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Aluminum-doped zinc oxide sol–gel thin films: Influence of the sol's water content on the resistivity

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ABSTRACT

Thin films of indium tin oxide (ITO) have gained substantial interest due to their optical and electrical properties. Since ITO is an expensive material and indium is a rare element, considerable attempts have been made to replace it by, e.g., aluminum-doped zinc oxide (ZnO:Al). The production of ZnO:Al is less cost-intensive, especially if the sol–gel technique is applied, while its properties are comparable to those of ITO. In this study, we demonstrate that the electrical properties of ZnO:Al thin films can be improved considerably by the addition of small amounts of ultrapure water to the dip coating solution during the preparation. The lowest resistivity obtained with a film prepared from a sol containing 0.2 M water is 2.8 10^{-3} Ωcm. Optical modeling thus indicates an improvement of the free carrier mobility of films prepared from sols in the presence of additional water. The films prepared have an average thickness of 340 nm and a solar transmittance above 85% after annealing in a forming gas atmosphere. Clearly, the addition of water to the sol has a positive impact on the resistivity of the final ZnO:Al thin film. We suggest the observed increase of the free carrier mobility to be due to an improved electron transfer at the grain boundaries between the spherical nanoparticles.

1. Introduction

Thin films of indium tin oxide (ITO) have gained a lot of interest due to their optical and electrical properties. ITO is a transparent conductive oxide (TCO) which is characterized by a low resistivity as well as by a high transmittance in the visible range [1]. Since ITO is an expensive material and its manufacture and processing can be harmful to the environment, considerable attempts have been made to replace it by materials that are less expensive and ecologically more compatible [2]. As its electronic properties are comparable to those of ITO, aluminum-doped zinc oxide (ZnO:Al) is expected to be a suitable alternative for many applications including solar cells, displays, optoelectronic, and electrochromic devices as well as gas sensors [3–8].

Thin films of ZnO:Al can be deposited by a number of different techniques: various sputtering methods, plasma-enhanced chemical vapor deposition, spray pyrolysis, or sol–gel processes [9–14]. The preparation of thin films by sol–gel techniques is advantageous because no cost-intensive vacuum technique is required. Furthermore, the method is suitable for a large range of substrate geometries [13].

The resistivity of ZnO:Al films prepared by sol–gel methods is usually found to be at least one order of magnitude higher than that of films obtained by other deposition methods [15]. Herein, we demonstrate how the electronic properties of ZnO:Al films can be improved by the addition of water to the initial dip coating solution in concentrations of up to 0.2 M depending on the amount of zinc. We have furthermore analyzed the free carrier concentration, the free carrier mobility, the optical constants, and the thickness of the films by spectroscopic ellipsometry. The resistivity has been determined by the four-point probe method. Transmittance and reflectance measurements have been performed by UV–VIS- and Fourier-transform-infrared-spectroscopy (FTIR), whereas scanning electron microscopy and X-ray diffraction measurements (XRD) provided information concerning the morphology of the ZnO:Al films.

2. Experimental details

2.1. Synthesis

For the preparation of the dip coating solution, in general, we followed the original method of Schuler and Aegerter [12]. Nevertheless, we implemented some modifications regarding the addition of water at the end of the sol preparation. According to Schuler, for a 0.1-M sol 5.49-g zinc acetate dihydrate ($Zn(OAc)_2$ 2 H_2O, Sigma–Aldrich) is dissolved in a mixture of 250-mL isopropyl alcohol (2-propanol, anhydrous, 99.5%, Sigma–Aldrich) and 2.63-g diethanolamine (DEA, Sigma–Aldrich). The molar ratio Zn/DEA is fixed to 1.0 according to Takahashi et al. [16]. The solution is stirred at ambient temperature until it becomes clear and homogeneous. Doping of the solution is obtained by the dropwise addition of an aluminum nitrate solution prepared by dissolving 0.094-g aluminum nitrate nonahydrate ($Al(NO_3)_3$ 9 H_2O, Sigma–Aldrich) in a small amount of ethanol (absolute, Spectranal®, reag. DAB, Sigma–Aldrich), resulting in

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a ratio of 1 at% for Al/Zn. Additionally, after 30 min of stirring, ultrapure water is added dropwise to the solution. After another 15 min of stirring, the solution is ready for use.

Obviously, the total amount of water in the sol consists of the water of crystallization introduced by the precursors as well as of any additional amount of water added during the sol's fabrication. The contribution of water of crystallization is 0.2 M for zinc acetate and 0.009 M for aluminum nitrate, and is consistent throughout all experiments performed in this work. Additional water in concentrations of 0.1 M and 0.2 M has been added during the sol's preparation and was chosen to be either the same as or twice the amount of the zinc content in the sol. The following discussion is concerned with the possible impact of the additional amount of water in the sol.

2.2. Film preparation

Alkali free glass substrate slides (AF45 from Schott, dimension 100 × 50 × 0.7 mm^3) are cleaned using first Mucasol® and thereafter ultrapure water in an ultrasonic bath for 15 min each. The cleaned glass substrates are coated with the solution at a withdrawal speed of 7 mm/s and are subsequently transferred to a continuous furnace (RTC LA-310 from Radiant Technology Corporation), where the film is annealed at 550 °C for 3 min at ambient atmosphere. This procedure is repeated up to 15 times until the desired film thickness is obtained. Finally, the films are annealed with forming gas in a tube furnace (self-constructed at ISFH) to reduce their resistivity. Before annealing, the tube furnace is first flushed with nitrogen gas for 60 min and afterwards with forming gas (N_2:H_2 = 90:10) for 30 min. The films are annealed at 400 °C for 2 h without gas flow and subsequently cooled down to temperatures below 35 °C in a stream of forming gas. The flow rate is 1.0 L/min for each gas.

