

Transparent Conducting Films in the Zn–Sn–O Tie Line

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Abstract. Coatings were obtained on borosilicate glass and fused silica substrates with thicknesses of up to 230 nm from solutions with compositions along the Zn–Sn–O tie line. The preparation of the sols was accomplished by combinatorial chemistry with a robotic sample processor using different Zn^{II}, Sn^{II} and Sn^{IV} salts and alkoxides, as well as salts of different doping agents (e.g. Sb^V, Ta^V, In^{III}) dissolved in various solvents and additives. The films were made by spin-coating followed by a thermal treatment in air, inert or reducing atmosphere at temperatures up to 1000°C. Except for a few cases, mixed crystalline phases of ZnO, SnO₂ and ZnSnO₃ or Zn₂SnO₄ are usually observed within the range $0.4 < [\text{Zn}]/([\text{Zn}] + [\text{Sn}]) < 0.75$. Pure Zn₂SnO₄ and ZnSnO₃ coatings exhibit good optical properties with a haze <0.2% and a transmission in the visible range >85%. In contrast to literature, results obtained for similar coatings by sputtering and pulsed laser deposition, all the sol–gel coatings showed a high resistivity of $\rho > 3 \Omega\text{cm}$ even after a forming gas treatment and/or doping.

Keywords: transparent conducting oxides, sol–gel, ZnSnO₃, Zn₂SnO₄, coating

1. Introduction

Today, transparent conducting oxides (TCOs) play a key role in numerous opto-electronic devices (e.g., flat panel displays, IR-reflective coatings). For these applications, TCOs such as In₂O₃:Sn (ITO), SnO₂:F or SnO₂:Sb (FTO or ATO) and ZnO:Al (AZO) are already established in industrial scale but it is crucial to find new approaches to existing or even new TCO materials to improve properties such as work function, electron mobility and transparency.

Various coatings of TCOs consisting of ternary compounds (e.g., Cd₂SnO₄, ZnSnO₃, Zn₂SnO₄, ZnGa₂O₄ and GaInO₃) have been reported in the literature, most of them fabricated by physical deposition methods such as sputtering or pulsed laser deposition [1–3]. Only a few references can be found on sol–gel deposited thin

films such as Cd₂SnO₄ [4, 5], ZnGa₂O₄ [6], In₆WO₁₂ [7] and Zn₂SnO₄ [8]. About 500 nm thick film sensors have been developed using Zn₂SnO₄ particles made by a sol–gel route [9].

A study was initiated with the aim to develop single-phase, multi-component TCO coatings in the systems ZnO–SnO₂ (ZnSnO₃, Zn₂SnO₄), ZnO–In₂O₃ (Zn₂In₂O₅), ZnO–Ga₂O₃ (ZnGa₂O₄) and Ga₂O₃–In₂O₃ (GaInO₃) via the sol–gel process. This paper presents the results obtained along the Zn–Sn–O tie line within the range $0.4 < [\text{Zn}]/([\text{Zn}] + [\text{Sn}]) < 0.75$. Until now no sol–gel literature has been reported to obtain ZnSnO₃ and Zn₂SnO₄ coatings for the use as transparent conducting films.

2. Experimental

The coating solutions for screening experiments were prepared with a robotic processor (TECAN

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Genesis RSP 150) by dissolving ZnCl_2 (Fluka, p.a.), $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (Riedel de Haen, pure), SnCl_2 (Fluka, 98%), $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ (Aldrich, 98%), $\text{SnCl}_2(\text{OAc})_2$ (DZD, prepared according to [10]), $\text{Sn}(\text{O}^i\text{Pr})_4 \cdot \text{HO}^i\text{Pr}$ (ChemPur, 99.99%), and $\text{Sn}(\text{O}^t\text{Bu})_4$ (ChemPur, 99.99%) in ethanol. All solutions have been prepared with a zinc to tin molar ratio $[\text{Zn}]/([\text{Zn}] + [\text{Sn}])$ ranging from 0.4 to 0.75 and total metal concentrations of 0.4 mol/L. For this purpose, a total amount of ~ 200 solutions with 2 mL each were prepared for the various Zn/Sn combinations of precursors. The solutions were then heated under reflux for 1 h and filtered ($0.2 \mu\text{m}$ PTFE) after cooling.

