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Novel transparent conducting sol–gel oxide coatings

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Abstract

This work focuses on the preparation of novel ternary transparent conducting oxide coatings on glass by the sol–gel method. The coatings were deposited by spin-coating from solutions of appropriate metal precursors and heat-treated at different heat-treatment procedures. An increase in electrical conductivity was achieved by a final forming gas treatment. Best electrical and optical properties have been obtained for coatings of crystalline Zn_2SnO_4, $Zn_3In_2O_6$ and $Zn_5In_2O_8$ and X-ray amorphous $ZnSnO_3$ with resistivities in the order of 10^{-2}–10^{-1} Ω cm, an average transmission in the visible of 85% and an average surface roughness of ~1 nm. $ZnGa_2O_4$ and $GaSbO_4$ coatings showed no electrical conductivity. For Zn_2SnO_4 coatings, a restricted crystallite growth was observed probably due to phase segregation effects. Electrical properties of coatings in the system $ZnO–In_2O_3$ were interpreted on the basis of the percolation theory.

Keywords: Transparent conducting oxide; Sol–gel; Zn_2SnO_4; $Zn_kIn_2O_{k+3}$

1. Introduction

Ever-increasing demands in modern electronic devices have initiated a worldwide search for alternative transparent conducting oxide (TCO) materials [1,2]. As certain applications require TCO coatings exhibiting tailored characteristics (high electron mobility, increased work function, low surface roughness), the search is not only limited to 'common' TCO materials and mixtures thereof [3], but was also extended to compositions consisting of new metal oxides [4,5].

In this work, as illustrated in Fig. 1, coating materials in the systems $ZnO–SnO_2$, $ZnO–In_2O_3$, $ZnO–Ga_2O_3$, $Ga_2O_3–Sb_2O_5$, and $Zn_2SnO_4–In_2O_3$ were prepared by the sol–gel process. The electrical, optical and morphological properties of the coatings are presented.

2. Experimental

Coating solutions in the systems $ZnO–SnO_2$, $Zn_2SnO_4–In_2O_3$, $ZnO–Ga_2O_3$, and $Ga_2O_3–Sb_2O_5$ were prepared by dissolving the appropriate amounts of metal salts in ethanol, and in the system $ZnO–In_2O_3$ from metal salts dissolved in 2-methoxyethanol with 10 vol.% 2-aminoethanol. All solutions had a total metal concentration of 0.2 to 0.4 mol/l. Before deposition, the mixed solutions were heated under reflux for 1 h and filtered (0.2 μm PTFE).

The coatings were deposited by spin-coating (1000 rpm) on 5×5 cm^2 Borofloat 33 (Schott/Jenaerglas) and fused silica and heated at a 5 K/min rate to 550 to 1000 °C for 0.25 to 96 h. A further annealing process was done in reducing atmosphere (80% N_2/20% H_2) during 1 h in a gas flow of 100 l/h at 300 °C.

X-ray diffraction (XRD) patterns were obtained on a Siemens D500 diffractometer ($10° < 2\theta < 70°$) at $\theta = 0.5°$ grazing incidence using $Cu_{K\alpha}$ radiation. Crystallite sizes were calculated from the Scherrer equation and the volume fraction of coating compounds was estimated from integrated intensities of the appropriate diffraction signals. Background subtraction was performed on XRD diagrams for illustration purposes only. Thickness measurements were performed with a surface profiler (TENCOR P-10) after etching a sharp edge with concentrated HCl and zinc powder. Haze and transmittance values were measured with a BYK Gardner Haze-gard plus equipment. Transmission and reflection spectra were collected on a spectrophotometer (Varian CARY 5E) in the range from 200 to 3000 nm with air as a reference. Optical band gaps were derived from plots of the calculated absorption coefficient spectra vs. energy. Resistivity, Hall mobility, and carrier concentration were measured by means of the Van der Pauw and Hall method (MMR Technologies) using a magnetic field of 1.0 T

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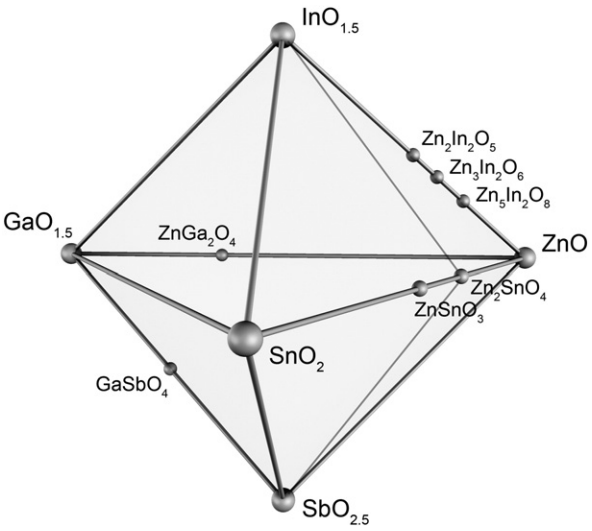

Fig. 1. Schematic multidimensional phase diagram of coating materials investigated in this study.

and the work function with a scanning Kelvin probe (KP Technologies [6]) over a surface area of 17.6×17.6 mm^2. The average surface roughness R_a was evaluated by AFM (Topomatrix Explorer TMX2000) in contact mode equipped with an ultra sharp Si_3N_4 cantilever (ND-MDT) over an area of 500×500 nm^2.

