

Solution Deposition of Amorphous IZO Films By Ultrasonic Spray Pyrolysis

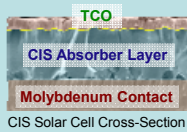
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Transparent Conducting Oxides (TCO)

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

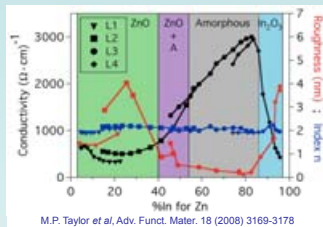
- Sputtering / Pulsed Laser Deposition
- Expensive
- High vacuum
- Difficult to scale

Solution Deposition Methods

- Spin Coating / Spray Pyrolysis / Inkjet Printing
- Inexpensive
- Atmospheric
- Scalable
- Simple



Our Approach

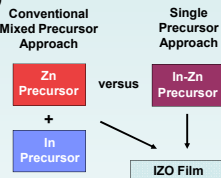


Combinatorially sputtered Indium Zinc Oxide (IZO) shows highest conductivity and smoothness in Indium-rich region

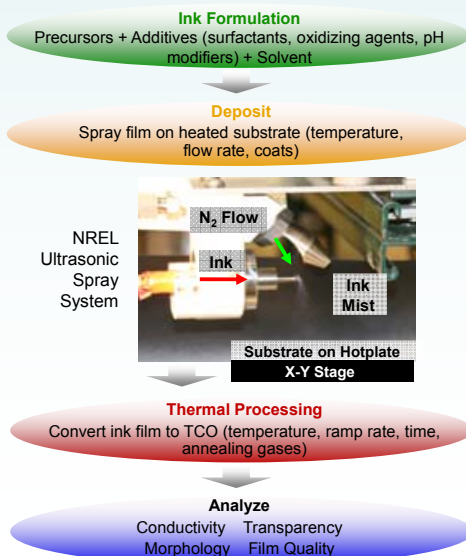
Current TCOs by solution routes have only focused on crystalline, Zinc-rich films (3-5% In)

Our Goals:

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



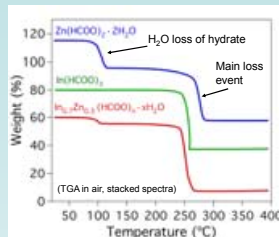
Solution Processing Scheme



Formate Precursor Synthesis

Zn Formate Zn hydroxy carbonate + formic acid at 80°C 1 week, white crystals	
In Formate In oxide + formic acid at 80°C 2 weeks, white with yellow tint powder	
In_(1-x)Zn_(x) Formate (IZF) hydroxy carbonate + In oxide + formic acid at 80°C 2 weeks, white powder	

Formate Characterization



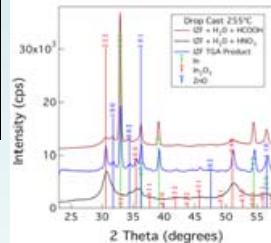
Thermal Gravimetric Analysis (TGA)

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

Ink Additives

Ink	Film
IZF + H ₂ O + HCOOH (reducing acid)	Gray (In ⁰)
IZF + H ₂ O + HNO ₃ (oxidizing acid)	Yellow (In ₂ O ₃)

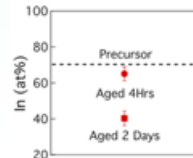
- IZF inherently reducing
- Acid addition required for IZF solubility
- Acid choice affects redox ink properties



Processing Details

Ink Formulation IZF + HNO ₃ + H ₂ O IZF + HNO ₃ + MeOH (0.1M)
Deposition Sprayed films on glass substrates at 140-210°C
Ar-RTP Processing Rapid Thermal Processing under Ar for 20min at 340°C with a 20°C/sec ramp film side up then down
Ar-H₂ Annealing Annealed in tube furnace under Ar-4%H ₂ at 300-400°C for 20min with a 3hr ramp

Precursor and Film Composition

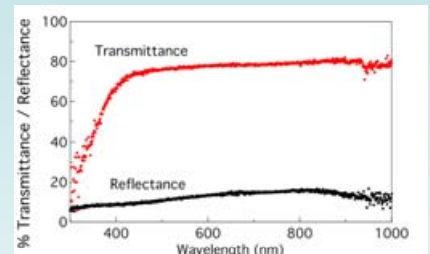


- Composition of IZF precursor (line) and annealed films (points) when ink aged 4 hrs versus 2 days:
- Measured by XRF
- Confirmed by ICP-AES
- Longer ink aging results in precipitation and reduction of In content (at%) relative to Zn

Film Quality and Optical Properties

	As Deposited	Post Processing
H₂O-based Poor Quality		
MeOH-based Good Quality		

• 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 300-400°C are amorphous
- Higher temperature processing and films with 65 at% In show In₂O₃ crystallization / phase separation
- No ZnO observed

Conclusions

- Spray deposition with an IZF+HNO₃+MeOH ink and Ar-H₂ anneal results in IZO films
 - Amorphous, In₂O₃ forms at higher In content and with annealing near 500°C
 - 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 260°C
 - 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