The final film is coated on both sides of the substrate due to the usage of the dip coating technique. As single side coating is preferred, the coating from the backside of the glass substrate is subsequently removed using 0.1 M HCl.

2.3. Characterization

Reflectance and transmittance data are measured both with a UV–VIS-NIR-spectrophotometer (Cary 5000 from Varian/Agilent Technologies) in the wavelength range from 0.25 μm to 2.5 μm, further reflectance data from 2.5 μm to 17.0 μm with an FTIR-spectrophotometer (Equinox 55 from Bruker). Both spectrophotometers are equipped with an integrating optical sphere. A spectroscopic rotating compensator ellipsometer (M-2000UI from J.A. Woollam, Inc.) is used for the determination of the film thickness and the optical constants. The WVASE32-software (J.A. Woollam, Inc.) is used to analyze the electronic properties of the films by simultaneous modeling of reflectance, transmittance, and ellipsometric data. The optical modeling of the ZnO:Al thin films is beyond the scope of this paper and is explained in detail elsewhere by Ehrmann and co-workers [17]. In addition to this work, the optical modeling contains a gradient of voids in order to characterize the porous structure. Four-point probe measurements are performed to determine the sheet resistance, from which the resistivity is calculated. As the resistivity is independent of the film thickness, it is a useful parameter for the comparison of the samples [3]. Information on the morphology of the film is obtained by scanning electron microscopy (SEM) using a Hitachi S-4800 as well as by XRD analysis performed at the Institute for Mineralogy (Leibniz University Hannover) (Philips PW1800 with a CuK_α-source).

3. Results and discussion

3.1. Structural properties and morphology

We have prepared films of sols with an additional water content of 0.0 M, 0.1 M, and 0.2 M, respectively, leading to an average film thickness of 340 nm after 15 dip coatings in all cases, as shown in Table 1.

Fig. 1 depicts an SEM image of the film's structure after annealing in forming gas atmosphere. The film consists of quasi-spherical nanoparticles. We analyzed X-ray diffraction patterns in order to follow changes of the morphology of the ZnO:Al films regarding the amount of additional water. All peaks are identified as being characteristic of ZnO in agreement with the JCPDS-database [19]. The particle sizes of the ZnO:Al films have been calculated employing the Scherrer equation [20] for a $CuK_{\alpha1}$ wavelength of 154.06 pm. The diameters of the particles are found to be 21 nm on average in accordance with the SEM image. Fig. 2 compares the XRD patterns of ZnO:Al thin films prepared with additional water contents between 0.0 M and 0.2 M at diffraction angles between 30° and 42°. No indications for morphology changes of the films induced by the different water content are observed. The lattice parameters have been determined using Rietveld refinement giving average values of a = (325.5 ± 0.2) and c = (521.4 ± 0.3).

The refractive index values of the films were determined by ellipsometric modeling of the dielectric function. Due to the porous structure of the films, we consider a gradient of voids in the film. Therefore, also the refractive index exhibits a gradient over the film thickness. For comparison of the different films, the refractive index values at a wavelength of 500 nm and a film thickness of 150 nm are chosen. Higher refractive index values indicate a denser structure due to fewer voids. The results in Table 1 indicate a more dense structure, i.e., a decrease in porosity, for films containing water especially before the annealing in forming gas atmosphere. The observed decrease of the refractive index values after treatment in the forming gas atmosphere indicates an increase of the porosity again, which could be attributed to the incorporation of hydrogen atoms. However, the tendency to a less porous structure with increasing water content in the sol still exists.

3.2. Optical properties

The transmittance and reflectance spectra of a ZnO:Al film prepared from a sol containing 0.2 M additional water (sample C) are compared to those of a film made from a solution without additional water (sample A), as illustrated in Fig. 3. All films are transparent in the visible range with a solar transmittance above 85% (see Table 1), whereas the transmittance of the uncoated glass substrate is 91.8%. Apparently, the reflectance of sample C – with 0.2 M additional water in the sol – in the infrared wavelength range above 4.0 μm increases after annealing in forming gas atmosphere. This effect is

Table 1
Structural and optical parameters of the films. The emissivity values represent wavelength-averaged data for a black-body radiation of 283 K; the solar transmittance data are according to ISO 9050:2003 taking into account global solar radiation with air mass 1.5 [18].

Sample	Film thickness d [nm]	Refractive index before FG[a] n	Refractive index after FG[a] n_{FG}	Emissivity e [%]	Solar transmittance T_{solar} [%]
A (without H_2O)	350 ± 5	1.872 ± 0.004	1.866 ± 0.005	72.7 ± 0.2	85.4 ± 0.4
B (0.1 M H_2O)	350 ± 5	1.935 ± 0.006	1.920 ± 0.006	64.4 ± 0.2	85.3 ± 0.4
C (0.2 M H_2O)	330 ± 5	1.965 ± 0.004	1.933 ± 0.005	61 ± 2	85.0 ± 0.4

[a] FG = forming gas.