3. Results and discussion

3.1. Coatings in the system ZnO–SnO$_2$

Coatings of high optical quality (haze<0.1%) and low surface roughness (R_a<1 nm) were obtained using $ZnCl_2$ and Sn(O^tBu)$_4$ in ethanol, irrespective of coating thickness (20… 100 nm). These coating solutions showed a shelf-stability of >100 d (3% increase of the viscosity).

3.1.1. Crystallization

In this system, only Zn_2SnO_4 could be observed as a ternary phase. For coatings annealed at 600 °C for 12 h (Fig. 2), Zn contents of the coating solution below 50 and above 80 mol% yielded crystalline SnO_2 and ZnO, respectively.

X-ray amorphous coatings were observed for a Zn content of 60 mol%, whereas single-phase Zn_2SnO_4 was found in the range 65 to 72 mol%. As can be seen in Fig. 3, the maximum Zn_2SnO_4 crystallite size was observed for a Zn content of 70 mol%, regardless of sintering temperature. Higher annealing temperatures (800 °C) lead to an extension of the Zn_2SnO_4 existence range to Zn contents from 50 to 80 mol%, whereas SnO_2 and ZnO co-existed for 50 and 80 mol%, respectively.

The investigation of thermal and temporal heat treatment parameters showed, besides an increase in Zn_2SnO_4 crystallite size (ca. 30 nm at 800 °C, 4 h), an acceleration of the crystallization at higher sintering temperatures. By varying the stoichiometry of the solution, a delayed crystal growth and reduced final crystallite size could be observed, leading to inferior electrical properties (see below).

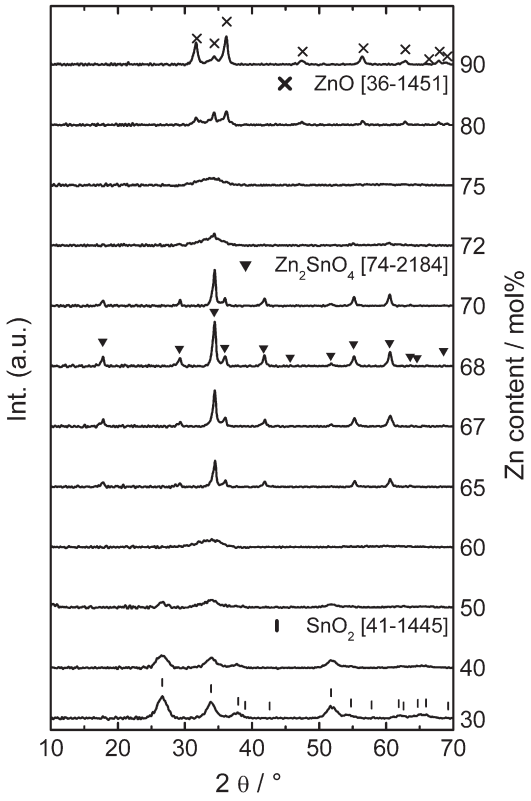

Fig. 2. XRD diagrams of 65 to 80 nm thick coatings of the system ZnO–SnO_2 on borosilicate glass substrates heat-treated at 600 °C for 12 h.

3.1.2. Electrical and optical properties

Hall measurements revealed two compositional regions of interest for coatings sintered at 600 °C. Whereas end members showed resistivities above 10 Ω cm with low charge carrier concentrations and mobilities, X-ray amorphous (55–60 mol% Zn) and crystalline Zn_2SnO_4 coatings (65–72 mol% Zn) lead to minima of 0.11 and 0.42 Ω cm, respectively, with high charge carrier concentration and mobility values (Fig. 4).

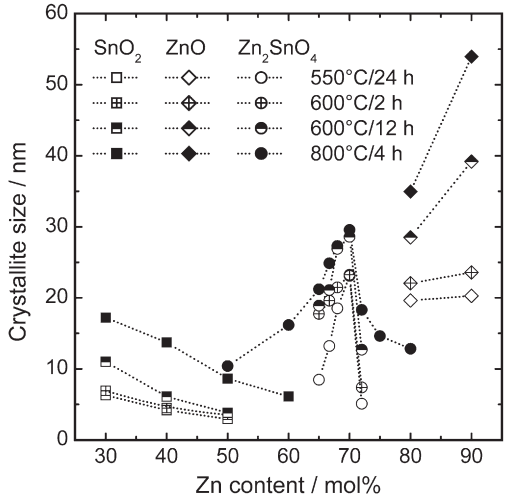

Fig. 3. Influence of temperature treatment and Zn content on Scherrer crystallite size of the observed crystalline phases in the system ZnO–SnO_2. Coating thicknesses 65 to 80 nm.