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Sol–gel synthesis, comparative characterisation, and reliability analyses of undoped and Al-doped zinc oxide thin films

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ABSTRACT

Thin films of sol–gel derived undoped and Al-doped zinc oxide material systems were fabricated for potential use in transparent conducting oxide modules. A comparative characterisation of the functional properties of the films was performed. Undoped zinc oxide thin films were obtained with desired properties. Al doping reduced the average crystallite size, and led to a denser and less porous morphology, and also caused an increase in transparency in the UV region. An improvement in electrical conductivity was achieved upon Al doping. Temperature cycling and accelerated delamination test results demonstrated the high physical reliability of the thin films of the material system obtained in this study.

1. Introduction

Transparent conducting oxides (TCOs) are widely used as electrodes on flat panel displays, sensors and solar cells; and to-date, indium tin oxide (ITO) has been the main material of choice [1]. However, a replacement for ITO is now required due to both cost and environmental issues. Both undoped and doped sol–gel derived zinc oxide is now attracting significant attention due to its wide range of electrical and optical properties [2–9].

In addition to characterisation of the functional properties, assessment of the physical reliability of optoelectronic devices is also of significant importance from application point of view. Temperature cycling tests in appropriate environmental laboratory test chambers, for instance, can be devised simulating the particular environmental conditions as described by the Generic Reliability Assurance protocol [10]. An accelerated delamination test can also be employed to provide a rapid evaluation of the susceptibility of a TCO [11]. The latter technique is based on stressing the TCO by applying heat, humidity, and a *direct current* (DC) bias to drive sodium ions to the TCO–glass interface to predict the probability of thin film TCO module failure via electrochemical delamination of the TCO.

In this study, functional properties of the sol–gel derived undoped and Al-doped zinc oxide films were comparatively characterised by means of *X-ray diffractometry* (XRD), *scanning electron microscopy* (SEM), UV/vis spectrophotometry, and electrical resistivity measurements, and their reliability analyses were performed in terms of temperature cycling and accelerated delamination tests.

2. Experimental details

2.1. Synthesis

$Zn(C_2H_3O_2)_2 \cdot 2H_2O$ (Sigma-Aldrich) was dissolved in the mixture of *isopropanol* (IPA; Rockwood, isoclean), as a solvent, and *2-aminoethanol* (MEA; Sigma-Aldrich), as both a complexing agent and a base, while stirring at 60 °C for 1 h. The molar ratio of Zn to MEA was kept constant at 1. Then, an adequate amount of IPA was added so as to attain a sol of [Zn] = 0.7 M. In the case of doping, a 0.2 M ethanolic Al solution was first prepared by dissolving the required amount of $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich) in absolute ethanol (Aldrich). This solution was then added to the sol directly after the dissolution of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in IPA + MEA, in such a way that the resultant Al concentration in the mixture was 5 mol% ([Al]/([Al] + [Zn]) × 100). In this case, the molar ratio of total metals (Zn + Al) to MEA was kept constant at 1. An adequate amount of IPA was then added so as to attain a sol of [Zn] + [Al] = 0.7 M. All sols, undoped or doped, were left to age for 1 day at ambient temperature in a closed vessel. The overall outline of the synthesis is given in Fig. 1.

2.2. Film preparation and processing

Following the sol ageing, the mixtures were spin-coated onto soda-lime glass slides (Menzel-Gläser, with a Na_2O content of ~14.30 mass%) using a WS-400A-6NPP/LITE Spin-Coater (Laurell Technologies) at a spin rate of 3000 rpm for 20 s. The coated slides were then transferred into a laboratory furnace (Heraeus Instruments, M104), which had been set to 275 °C. After 10 min, the furnace was heated to 550 °C, using an approximate heating rate of 10 °C min^{-1}. Following an annealing of 1 h, the furnace was left to cool down to ambient temperature. The film preparation and processing are outlined in Fig. 2.

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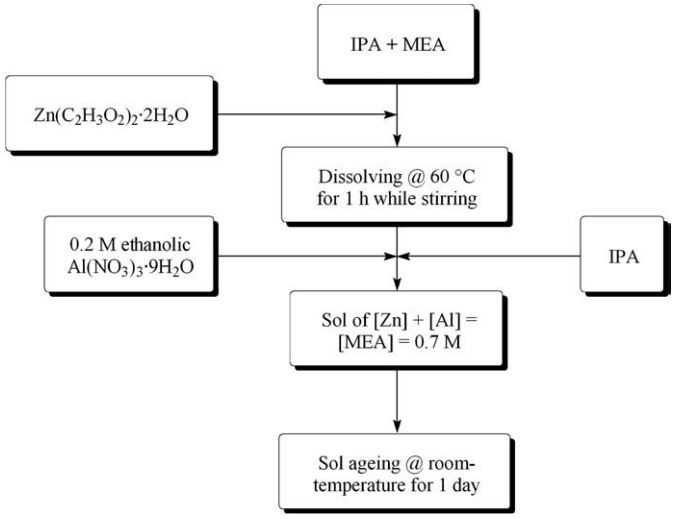

Fig. 1. Overall outline of the synthesis.