Spin-coating with rotation speeds ranging from 200–4000 min^{-1} was used to coat glass substrates (Borofloat 33 Schott/Jenaerglas, AF45 Schott-DESAG, fused silica) with sizes up to $10 \times 10 \text{ cm}^2$. Sintering was performed in air in a furnace either by direct heating (heating rate $\sim 100^\circ\text{C}/\text{min}$) or with a heating rate of $5^\circ\text{C}/\text{min}$. Further annealing in inert (N_2) or reducing gas (92% $\text{N}_2/8\% \text{H}_2$) was performed during 1 to 12 h in a gas flow of 100 l/h at temperatures from 300 to 500°C and a heating rate of $5^\circ\text{C}/\text{min}$. The samples were allowed to cool below 50°C under flowing gas before removal from the furnace.

X-ray diffraction (XRD) patterns were obtained on a Siemens D500 diffractometer equipped with a thin film sample holder in the 2θ range from 10° to 70° at grazing incidence ($\theta = 0.5^\circ$) using the $\text{Cu}_{K\alpha}$ radiation. The crystallite size has been calculated from the Scherrer equation.

Thickness measurements were performed with a surface profiler (TENCOR P-10) after etching a sharp edge with concentrated HCl and zinc powder. The same instrument was used to determine the average roughness over a length of 0.5 mm at several positions of the samples. To visualize the surface of the coatings, SEM images were recorded by a high-resolution electron microscope (JSM 6400 F, JEOL) at an excitation energy of 10 keV.

Haze and transmittance values were measured on a haze-meter (BYK Gardner Haze-gard plus) in reference to haze and clarity standards provided by the manufacturer. Transmission spectra were collected on a UV-Vis-NIR spectrophotometer (Varian CARY 5E) in the range from 250 to 3000 nm with air as reference.

The resistivity of the coatings was measured by the 4-point technique.

3. Results and Discussion

3.1. Search for Zn_2SnO_4 ($0.63 < [\text{Zn}]/([\text{Zn}] + [\text{Sn}]) < 0.75$)

In initial screening experiments, crystalline Zn_2SnO_4 could only be observed in coatings made from solutions having $[\text{Zn}]/([\text{Zn}] + [\text{Sn}])$ molar ratios ranging from 0.63 to 0.75 (theoretical ratio for Zn_2SnO_4 at $[\text{Zn}]/([\text{Zn}] + [\text{Sn}]) \sim 0.67$). Phase compositions, optical and electrical properties and surface morphologies of coatings prepared within this range were determined. The appropriate choice of the precursor system was found to be of particular importance to obtain the formation of pure Zn_2SnO_4 . As a typical example, Fig. 1 shows the various crystalline phases encountered for coatings sintered at 550°C during 24 h with a heating rate of $5^\circ\text{C}/\text{min}$. Most of them are mixed phases of ZnO, SnO_2 and Zn_2SnO_4 . However, monophasic Zn_2SnO_4 coatings are obtained by the use of polymerizable tin precursors which tend to form a rigid network on condensation, such as $\text{SnCl}_2(\text{OAc})_2$, $\text{Sn}(\text{O}^i\text{Pr})_4$ and $\text{Sn}(\text{O}^t\text{Bu})_4$.

The hydrolysis reaction mechanisms of $\text{SnCl}_2(\text{OAc})_2$ have not yet been examined, whereas

