Aqueous solution-based synthesis and deposition of crystalline In-Ga-Zn-Oxide films via spin-coating

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KNOWLEDGE IN ACTION

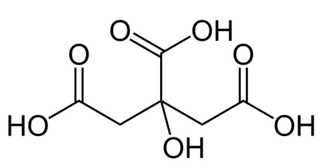
Introduction:

The last decade has seen an increased attention towards the implementation of InGaZnO (IGZO) as a metal oxide channel material in TFT-devices. Crystalline IGZO shows a high electron mobility and low off-state leakage current, which results in an improved device performance compared to amorphous IGZO. Thin film deposition of the IGZO superlattice structure requires a good layer homogeneity in addition to control of the stoichiometry, which can be achieved by using a solution-based process. In general, this is usually achieved using 2-methoxyethanol (2-ME) based precursors. However, due to its harmful and teratogenic properties, alternative solvents are being explored.

In this work, an aqueous precursor system is developed, starting from the individual metal (hydr)oxides. A stable multimetal precursor is acquired, in which the metal ions are stabilized by α-hydroxy carboxylic acids which fulfill the role of ligands. Through an optimized multi-step thermal treatment, crystalline thin films of IGZO are obtained that show a preferential c-axis orientation after rapid thermal annealing at 1000°C in inert conditions. Preliminary electrical characterization of the deposited thin films already shows promising resistivities well below 5 mΩ*cm, which can apply to several areas of interest.

Precursor synthesis:

$In(OH)_3$ Ga_2O_3 ZnO



Reflux setup:

a) 120°C under acidic conditions
b) 110°C under neutral conditions

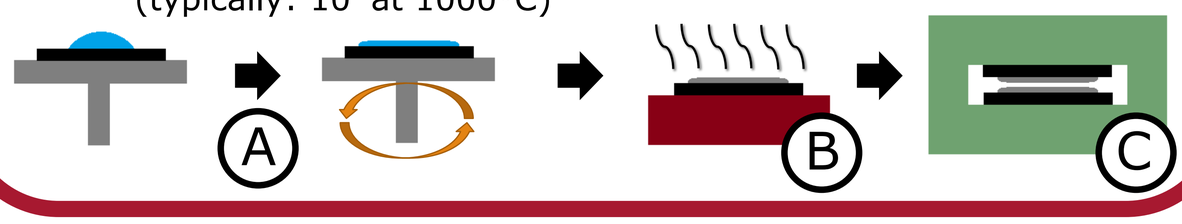
Mixed In^{3+}, Ga^{3+}, Zn^{2+} citrate system

Film processing:

A Spin-coating of aqueous precursor solution (repeat x times after B)

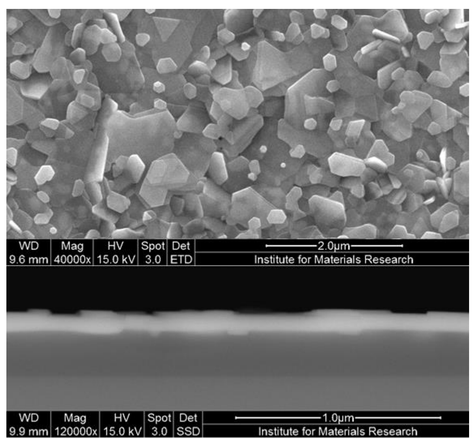
B Intermediate annealing using several hotplate steps (typically: 2' at 200°C, 2' at 400°C, 2' at 580°C)

C Rapid Thermal Processing (RTP) under inert conditions using a "double-substrate" setup to prevent metal volatilization (typically: 10' at 1000°C)



Results:

