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Preparation, analysis and characterization of ITO nanostructures

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Conductive and highly transparent indium tin ox- ide (ITO) thin films were prepared on photosensitive glass substrates by the combination of sol–gel and spin-coating techniques. First, the substrates were coated with amorphous Sn-doped indium hydroxide, and these amorphous films were then calcined at 550° C to produce crystalline and electrically conductive ITO layers. The resulting thin films were characterized by means of scanning electron microscopy, UV-Vis spectroscopy, X-ray photoelectron spectroscopy and spectroscopic ellipsometry. The measurements revealed that the ITO films were composed of spherical crystallites around 20 nm in size with mainly cubic crystal structure. The ITO films acted as antireflection coatings increasing the transparency of the coated substrates compared to that of the bare supports. The developed ITO films with a thickness of 170–330 nm was highly transparent in the visible spectrum with sheet resistances of 4.0–13.7 kQ/sq. By coating photosensitive glass with ITO films, our results open up new perspectives in micro- and nanotechnology, for example in fabricating conductive and highly transparent 3D microreactors.

Keywords: Analysis; Characterization; ITO; Nanostructure.

1.INTRODUCTION

By virtue of its excellent optical and electrical properties, indium tin oxide (ITO) is one of the most extensively stud- ied transparent conductive oxides [1]. ITO thin films with high transmittance in the visible spectral range and with low resistivity have previously been prepared by several methods, such as sputtering [2], spray pyrolysis [3], chemical vapor deposition [4], electron-beam evaporation [5], screen printing [6], pulsed-laser deposition [7],

and the sol-gel process [8]. The sol-gel method is a popular technique to pro- duce highquality thin films as it has a number of advantages, such as relatively low cost, a need for only simple equipment, and a high degree of control over the chemical composition of the resulting metal oxides. Sol-gel-based ITO films can be prepared either by the deposition of coating solutions [9] or from sols containing colloids [10]. In the coating solutions, the precursors are not hydrolyzed before the film deposition step [11]. In this case, after film deposition, the resulting, partially hydrolyzed pre- cursors transform to ITO upon calcination. The coating solutions are frequently used to prepare ITO films, but they contain inorganic ions of the precursors, which could be unfavorable during calcination. Sols (or colloidal dispersions) containing ITO [12] or other types of nanoparticles (e.g. indium tin hydroxide, ITH) can also be used for thin- film preparation [10]. ITH sols are generally synthesized by the hydrolysis of InCl₃ or In(NO₃)₃ and SnCl₄ in aqueous medium [13]. Since the hydrolysis and condensation of the precursors result in colloidal particles, the undesired ions (Cl⁻ and NO_{3}) can be removed from the media of the sol by washing or use of dialysis. Another advantage of the sol- based process is that the morphology or crystal phase of the ITO particles can be controlled via the synthesis temperature and pH. Sol-gel-based films are usually prepared on a glass or quartz substrate by dip- or spin-coating techniques. During film deposition, the medium of the sol evaporates and subsequently a metal oxide/hydroxide xerogel film is formed [10]. The as-prepared layers are often amorphous,

and heat treatment at $500-550^{\circ}$ C is therefore necessary to obtain crystalline and conductive ITO films. This heat treatment is an important step because it causes particle sintering, which leads to a decrease in the electrical resistance of the ITO layers. For sol preparations, the well-known hydro [14] and solvothermal [15] methods can also be employed. These synthesis methods, with the application of elevated temperature and pressure, can produce ITO nanoparticles directly instead of ITH [16].

In a recent study [10], we presented a short survey of the preparation of ITO films with wellcontrolled layer thick- ness (~40-1160 nm) by applying a combination of sol-gel and dipcoating methods. The adhesive ITH sols applied allowed the rapid preparation of high-quality ITO films. It was revealed that the sheet resistance of the ITO films was significantly lower when the ITH sols contained polyvinylpyrrolidone (PVP). In another study [17], we demonstrated a novel concept through which to achieve embedded 3D conductive and completely transparent structures in glass microchips by using a combination of femtosecond laser microfabrication and a sol-gel method. The application of ITO coatings on photosensitive glass can be a breakthrough toward the further exploitation of microchip technology by fabricating microchips with novel features. The idea relies on the wide- ranging applicability and sensitivity of ITO films of value for sensitive biochemical analysis and biological, chemical, and medical inspections based on the development of highly functional microdevices. Photosensitive glass (under the trade name Foturan®) has all of the unique properties of traditional glass (e.g. transparency, hardness, chemical, etc.) and is an excellent material with which to embed hollow microchannels and other complicated 3D structures by using femtosecond laser direct writing [18–20]. Moreover, Foturan glass can withstand thermal treatment at 550°C, which is a requirement for the production of sintered, conductive ITO films.