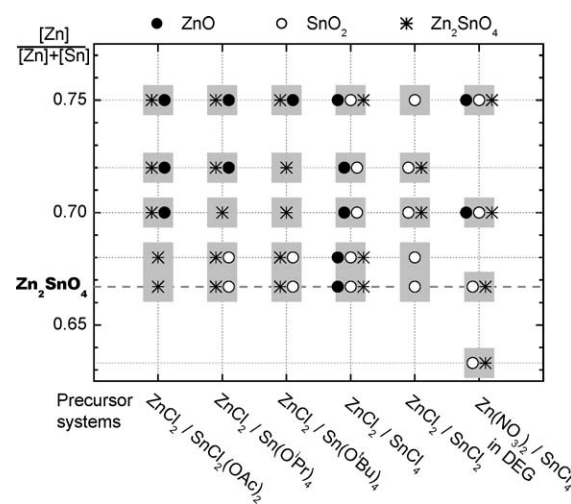


Figure 1. Dependence of precursors and zinc to tin ratio (0.63–0.75 range) in coating solutions on the thin film phase formation (solvent ethanol except column six diethylene glycol (DEG), heat-treatment 550°C for 24 h, $5^\circ\text{C}/\text{min}$). Each square represents a coating. The crystalline phases observed for each film are shown by the symbols, (ZnO), (SnO_2) and (Zn_2SnO_4), the amount of the phase decreasing from left to right in each square. The dashed horizontal line represents the theoretical ratio of zinc to tin in Zn_2SnO_4 .

the condensation of tin(IV) alkoxide compounds has been investigated extensively [11]. From these investigations it is known that $\text{Sn}(\text{O}^i\text{Pr})_4 \cdot \text{HO}^i\text{Pr}$ condenses by forming tin oxo-alkoxide polymers. During deposition, the condensation of the coating solution begins and other metal ions like Zn^{II} can be easily incorporated into the tin oxo-alkoxide network leading to a homogeneous distribution of Sn^{IV} and Zn^{II} in the wet film. Thus, a phase separation is avoided resulting in a single phase of Zn_2SnO_4 . The reasons to have an excess of zinc (compared to $\text{Zn}/\text{Sn} = 2$ in Zn_2SnO_4) in the solutions containing tin alkoxides are still under investigation.

Measurements of the optical properties of the coatings show that the sols made with tin(IV) alkoxides lead to a lower haze (minimum 0.2%) and a higher transmittance (maximum 94%) than those made from $\text{SnCl}_2(\text{OAc})_2$ (4.8% and 90%, respectively), as seen in Fig. 2 for various zinc to tin ratios (same solutions as the first two columns in Fig. 1). Higher zinc content in the coating solution leads to a decrease of the haze. This is due to a stabilization effect of the zinc chloride during the alkoxide hydrolysis reactions leading to smoother surfaces and less light scattering. Furthermore, the coating solutions made with tin alkoxides produced films with low average roughness (R_a) and a high transmission (T) in the visible. The values for a four layer (230 nm) coating were typically $R_a \sim 1$ nm and $T > 85\%$. S.E.M. images taken of an area of $2 \times 2 \mu\text{m}^2$ show no visible inhomogeneities. For these reasons, coating solutions containing tin(IV) alkoxide precursors were mainly used in the following investigations.

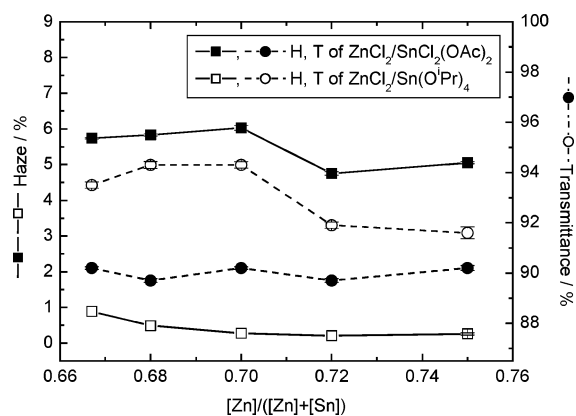


Figure 2. Values of haze H (squares) and transmittance T (circles) of coatings obtained by spin-coating from ethanolic solutions containing 0.4 M $\text{ZnCl}_2/\text{SnCl}_2(\text{OAc})_2$ (solid) and $\text{ZnCl}_2/\text{Sn}(\text{O}^i\text{Pr})_4$ (open) (first two columns of Fig. 1).

