



Thermal processing of aqueous AZO inks towards functional TCO thin films



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ARTICLE INFO

Article history:

Received 10 May 2016

Received in revised form

26 July 2016

Accepted 15 August 2016

Available online 18 August 2016

Keywords:

Al-doped ZnO

Thin film

Inkjet printing

Transparent conductors

Sol-gel

ABSTRACT

Aluminium doped zinc oxide is considered an interesting, earth abundant alternative to the transparent conductor indium tin oxide. In this respect, we synthesized Al-ZnO (AZO) thin films by a chemical solution deposition approach. Using water-based inks, the AZO thin films were printed in one single step on glass substrates in non-vacuum conditions. The drying process and the humidity of the atmosphere proved to be crucial during the thermal processing of the wet deposited thin films. To improve the understanding of the phenomena involved, the influence of these processing parameters on the final properties of the AZO thin films are investigated by FTIR, XRD, SEM, ¹H and ²⁷Al NMR and resistivity measurements. Optimal conditions were obtained by drying the wet thin film at 120 °C, followed by heating in a tube furnace until 500 °C under a 200 ppm O₂/N₂ atmosphere with a humidity controlled by bubbling the gas flow through 2 glass bottles containing water at 20 °C. AZO thin films with an resistivity of $2.54 \times 10^{-2} \Omega \text{ cm}$ were obtained.

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1. Introduction

Indium tin oxide (ITO) is generally accepted as the leading transparent conductive oxide (TCO) [1]. However, an expanding market of TCOs and an unstable supply of indium stirred research efforts towards indium free TCOs. Indeed, indium's natural scarcity and the increasing demand for ITO resulted in a soaring market value for indium. Before 1960 the price of indium metal was steady at \$72/kg but rose to \$735/kg in 2014. N-type doped ZnO is an attractive candidate for indium free TCO with Al and Ga as promising dopants [2–4]. Doping ZnO with group IIIA elements such as B, Al, Ga, In lowers the resistivity and increases the carrier density. Al, Ga, and In are the most frequently used dopants. We favour Al as dopant for the ZnO host matrix for several reasons. (1) The introduction of Al in the host matrix under reducing conditions creates

defect levels close to the ZnO conduction band [5]. (2) The experimental solubility limit of 3–4 at% allows the introduction of a large quantity of charge carriers [6–8]. (3) Al is the most cheap and abundant element of group IIIA [9].

A dopant can occupy diverse sites in the crystal structure of the host matrix; (i) empty octahedral or (ii) empty tetrahedral sites. Alternatively, (iii) a dopant ion can substitute Zn in the regular lattice. In the latter case, the dopant occupies a tetrahedral site and can donate a free electron to the conduction band of ZnO [10]. In contrast, if an *interstitial* tetrahedral site is occupied, the dopant is inactive, whereas occupied octahedral sites act as electron acceptors [10,11]. These doped ZnO materials have the capacity to reach competitive opto-electrical properties compared to ITO [12,13]. Nevertheless, the manufacturing process of doped ZnO thin films still lacks high throughput capacity. In addition, commonly used vacuum deposition methods such as chemical vapor deposition (CVD), sputtering, pulsed laser deposition (PLD) suffer from by high cost associated with maintaining vacuum during production [14].

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Although the nowadays studied chemical solution deposition (CSD) processes are better, they often apply multiple coatings steps with an intensive thermal treatment in between [15–18].

In this paper, we opted to investigate the synthesis of Al doped ZnO (AZO) thin films due the high abundance and low cost of Al and Zn and its excellent opto-electrical properties [9]. Our goal is to deposit AZO thin films through CSD processing in an environmental friendly and scalable manner. As deposition method, ink jet printing is selected and the AZO thin films are synthesized through the single deposition of an aqueous ink. Ink jet printing is a scalable and versatile technique which allows a controlled deposition of thin films and patterns on small or large surfaces [19,20]. Ink jet printers have a closed cartridge which reduces any chance of contamination and the precise deposition of the droplets reduce undesired waste of the ink. The synthesis of aqueous inks avoids the commonly used toxic organic solvents such as 2-methoxyethanol. However, dissolving metal precursors in water enhances the possibility of metal hydroxide precipitation at neutral pH levels [21–23]. Stable inks are obtained by adding chelating components such as ethylenediaminetetraacetic acid (EDTA), citric acid (CA), nitrilotriacetic acid (NTA), etc. These additives make the thermal processing of wet thin films more complex. The development and characterisation of the inks and the printing itself was studied in detail in a previous paper [24]. Optimising the processing steps such as drying time, synthesis temperature, humidity of the used atmosphere aims to further improve the final morphology and properties of the films and is the subject of this paper.

2. Experimental section

2.1. Synthesis

The preparation of the AZO ink, cleaning of the substrates and deposition of the ink are discussed in detail elsewhere [24]. Two separate aqueous solutions were prepared containing stabilized Zn^{2+} and Al^{3+} ions. The Zn solution contains zinc acetate (0.5 mol L^{-1}), ethanolamine, formic acid, while the Al solution contains aluminium nitrate (0.5 mol L^{-1}), malonic acid, ethanolamine and formic acid. Mixing both solutions resulted in a stable AZO aqueous ink which could be printed by the addition of 10 v% of ethanol.

