Effect of the H$_2$ Annealing on the Electrical Properties of In$_2$O$_3$-SnO$_2$ Thin Films

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Abstract. Single-layered In$_2$O$_3$-SnO$_2$ coatings, with a Sn/(Sn + In) ratio of 25–50 at.%, were fabricated by a spin-coating method using coating solutions prepared from tin and indium 2-isopropoxyethoxides. The electrical conductivity of the air- and H$_2$-annealed samples were analyzed. The maximum conductivity for the air-annealed samples, 24 S/cm, were obtained with the smallest Sn content. H$_2$ annealing induces a remarkable permanent increase in the conductivity of the films with a specific Sn content of 30–40 at.%. The highest relative conductivity increase was 7600% (1 S/cm $\rightarrow$ 76 S/cm). The effect of the H$_2$ annealing on the chemical composition and the crystal structure of the fabricated films having a Sn/(Sn + In) ratio of 35.5 at.% was followed using XPS and XRD, respectively.

Keywords: transparent conductive oxides, ternary compounds, reductive annealing

1. Introduction

Impurity-doped indium oxide (ITO, where Sn/(Sn + In) $\sim$ 9 at.%) is conventionally used in transparent conducting films in optoelectronic devices. However, research and development of alternative materials with enhanced physical properties and reduced cost due to lower amounts of expensive indium is rapidly expanding as well. For this purpose ternary oxides, such as GaInO$_3$, Zn$_2$In$_2$O$_5$, In$_4$Sn$_3$O$_{12}$, ZnSnO$_3$, and Zn$_3$SnO$_4$, might be potential materials [1, 2].

Thin conformal ternary oxide films are typically fabricated via sputtering or MOCVD techniques. Liquid-phase processing, such as sol–gel techniques, would enable molecular mixing of the precursor compounds, facilitating the fabrication of homogeneous multi-component materials. However, sol–gel processing of such oxides has only been reported for In$_6$WO$_{12}$ thin
The expected ternary \( \text{In}_2\text{Sn}_3\text{O}_{12} \) oxide phase [9, 10] was not detected in X-ray powder diffraction (XRD) measurements. However, the \( \text{H}_2 \) annealing was found to strongly affect the conductivity of films having \( \text{Sn}/(\text{Sn} + \text{In}) \) ratios between 30 and 40 at.%. In this paper we report on the effects of the precursor composition and annealing on the electrical properties of the \( \text{In}_2\text{O}_3\text{-SnO}_2 \) films fabricated via the single layer sol-gel process. Reasons for the increased conductivity of these specific films are also discussed.

2. Experimental

Alkoxide solutions were prepared by dissolving commercial indium(III)isopropoxide (\( \text{In}(\text{OPr}^\prime)_3 \)) and tin(IV)isopropoxide (\( \text{Sn}(\text{OPr}^\prime)_4 \)) by Chemat, into dry 2-isopropanol-ethanol. Two separate 0.5 M solutions were made. This was done under a \( \text{N}_2 \) atmosphere in order to avoid the hydrolysis of the precursors. The coating solutions were then prepared by mixing the two solutions to obtain \( \text{Sn}/(\text{Sn} + \text{In}) \) ratios ranging from 25 to 50 at.%. Sample films were prepared from filtered solutions via spin coating under an ambient clean room atmosphere at 25°C and 45% relative humidity. Single layered films were spun-on for 20 s at 1250 rpm. The deposited films were then dried at 140°C for 30 min, after which they were further annealed in a belt furnace under an air atmosphere in order to crystallize the materials (total annealing time was 100 min, with 20 min at 600°C). In addition to this, some samples were further annealed in a \( \text{H}_2/\text{N}_2 \) atmosphere using the same furnace and temperature program. During the second annealing cycle the \( \text{H}_2/\text{N}_2 \) flow was 5/200 litres/min and the \( \text{O}_2 \) levels were below 5 ppm.

Electrical and optical measurements were recorded for the air and air + \( \text{H}_2 \) annealed slab films deposited on boro-silicate glass substrates. Film thicknesses were also measured using a Filmetrics F20. Optical transmissions were measured using an optical power meter (ANDO AQ-6135E) and applying collimated 350-1350 nm radiation from a tungsten lamp. Sheet resistances were measured using a linear four-point method.

The composition of films deposited on Si-substrates were determined by XPS using a Kratos AXIS 165 electron spectrometer. All spectra were recorded with monochromatized Al \( \text{K}_\alpha \) irradiation at 100 W. Surface chemical compositions were studied using high-resolution measurements with 0.1 eV energy step and 20 eV pass energy. Low-resolution sputter profiles through the films were also recorded using 4 kV Ar ion bombardment and a differentially pumped, rastering MinibeamIII ion gun [11].

X-ray powder diffraction data was taken to analyze the crystal structures of the films deposited on Si-substrates. Data was collected at room temperature, 25°C, using a Siemens D5000 powder diffractometer. Cu \( \text{K}_\alpha \) irradiation at 30 kV and 40 mA was used for the experiments and diffractograms were recorded by step scanning in the 2θ range of 20° to 60°, with steps of 0.02°. Diffraction patterns were identified using ICDD 1999 data sets.

3. Results

3.1. Electrical and Optical Properties

The film thicknesses obtained for air- and air + \( \text{H}_2 \) annealed coatings were between 60 and 70 nm with optical transmission values higher than 85% at visible wavelengths.

The electrical conductivities of the air-annealed films increased with decreasing Sn levels as shown in Fig. 1. The maximum conductivity value for air-annealed samples was 24 S/cm, which corresponds to a sheet resistance value of 6200 \( \Omega /\square \).

In the case of the air + \( \text{H}_2 \) annealed samples, the conductivities were not monotonically related to the decreasing Sn levels. For the films with high Sn contents, hydrogen annealing did not promote changes in their conductivities. Films with low Sn contents yielded conductivities below those measured for the samples annealed in air only. However, at around \( \text{Sn}/(\text{Sn} + \text{In}) \) ratios of 35 at.%, the \( \text{H}_2 \) annealing had a marked effect on the films’ conductivities. The maximum conductivity measured, 76 S/cm at 35.5 at.% corresponds to a sheet resistance of 1950 \( \Omega /\square \).