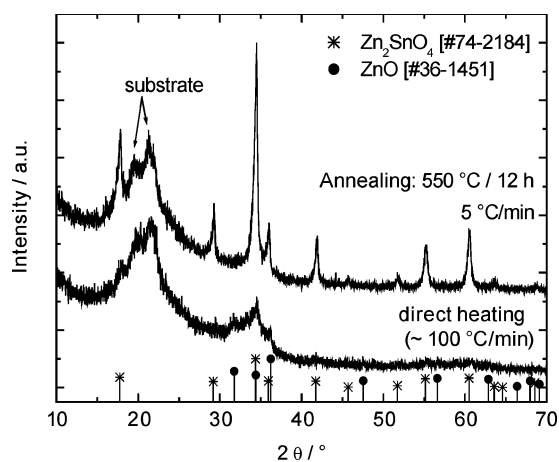


Figure 3. XRD patterns of spin-coated films after different sintering procedures. For each one, a final temperature of 550°C was maintained for 12 h. Coating solution 0.4 M $\text{ZnCl}_2/\text{Sn}(\text{O}^i\text{Bu})_4$ in ethanol $[\text{Zn}]/([\text{Zn}]+[\text{Sn}]) = 0.7$.

Top: heating rate of $5^\circ\text{C}/\text{min}$, bottom: direct heating ($\sim 100^\circ\text{C}/\text{min}$)

The heating procedure was also found an important factor for the phase formation. As an example, Fig. 3 shows XRD diagrams obtained for Zn_2SnO_4 coatings made with a solution containing ZnCl_2 and $\text{Sn}(\text{O}^i\text{Bu})_4$ with a ratio $[\text{Zn}]/([\text{Zn}]+[\text{Sn}]) = 0.7$.

The sample put directly into the hot furnace at 550°C and kept at this temperature during 12 h shows a weak crystallization of Zn_2SnO_4 (crystallite size about 5 nm) together with a ZnO phase. As a consequence of the films fast solidification, small crystallites < 5 nm grow immediately and phase separation occurs preventing the further growth of Zn_2SnO_4 particles. On the other hand, the sample heat treated with a heating rate of $5^\circ\text{C}/\text{min}$ shows more intense diffraction peaks of Zn_2SnO_4 with a crystallite size of about 39 nm. The peaks in the 2θ range from 19° to 23° are from the substrate as the penetration depth of the X-rays ($3\text{--}4 \mu\text{m}$) into the sample is much larger than the film thickness (~ 60 nm).

The time-dependant structural evolution of the same coating is presented in Fig. 4. Coatings sintered at 550°C up to 4 h are still amorphous. The first diffraction peaks of polycrystalline Zn_2SnO_4 appear after a sintering time of 4 to 5 h and a subsequent growth of the crystallites is observed with increasing sintering time resulting in Zn_2SnO_4 crystallite sizes of 39 nm at 12 h and 85 nm at 24 h. In comparison, Young et al. [2] observed the crystallization of Zn_2SnO_4 at temperatures above 660°C for 30 min in flowing Ar.

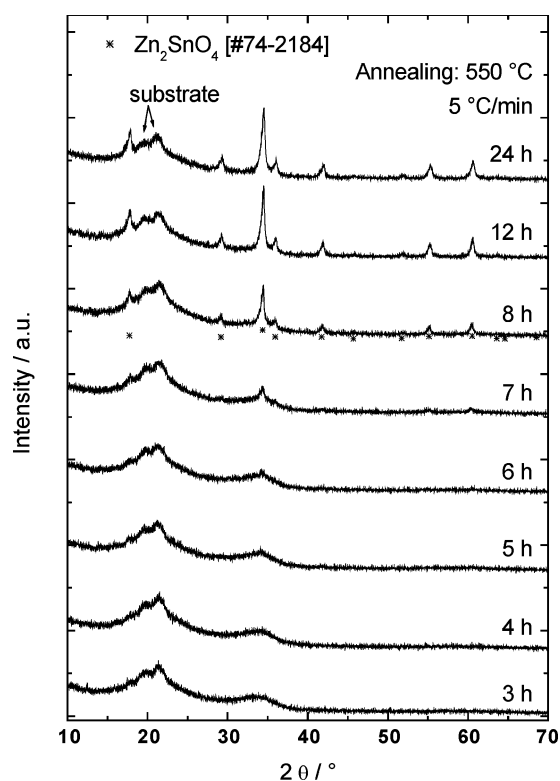


Figure 4. Time evolution of the XRD patterns of films prepared with heat treatments at 550°C (same coating solution as in Fig. 3).

