National Renewable Energy Laboratory

Colorado School of Mines

Innovation for Our Energy Future

Solution Deposition of Amorphous IZO Films By Ultrasonic Spray Pyrolysis

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Transparent Conducting Oxides (TCO)

Dual Function in Solar Cell

- Transparent - allows light to enter solar cell to reach the absorber
- Conducting - electrical contact for collecting charge carriers

CIS Solar Cell Cross-Section

M.A. Contreras, et. al, 24th PVSC IEEE December 5-9 (1994)

Why Solution Processing ?

Current Deposition Methods

Sputtering / Pulsed Laser Deposition

- Expensive
- High vacuum
- Difficult to scale

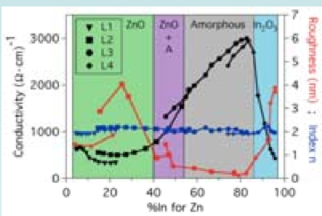
Solution Deposition Methods

Spin Coating / Spray Pyrolysis / Inkjet Printing

- Inexpensive
- Atmospheric
- Scalable
- Simple

Our Approach

Combinatorially sputtered Indium Zinc Oxide (IZO) shows highest conductivity and smoothness in Indium-rich region



M.P. Taylor *et al*, Adv. Funct. Mater. 18 (2008) 3169-3178

Current TCOs by solution routes have only focused on crystalline, Zinc-rich films (3-5% In)

Our Goals:

- Amorphous IZO film
- Indium-rich composition
- Overcome solubility problems with conventional Indium metal-organic compounds
- Develop new In-Zn precursors

Conventional Mixed Precursor Approach: Zn Precursor + In Precursor → IZO Film

versus

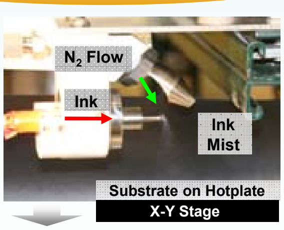
Single Precursor Approach: In-Zn Precursor → IZO Film

Solution Processing Scheme

Ink Formulation
Precursors + Additives (surfactants, oxidizing agents, pH modifiers) + Solvent

Deposit
Spray film on heated substrate (temperature, flow rate, coats)

NREL Ultrasonic Spray System



Thermal Processing
Convert ink film to TCO (temperature, ramp rate, time, annealing gases)

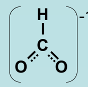
Analyze
Conductivity Transparency
Morphology Film Quality

Formate Precursor Synthesis

Zn Formate
Zn hydroxy carbonate + formic acid at 80⁰C 1 week, white crystals

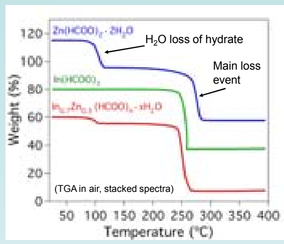
In Formate
In oxide + formic acid at 80⁰C 2 weeks, white with yellow tint powder

$In_{(1-x)}$-$Zn_{(x)}$ Formate (IZF)
Zn hydroxy carbonate + In oxide + formic acid at 80⁰C 2 weeks, white powder



Formate Ion

Formate Characterization

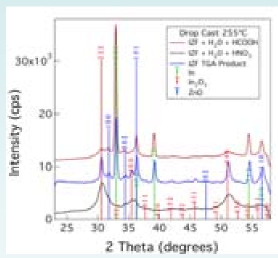


Thermal Gravimetric Analysis (TGA)

- Formates decompose at temperature similar to acetates
- Single / close decomposition temperatures preferred to avoid separate phase formation

Ink Additives

Ink	Film
IZF + H_2O + HCOOH (reducing acid)	Gray (In^0)
IZF + H_2O + HNO_3 (oxidizing acid)	Yellow (In_2O_3)



- IZF inherently reducing
- Acid addition required for IZF solubility
- Acid choice affects redox ink properties

Processing Details

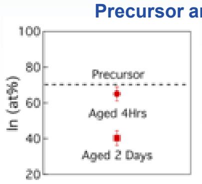
Ink Formulation
IZF + HNO_3 + H_2O IZF + HNO_3 + MeOH (0.1M)

Deposition
Sprayed films on glass substrates at 140-210⁰C

Ar-RTP Processing
Rapid Thermal Processing under Ar for 20min at 340⁰C with a 20⁰C/sec ramp film side up then down

Ar-H_2 Annealing
Annealed in tube furnace under Ar-4%H_2 at 300-400⁰C for 20min with a 3hr ramp

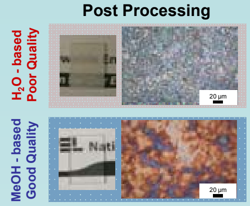
Precursor and Film Composition

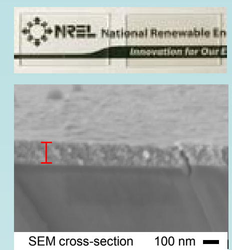


Composition of IZF precursor (line) and annealed films (points) when ink aged 4 hrs versus 2 days:

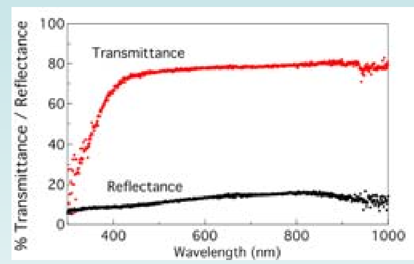
- Measured by XRF
- Confirmed by ICP-AES
- Longer ink aging results in precipitation and reduction of In content (at%) relative to Zn

Film Quality and Optical Properties

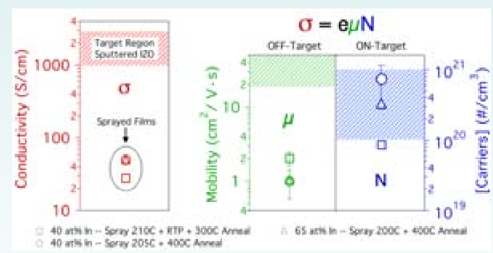




- MeOH prevents cracking
- 150-200 nm thick
- SEM suggests porous film or small grains
- AFM RMS roughness 18 nm
- Sprayed films 5-40X rougher than sputtered IZO film



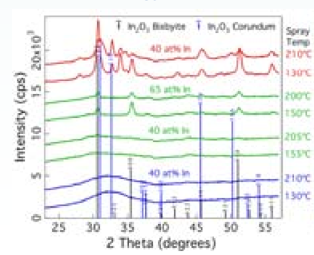
Conductivity



- Need to boost mobility by ~1 order of magnitude to be in range of sputtered IZO
- Desired carrier concentration can be achieved with 40 and 65 at% In

Film Morphology

- XRD suggests 40 at% In films annealed at 300-400ºC are amorphous
- Higher temperature processing and films with 65 at% In show In_2O_3 crystallization / phase separation
- No ZnO observed



Conclusions

- Spray deposition with an IZF+HNO_3+MeOH ink and Ar-H_2 anneal results in IZO films
  - Amorphous, In_2O_3 forms at higher In content and with annealing near 500ºC
  - Thin, crack-free
  - Good optical transmittance (>75%)
  - Conductive (~60 S/cm)
- Successfully synthesized and characterized In, Zn, and In-Zn formates
- In-Zn formate (IZF) can serve as a precursor for In-Zn oxide films
  - 70:30 In:Zn atomic ratio
  - Decomposes near 260ºC
  - Ink composition dependent on aging

Future Work

- Explore processing to produce denser films and increase mobility
- Narrow processing temperature and time windows
- Factorial design to determine critical processing parameters
- Explore other precursors

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