac{P - 1}{n - 1} \times 100 \]
Solar cells fabricated using ZnO from CBD show identical performances when compared to devices incorporating sputtered ZnO layers.

### Table: Performance Comparison

<table>
<thead>
<tr>
<th></th>
<th>ZnO CBD</th>
<th>ZnO Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{OC}$ (V)</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>$J_{SC}$ (mA/cm²)</td>
<td>32.1</td>
<td>32.0</td>
</tr>
<tr>
<td>FF (%)</td>
<td>55.5</td>
<td>56.3</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>7.3</td>
<td>7.4</td>
</tr>
</tbody>
</table>

van Embden et al. "CZTSSe Solar Cells from Polar Nanocrystal Inks", submitted
Della Gaspera et al. "Mimicry of sputtered ZnO thin films through aqueous deposition", in preparation
Conclusions and Acknowledgements

Summary

- High quality ZnO films have been prepared using a low temperature aqueous deposition.

- These ZnO films have very similar morphology and properties compared to sputtered ZnO.

- High efficiency (> 7%) solar cells have been obtained using both sputtered and CBD ZnO.

Acknowledgements

Dr. Jacek Jasieniak
Dr. Joel van Embden
Dr. Anthony Chesman
Dr. Noel Duffy

Flexible Electronics Theme

Funding
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- High efficiency (> 7%) solar cells have been obtained using both sputtered and CBD ZnO.

If you want to know more about our solution-processed inorganic materials:

<table>
<thead>
<tr>
<th>Speaker</th>
<th>Session Details</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Enrico Della Gaspera</td>
<td>Today (Wed) 5-6 pm, Poster #154, Halls F&amp;G</td>
<td>“Non injection, high concentration synthesis of Ga-doped ZnO colloidal nanocrystals”</td>
</tr>
<tr>
<td>Dr. Joel van Embden</td>
<td>Today (Wed) 5-6 pm, Poster #82, Halls F&amp;G</td>
<td>“CZTSSe thin films solar cells” and “Near infrared absorbing copper antimony sulphide nanocrystals”</td>
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<tr>
<td>Dr. Anthony Chesman</td>
<td>Tomorrow (Thu), 11 am, Session TH 1.1, MR 4-5</td>
<td>“One-pot, multigram synthesis of CZTS and CZGS nanocrystals using a dual precursor approach”</td>
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</table>
Thank you

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ZnO films by CBD

Effect of amines

Dimethyl amino borane: CBD at low temperatures (60 °C) but uncontrolled growth of big crystals resulting in very rough films

Diethylene triamine: Need much higher temperatures (90 °C) and gives nanoparticulate coatings

Hexamethylene tetraamine: CBD at low temperatures (60 °C) and nice tuning of the rods growth according to reaction temperature