The electrical conductivity of Zn_2SnO_4 thin films made by sputtering and PLD was reported to originate mainly from oxygen vacancies [12], which are generated during the deposition process [3]. Post-annealing of sintered Zn_2SnO_4 pellets in a reducing atmosphere (25% H_2 /75% N_2) for 14 h at 450°C was found to decrease the resistivity from $10^9 \Omega\text{cm}$ down to $10^2 \Omega\text{cm}$ [13].

Like in common TCOs, the introduction of charge carriers may also be achieved by doping the host material with elements of different valency. Palmer et al. [14] prepared powders of Zn_2SnO_4 doped with In_2O_3 and observed a resistivity of 0.5 Ωcm only with high In-content (16.67%) and harsh reduction processes. On the contrary, the room temperature resistivity of Nb_2O_5 -doped Zn_2SnO_4 ceramics increases on doping probably due to the precipitation of $3\text{ZnO} \cdot \text{Nb}_2\text{O}_5$ at the grain boundaries [15].

The resistivity of all the as-deposited sol-gel coatings is high (not measurable). However it can be decreased by a heat treatment in a reducing atmosphere. The lowest resistivity, $\rho = 3 \Omega\text{cm}$, was obtained for a 5 h, 300°C annealed pure Zn_2SnO_4 coatings. Further-

more, no decrease in resistivity was yet observed by doping the solutions made with tin alkoxides up to a concentration of 2 mol% with different metal ions such as Sb^{V} , Ta^{V} , Nb^{V} , Ga^{III} and In^{III} .

3.2. Search for ZnSnO_3 ($0.4 < [\text{Zn}]/([\text{Zn}]+[\text{Sn}]) < 0.6$)

The presence of a crystalline ZnSnO_3 phase expected for the coatings made with solutions having a zinc to tin ratio of 1:1 is difficult to proof because of the poor crystallinity of the coatings. This is also observed during the decomposition of powder samples of $\text{ZnSn}(\text{OH})_6$. Undoped ZnSnO_3 coatings made with solutions containing $\text{ZnCl}_2/\text{Sn}(\text{O}^i\text{Pr})_4$ and having a $[\text{Zn}]/([\text{Zn}]+[\text{Sn}])$ molar ratio ranging from 0.4 to 0.6 show a resistivity in the range of 10 Ωcm without annealing in reducing atmosphere. The optical and morphological properties are similar to those observed for Zn_2SnO_4 coatings.

4. Conclusions

Single- and multilayer zinc stannate (Zn_2SnO_4 , ZnSnO_3) coatings were prepared on glass substrates by sol-gel spin-coating with good optical properties, i.e. a haze of 0.2% and a transmission of 85% in the visible range for 230 nm thick coatings. Good morphological quality is achieved with average roughness values of 1 nm. The resistivity of undoped monophasic sol-gel Zn_2SnO_4 coatings is very high (not measurable), but a value of 3 Ωcm is obtained after annealing in reducing gas (92% N_2 /8% H_2) for 5 h at 300°C. A crucial point to get pure Zn_2SnO_4 and ZnSnO_3 phases is the appropriate choice of precursors. Only those which polymerize by condensation yield pure films of Zn_2SnO_4 . The size of the Zn_2SnO_4 crystallites grows with the sintering time. Value up to 85 nm was found for a sintering at 550°C for a time longer than 5 h. An increase of the heating rate from 5 to 100°C/min leads to small Zn_2SnO_4 crystallites in the range of 5 nm and phase separation resulting in the appearance of ZnO. ZnSnO_3 coatings exhibit promising resistivity of 10 Ωcm without post-annealing and doping.

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