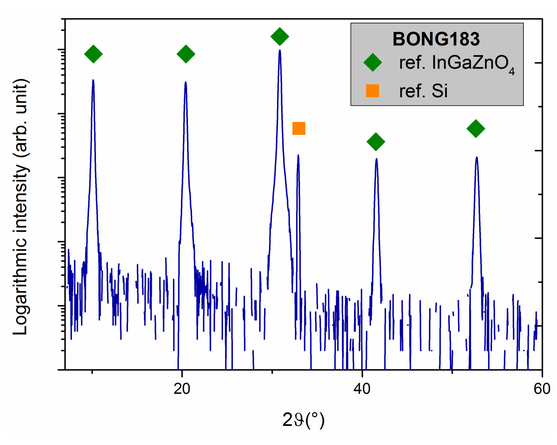
Morphology:



- Deposited on top of Si substrate with a 200 nm thermal oxide layer.
- Formation of large grains throughout the film during crystallization.
- Preferential c-axis orientation of crystallites can be seen by EBSD.
- Films are dense and relatively uniform in thickness.

Picture: SEM-micrographs of 100 nm crystalline $InGaZnO_4$-film annealed at 1000°C. Top: SE-image; Bottom: BSE-image.

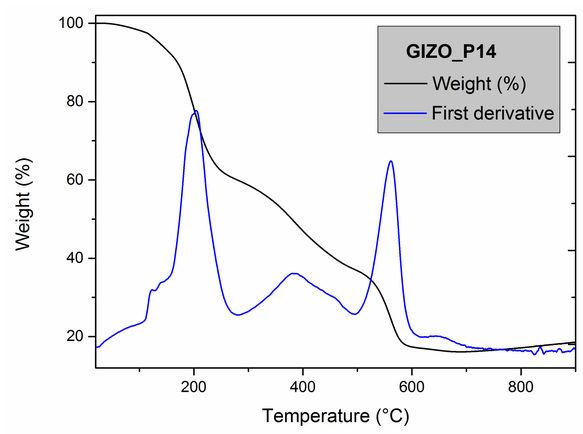
Phase formation:



- Despite short processing times, a very crystalline layer is observed.
- $InGaO_3(ZnO)_m$ superlattice [00N] peaks are detected, in this case m=1. (N: 3, 6, 9, …)
- No apparent secondary phases are seen.

Picture: XRD-diffractogram of crystalline IGZO-film annealed at 1000°C. Legend: ◆ $InGaO_3(ZnO)_1$ ■ Si.

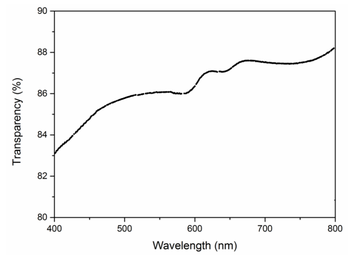
Thermal decomposition:



- Decomposition in dry air takes place in 3 steps.
- The gel is fully decomposed at around 600°C.
- Residual weight fraction is around 17% → Rather extensive mass loss during hot plate treatments.

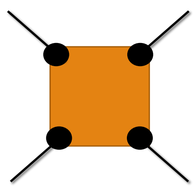
Picture: Thermogravimetric analysis of IGZO-precursor gel dried at 80°C. Heating was done at a ramp rate of 10°C/min under dry air atmosphere.

Opto-electrical properties:



- Sample deposition on transparent fused silica substrate.
- Transparency in the visible range (400-800 nm) averages at 86,1%.

Picture: Visible-light transmission spectrum of crystalline IGZO-film deposited on a fused silica substrate (background: air).



- Calculated resistivity of $2,3*10^{-3}$ Ω*cm. (4-point VdP setup, film thickness of 100 nm)
- Hall-effect measurement at 290K yields:
  - Carrier conc.: $1,0*10^{20}$ cm^{-3}
  - Hall mobility: 27,2 cm^2/Vs

Summary:

- We are able to deposit IGZO films using CSD by spin-coating, an aqueous precursor route was chosen.
- A phase-pure crystalline $InGaZnO_4$ was seen after annealing at 1000°C.
- The macroscopically uniform film shows a preferential c-axis orientation.
- Promising electrical properties with resistivities around $2*10^{-3}$ Ω*cm and Hall mobility values of 27 cm^2/Vs.

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