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Solution Deposition of Amorphous IZO Films by Ultrasonic Spray Pyrolysis

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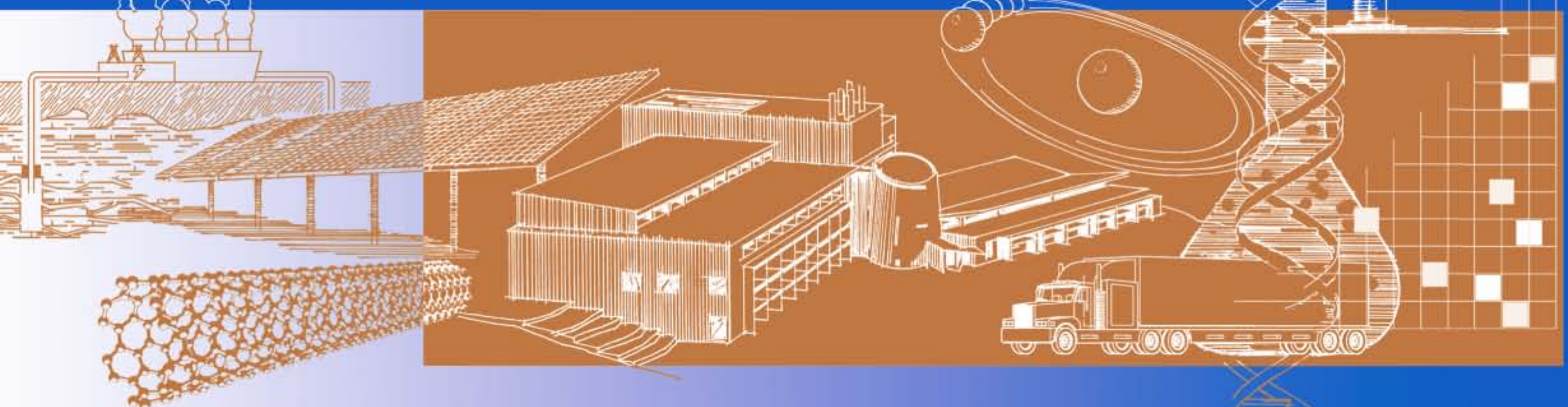

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SOLUTION DEPOSITION OF AMORPHOUS IZO FILMS BY ULTRASONIC SPRAY PYROLYSIS

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ABSTRACT

Atmospheric-pressure solution deposition of the transparent conducting oxide (TCO), amorphous indium-zinc oxide (α-IZO), was investigated as an alternative to traditional vacuum-based physical vapor deposition techniques for photovoltaic applications. Solution processing is attractive due to its ease and potential to lower device manufacturing costs. Here we report on α-IZO films prepared by ultrasonic spray pyrolysis from solutions of an indium-zinc formate (IZF) precursor. Thin, crack-free, amorphous IZO films with good optical transmittance (>75%) and conductivities of ~34 S/cm were produced from an IZF-HNO_3-methanol ink using joint RTP and Ar-H_2 annealing.

INTRODUCTION

Currently, the thin film transparent conducting oxides (TCOs) used for CIGS are deposited by vacuum-based physical vapor deposition techniques such as sputtering. This study investigates atmospheric-pressure solution deposition routes as an alternative to these traditional high-vacuum techniques. Solution processing is attractive due to its ease and potential to lower device manufacturing costs.

ZnO, typically used for the TCO layer, has poor resistance to water vapor. Recently, it has been demonstrated that amorphous indium-zinc oxide (α-IZO) has qualitatively better resistance to degradation at 85°C / 85% relative humidity. Sputtered IZO shows the highest conductivity and smoothness in the indium-rich region (~80 at% In) where the films are amorphous. However, current TCOs deposited by solution routes have only focused on crystalline, zinc-rich films (3-5 at% In) [1-4]. In nearly all these cases, acetate precursors are used, but the high indium content of α-IZO is difficult to achieve due to the poor solubility of indium acetate. Here we report on α-IZO films prepared by ultrasonic spray pyrolysis from solutions of an indium-zinc formate (IZF) precursor. Thin, smooth, crack-free amorphous IZO films with good optical transmittance (>75%) and conductivities of ~34 S/cm were produced from an IZF-HNO_3-methanol ink using joint RTP and Ar-H_2 annealing.

EXPERIMENTAL

Indium-zinc formate (IZF) was prepared (70:30 mol In:Zn) using a synthesis procedure developed in our laboratory. The procedure and characterization of the precursor are subjects of a manuscript in progress. 0.1M IZF inks were prepared with 1 vol% of conc. HNO_3 in both water and a methanol/water (10:1) mixture. Inks were aged 1-3 days and filtered prior to use. Films were ultrasonically sprayed in open atmosphere onto O_2-plasma cleaned glass microscope slides mounted on a substrate heater and X-Y stage. Typical deposition parameters were as follows: substrate surface temperatures 140-210°C, 7 SLPM N_2 carrier flow, and a 0.25 mL/min ink flow rate.

