



Synergy **RTD 2013** Mechanism of low temperature, aqueous solution deposition of conductive Al-doped ZnO Peter Fuchs, Jan van den Broek, Patrick Stücheli, Harald Hagendorfer, Yaroslav Romanyuk and Ayodhya N. Tiwari EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for EMPA Thin Films and Photovoltaics, Ueberlandstrasse 129, CH-8600 Duebendorf Introduction **CBD** solution chemistry - Al doped ZnO (AZO) is a transparent conducting oxide (TCO) and commonly used as an Solution chemistry: ~1M NH<sub>3</sub> (ligand, pH control), ~ 35 mM Zn, ~1 mM NH<sub>4</sub>Citrate (SDA), ~ electrode in thin film solar cells. 50 mM NH.NO. (pH control) - State of the art deposition methods (sputtering, chemical vapour deposition, pulsed laser At elevated temperature ZnO precipitation is iniated by the retrograde solubility of deposition) require vacuum equipment. [Zn(NH<sub>3</sub>)<sub>x</sub>(OH)<sup>-</sup><sub>y</sub>]<sup>2+(-y)</sup> complexes. - There is the need of a non-vacuum, low cost deposition method with potential for scale up. Chemical bath deposition (CBD) is therefore one of the most promising options:  $ZnO + 4NH_3 + H_2O \implies [Zn(NH_3)_4]^{2+} + 2OH^{-} pH \approx 11.5$ Glass or polyme Seed laye Chemical bath deposition (CBD) UV treatment  $Zn(NO_3)_2 + 4NH_3 \implies [Zn(NH_3)_4]^{2+} + 2NO_3^{-} \text{ pH} \approx 10.8$ substrate hh 222 ZnO is favoured over Zinc salts as a Zn precursor as its dissolution process is intrinsically basic, lead-UV treatment to improve -Spin coating of zinc ammine CBD at elevated temperature: T≈ 80 °C ing to a pH>11 which is favourable for deposition rates as well as the solubility of aluminium aqueous solution - drying at T = 100°C - Al doping by co-precipitation - Morphology control by structure direct -electronic properties (T < 150 °C) no carbon impurities ing agents (SDA) Al dopant supply routes 1. Al salt with constant concentration Dopant supply Resistivity o Carrier density N Mobility L Al in film [cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> [at.%] gradient [Ωcm] [cm<sup>-3</sup>] 0.9 mM AI(NO<sub>3</sub>)<sub>3</sub> 0.5 mM AI(NO<sub>3</sub>)<sub>3</sub> Constant Al con-Citrate 0.0105 -5 6E+19 10.5 0.0  $\rho = 0.44 \ \Omega cm$ = 0.11 Ωcm centration 0 0 Al metal foil 0.0087 -8 9F+19 81 0.4 Constant Citrate 0 AI(NO<sub>2</sub>) 0.0065 -9.8F+19 9.8 04 Citrate (SDA) inconcentration hibits growth on (0002) plane Al(NO<sub>3</sub>)<sub>3</sub> + Citrate 0.0034 -1.68E+20 10.7 0.6 2 um 2 um 10 mM AI(NO<sub>3</sub>), 2 mM AI(NO<sub>3</sub>) ρ > 20 Ωcm Resistivities  $< 10^{-2} \Omega$ cm could be achieved for film thicknesses down to  $\sim 700 \text{ nm}$ Reproducible resistivities in the 0.004-0.006  $\Omega$ cm range, record low of **0.003 \Omegacm** 2 un 2 um [Al(OH),] inhibits growth on {1010} faces

 $\rho = resistivity$ 

A gradient in the AI dopant supply is necessary to enable the onset of columnar growth, while maintaing a low resistivity through increased doping in the top part of the layer

# 2. Al metal foil for gradual dissolution



- Resistivities  $< 10^{-2} \Omega$ cm for film thicknesses  $> 2 \mu$ m - Reproducible resistivities in the 0.007-0.009  $\Omega$ cm range, record low of 0.005  $\Omega$ 

### 3. Al salt supplied gradually

The corrosion rate of the immersed aluminium foil can be mimicked by the continuous addion of Al(NO<sub>3</sub>)<sub>3</sub> through a syringe pump. 100





### **Applications**

Culn<sub>x</sub>Ga<sub>(1-x)</sub>Se<sub>2</sub>thin film solar cells





1600

FF [%] PCE [%]

> 62.7 7.6

> 576 69

> 52.2 6.4

2000

um

Organic solar cells



## Conclusions

- $\rho = 3.4 * 10^{-3} \Omega cm$  (with gradual supply of Al(NO<sub>3</sub>)<sub>3</sub> / Citrate)
- Process temperatures < 150°C

- Transmission > 80% in visible range for film/glass stack

#### Corresponding author

Peter Fuchs, peter.fuchs@empa.ch, Phone: +41 58 765 6124