The AZO thin films were printed on cleaned EAGLE²⁰⁰⁰ glass substrates (Präzisions Glass&Optics) with a piezoelectric drop-on-demand printing system and a computer controlled XY plotter. The orifice used (Microfab, MJ-ABP-01) had a diameter of 30 μm . The ink was jetted at 2 kHz. The applied waveform had a maximum of 14 V that was maintained for 4 μs . A thin film was printed with a line and drop spacing of 50 μm .

The printed layers were dried on a preheated hotplate for 10 min at varying temperatures (90–250 °C) before thermal treatment in a tube furnace till 500 °C in a wet or dry 200 ppm O_2/N_2 atmosphere. The heating rate was kept at 10 °C/min with a dwell at 250 °C and 500 °C for 1 h. The wet atmosphere was established by bubbling the dry atmosphere through 2 glass bottles containing water at varying temperatures. By controlling the water temperature, the amount of water vapour carried with the atmosphere was altered. Finally, samples were postheated at 450 °C during 30 min in a dry $\text{Ar}/5\% \text{H}_2$ atmosphere to create more charge carriers in order to enhance the electrical properties [25,26].

2.2. Characterization

The precursor solutions were studied by NMR (Bruker Avance III Spectrometer operating at a ^1H frequency of 500.13 MHz and equipped with a BBL_Z gradient probe) and ATR-FTIR (Perkin Elmer

Spectrum 100). Except mentioned otherwise, the FTIR measurements were performed on dried inks and metal-ion free blanks at 75 °C. The 1D ^1H NMR spectra recorded after heating the ink and required dilution in D_2O till the initial concentration of the precursor was obtained. Diffusion NMR measurements (2D DOSY) were performed on as prepared metal-ion free blanks and inks using a double stimulated echo sequence for convection compensation and with monopolar gradient pulses. Smoothed rectangle gradient pulse shapes were used throughout. The gradient strength was varied quadratically from 2 to 95% of the probe's maximum value (calibrated at 50.2 G/cm) in 32 or 64 steps, with the gradient pulse duration and diffusion delay optimized to ensure a final attenuation of the signal in the final increment of less than 10% relative to the first increment.

^{27}Al MAS NMR was used to study the influence of dry and wet thermal processing on the Al incorporation in the ZnO matrix. AZO bulk powders were synthesised in dry or wet air at 500 °C. The wet processed AZO powders were synthesised by bubbling the used gas flow through 2 glass bottles at 20 °C during synthesis. The spectra were recorded on a Bruker Avance400 spectrometer, using a 4 mm MAS probe and a spinning frequency of 10 kHz. The length and power level of the rf-pulses were carefully optimised on the sample itself. The collected data are an accumulation of 1536 scans with a recycle delay of 5s.

TGA/DTA measurements were performed on a Netzsch STA449 F3 Jupiter setup. The samples were dried at 75 °C during 1 h prior to analysis. A quantity of ± 10 mg of material was heated at 10 °C/min under a 120 mL/min air flow.

The morphology of the processed AZO coatings was analysed with a FEI Nova 600 Nanolab Dual Beam FIB-SEM. The crystalline phases of the obtained AZO coatings were characterised using a powder X-ray diffractometer equipped with a line detector and $\text{Cu K}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation (Bruker D8 Discover). The sheet resistance was measured by a four point wafer prober (Veeco, FPP-5000) while the carrier concentration and mobility were measured with a home-built setup in the Hall-Van der Pauw configuration (Keithley 6220 Precision Current Source, HP 3478 A Multimeter, electromagnet Varian V 3603).

3. Results and discussion

Previous results showed that the synthesized AZO thin films have a minimum resistivity when doped with 3 at% of Al. The final processed AZO layer using the printing parameters mentioned in the experimental section had a thickness of 80 nm. The doping percentages nor the printing parameters were varied in this paper.

3.1. Influence of the drying temperature on the formation of AZO thin films

After ink-jet printing of the precursor solution, the samples were first dried on a hotplate before the final thermal treatment in a tube furnace. This drying step was performed at various temperatures and related to the resistivity of the final layer (Fig. 1). From the figure, it is clear that the optimal drying temperature was 120 °C as this coincides with a minimum in resistivity.

To elucidate the chemical reactions that occur during the drying step, we studied the AZO films with a combination of FTIR and NMR. The inks were studied first to identify the formed complexes. The FTIR spectra of the ink dried at 75 °C (Fig. 2A) did not show a clear presence of the possibly formed Zn complexes and signals of Al complexes are absent due to the low concentration of these species in the ink. A small shift in the $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ of the formate and the acetate group suggest the formation of Zn acetate and formate complexes (Table 1). Therefore, the Al and Zn

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