Additionally, in order to investigate the influence of further annealing in inert atmosphere on the electrical properties of zinc oxide, some undoped film samples were subjected to a *forming gas process* (FGP) performed at 500–550 °C for 1 h. The gas mixture employed contained 8% H_2 in N_2. The samples were also allowed to cool down in this atmosphere.

2.3. Characterisation

A Philips (PW3719) X'pert Materials Research X-ray diffractometer, operated at 40 kV and 35 mA, with a Cu-Kα radiation source, was employed for XRD. All diffractograms were applied a smoothing process of 10-point Fast Fourier transform followed by an appropriate baseline correction. Scherrer's equation was used to estimate the average crystallite sizes, where the value of λ was taken as 0.154 nm.

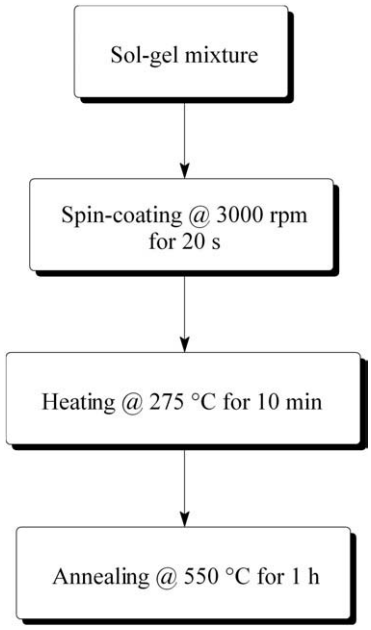

Fig. 2. Outline of the film preparation and processing.

In order to quantify the intensity ratio of the (002) crystal orientation, $\alpha_{(002)}$, was defined as:

$$\alpha_{(002)} = \frac{I_{(002)}}{I_{(002)} + I_{(100)} + I_{(101)}}$$

where $I_{(002)}$, $I_{(100)}$, and $I_{(101)}$ denoted the intensities of (002), (100), and (101) crystal orientations, respectively. Top-view and cross-sectional SEM images of the films were collected using a Hitachi S-4000 Field Effect SEM instrument, whose operating voltage was 20 keV. Film thickness was estimated from the cross-sectional SEM images. UV/vis spectroscopy was performed with a Shimadzu 2401 PC UV/vis spectrophotometer. Electrical resistivity measurements were carried out using a Keithley 617 electrometer evaporating two coplanar Al contacts with a width of 4 mm and a separation of 1 mm, in vacuum, at ambient temperature.

2.4. Reliability analyses

In order to asses the physical reliability of the obtained films, two separate tests were devised: Firstly, a temperature cycling test was carried out employing a Sun Electronic Systems EC11 Chamber. The temperature range and number of cycle applied were −40–65 °C and 100, respectively. The specimens were kept at these temperatures for 5 min, between which a heating or cooling rate of 10 °C min^{-1} was applied. Secondly, an accelerated delamination test was performed in a laboratory set-up, a schematic representation of which is shown in Fig. 3. The size of each specimen subjected to this test was ~9 cm^2. The applied bias and temperature were 100 VDC (10 min) and ~200 °C, respectively. A Keithley 237 High Voltage Source Measure Unit was employed as the voltage source, and for reading the electric current passing through the system. Following the treatment, the specimens were immediately taken out of the set-up, and allowed to cool down in ambient atmosphere (with an approximate relative humidity of 80–90%). The specimens were then observed for indications of delamination.

3. Results and discussion

3.1. Comparative characterisation

3.1.1. Sem

Top-view ((a) and (b)) and cross-sectional ((c) and (d)) SEM images of the undoped ((a) and (c)) and Al-doped ((b) and (d)) films are shown in Fig. 4. The top-view SEM images showed a well-developed grain structures for undoped films. However, denser and less porous films with smaller visual crystallite sizes were obtained upon Al doping, as anticipated [6,7]. Cross-sectional SEM images also confirmed that both types of films could be obtained crack-free. The

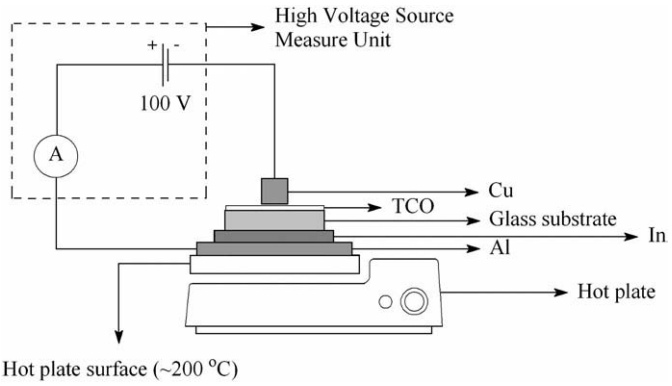

Fig. 3. Schematic representation of the set-up used in the accelerated delamination test.