Films were aged for 2 days prior to annealing. Annealing was performed in a tube furnace under Ar-4%H_2 at 300°C for 20min with a 3hr ramp. Additional samples were processed prior to anneal by rapid thermal processing (RTP) under Ar for 20min at 340^0C on a Si susceptor with a 20^0C/sec ramp film side up and then down.

RESULTS AND DISCUSSION

Precursor Characterization and Ink Formulation

The In:Zn ratio for the prepared IZF was determined to be 70:30 at% by ICP-AES. This composition is near the peak conductivity of 80:20 for IZO. In order to determine the processing temperatures required to convert the IZF precursor into IZO, thermal gravimetric analysis (TGA) was performed in air. The decomposition temperature was determined to be ~255°C. Spraying was performed above the solvent boiling point but below the decomposition temperature. Annealing was performed at 300°C to ensure full decomposition.

The effect of additives to the ink not only influences ink properties (such as wetting) but also influences the ink chemistry. The addition of nitric acid was required to ensure solubility of the precursor. Nitric acid was chosen over other acids to promote oxide formation, as it is an oxidizing acid.

Film Morphology and Optical Properties

Sputtered IZO has been shown to be amorphous at a 70:30 In:Zn composition. XRD was performed to determine whether spray deposited films are amorphous as well. Fig. 1 shows that films annealed at 300ºC are amorphous. Processing at higher temperature (500°C) resulted in crystallization during decomposition and/or phase separation of In_2O_3. Deposition temperature affected the morphology of the final films as spraying at 210°C showed greater resistance to In_2O_3 formation.

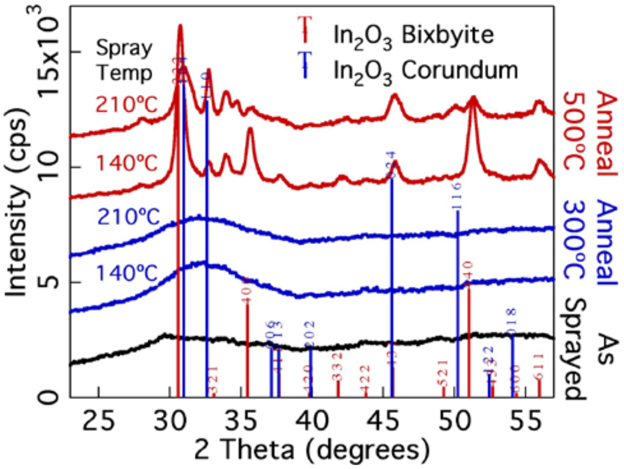

Fig. 1. XRD of sprayed films post-deposition at 140^0C and 210^0C and post-anneal at 300^0C and 500^0C.

Transparency is a critical property for thin film transparent conductors. Film morphology is crucial in determining the optical properties of solution deposited films as cracks, pores, and surface roughness can result in scattering.

The ink solvent was found to affect the quality of the film produced. The water-based ink (Fig. 2a) resulted in a loss of optical transparency due to film cracking. However, the methanol/water mixed solvent (Fig. 2b) produced a crack free film with good optical properties. Little optical loss was observed after processing, with a respectable transmittance of >75% as shown in Fig. 3.

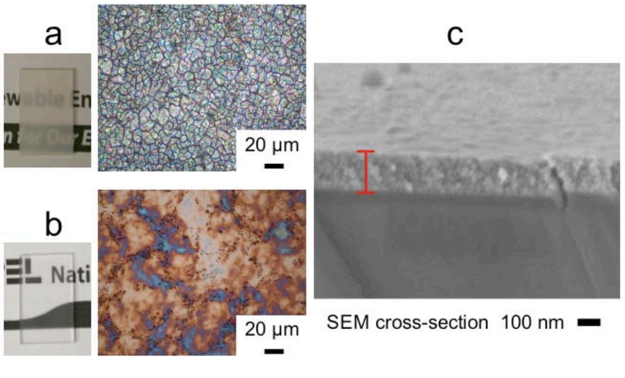

Fig. 2. Optical micrographs of films a) post-anneal sprayed from water-based ink, b) post-anneal sprayed from methanol/water-based ink, c) SEM cross-section of film post-anneal sprayed from methanol/water-based ink.

Spray depositing with 8 coats resulted in a smooth film with a thickness of 150-200 nm as seen in the SEM image in Fig. 2c. AFM studies are in progress to quantify the surface morphology and roughness.

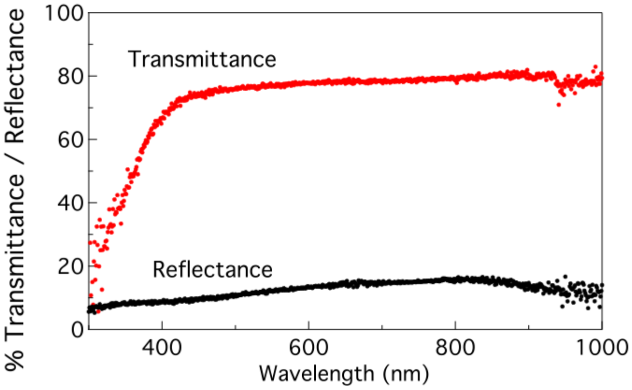

Fig. 3. Transmission-Reflectance of IZO film.

Electrical Properties

Conductivity is another critical property for thin film transparent conductors. Conductivity of the films was determined from 4-point probe sheet resistance and by Hall measurements. In general, it was observed that films sprayed at 210ºC had higher conductivities.

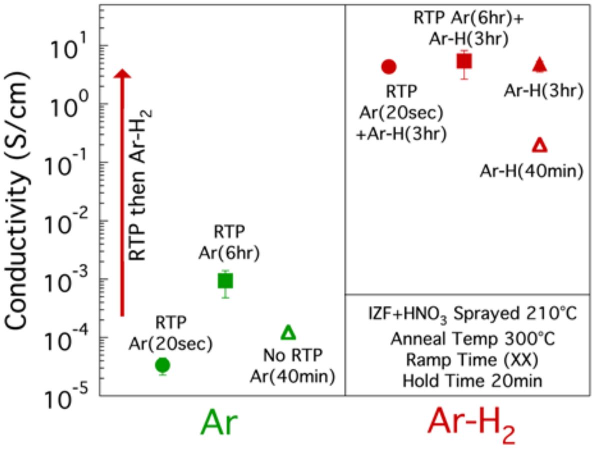

Fig. 4. Conductivity (σ) of IZO films as a function of annealing gas and processing conditions. *RTP* denotes σ after RTP step, and *RTP+* denotes σ after RTP and tube furnace anneal. Parenthesized value indicates ramp rate.

Fig. 4 shows the conductivity of films as a function of thermal processing atmosphere (Ar and Ar-4%H_2), ramp time, and thermal processing scheme (RTP, tube furnace anneal, and RTP followed by a tube furnace anneal). First, conductivity increases with longer anneal times and with more reducing annealing atmospheres. This effect is attributed to the production of more carriers. Second, rapid thermal processing demonstrates promise as a quick production method for solution deposited TCOs. Lower conductivity films were observed because the RTP could only be performed under Ar flow in the current setup. More importantly, it was demonstrated that the conductivity could be increased by 4-5 orders of magnitude following a secondary Ar-H_2 anneal.

Fig. 5 compares the Hall conductivity (34 S/cm), carrier concentration (8.5 x10^{19} #/cm^2), and mobility (2.0 cm^2/Vs) of the best-sprayed IZO film to date with the typical property range for sputtered IZO (illustrated by bars). The carrier concentration and especially mobility each need to be increased by ~1 order of magnitude to be in range of sputtered IZO. The low mobility is attributed to porosity or small grains as seen in the SEM cross-section of the film (Fig. 2c).

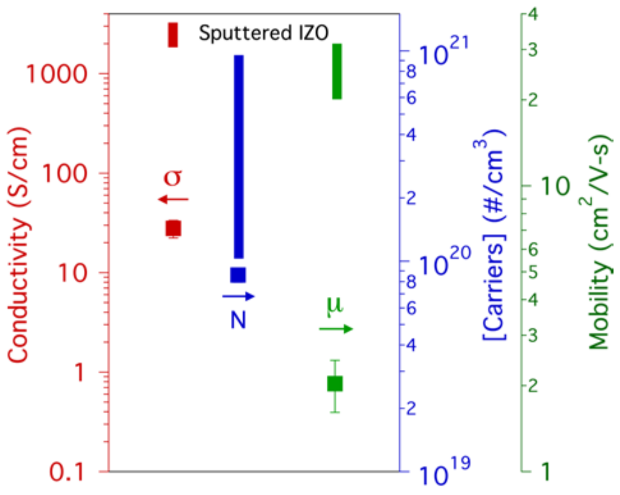

Fig. 5. Hall conductivity, carrier concentration, and mobility of best sprayed IZO film (points) compared to typical property range for sputtered IZO (bars).

CONCLUSIONS

In summary, In-Zn formate (IZF) can serve as an In-rich precursor for IZO films. Ultrasonic spray deposited IZF-HNO_3-methanol ink using joint RTP and Ar-H_2 annealing results in thin, smooth, crack-free amorphous IZO films with good optical transmittance (>75%). Current film conductivity (~34 S/cm) requires increases in both carrier concentration and mobility by ~1 order of magnitude to be comparable to sputtered IZO. Taken together, with the potential for lower production costs that solution processing offers, these attributes make ultrasonic spray deposited α-IZO thin film TCOs an attractive choice for many PV applications.

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