In the present study, we report on the preparation of sol- gel-based ITO thin films on photosensitive glass from PVP- containing amorphous ITH sol through use of spin-coating

method and subsequent calcination. The structural, optical and electrical properties of the resulting ITO thin films are reported and the effects of the aging time on the crystallinity and crystal phase composition are discussed.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of ITH sols

1.1727 g of InCl₃ 4H₂O and 0.1402 g of SnCl₄ 5H₂O were dissolved in 100 ml of deionized water, and the precursors were hydrolyzed at room temperature by the addition of 2.0 ml of 25% NH₃ solution during intensive stir- ring. The resulting dispersion was centrifuged and the sediment obtained was washed with water and subsequently with ethanol. After the washing procedure, a stable sol was prepared by redispersion of the sediment in 25 ml of ethanol with the addition of PVP in a final concentration of 0.1 w/v%. This sol was designated ITH-NA. The ITH-A sol was prepared as previously reported [10]. In this synthesis the aqueous dispersion of the as-prepared precipitate was dialyzed against deionized water until the conductivity had decreased below 1 μ S cm⁻¹. The dialysis was continued for a further 3 days, during which the precipitate was aged. After dialysis, the dispersion was centrifuged and the sediment obtained was washed with ethanol. Finally, the resulting precipitate was dispersed in 50 ml of ethanol with the addition of PVP as described above.

2.2 Preparation of ITH and ITO thin films

ITH thin films were prepared on Foturan glass substrates (10 10 2 mm) by the spin-coating method. 50 μ l of ITH-NA or ITA-A sol was dropped onto the substrate rotating with 3000 rpm and the as-prepared layer was subsequently dried for 30 s in the spin-coater. To prepare multi- layer films the above deposition step was applied again with the desired number of repetitions. To obtain ITO thin films, the deposited ITH layers were calcined for 30 min in air at 550°C in a preheated furnace.

2.3 Characterization

Thermogravimetric (TG) investigations were carried out in air with a TGA/SDTA 851e (Mettler Toledo) derivatograph at a heating rate of 5°C min⁻¹. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer equipped with a Göbel mirror. The measurements were made in θ - θ configuration using CuK_{α} radiation. The operating voltage and current were 40 kV and 40 mA, respectively. Transmission electron microscopy (TEM) im- ages were obtained with a Philips CM-10 electron micro- scope at an accelerating voltage of 100 kV. Scanning electron microscopy was performed with a Hitachi S-4700 FE-SEM cold-field emission electron microscope operated at 5 kV. UV-Vis spectrophotometry was performed with an Ocean Optics Chem2000-UV-VIS diode array spectrophotometer at wavelengths in the range 250–800 nm.

The X-ray photoelectron spectroscopy (XPS) was carried out with VG ESCALAB 250 spectrometer (Thermo Fisher Scientific K.K.) using monochromatic Al K X-ray radiation. The X-ray gun was operated at 200 W (15 kV, 13.3 mA). The C 1s binding energy of adventitious carbon was used as energy reference; it was taken at 284.8 eV.

Ellipsometry measures the complex reflection ratio ($\rho \tan(\Psi) e^{i\Delta}$, where Ψ and Δ are the ellipsometric angles), the ratio of the reflection coefficients of light polarized parallel and perpendicular to the plane of incidence [21]. By sensitively measuring phase changes of the light passing through the deposited layers, ellipsometry has a sensitivity of 0.1 nm and 0.0001 in the thickness and the in refractive index, respectively. However, as it is an indirect method,

The accuracy depends on the choice of an appropriate optical model. The ellipsometric measurements were performed with a Woollam M-2000DI rotating compensator spectroscopic ellipsometer in the wavelength range 400–800 nm, at angles of incidence ranging from 50° to 70°. A microspot was used to avoid backside reflection from the transparent substrate. The refractive index of the bare Foturan substrate was determined by using the multiple-angle spectra with backside roughening.

The sheet resistance of ITO films was determined by four-point probe measurements with a Keithley 2400 source- meter and a cylindrical four-point probe head (Jandel Engineering Ltd). The tip array was linear with a probe spacing of 1.0 mm. The 100-micron radius tips were made of tungsten carbide. The spring load was 60 g per tip. The sheet resistance (R_s) was calculated via the following relation- ship: $R_s = \pi/\ln 2 \times (V/I)$ where V and I are the voltage and the current, respectively.

3. RESULTS AND DISCUSSION

3.1 Structure, morphology and surface composition

ITO thin films were prepared by a combination of conventional sol–gel and spin-coating techniques. In the first part of the procedure, indium tin hydroxide (ITH) sol was synthesized, while in the second step ITH thin films were prepared by a spin-coating. Finally, the ITH films were calcined at 550° C. To synthesize ITH, the precursors (InCl₃ and SnCl₄) were hydrolyzed in aqueous medium by the addition of NH₃ solution until the pH reached 9. Following the hydrolysis of In³⁺ and Sn⁴⁺ and the condensation of the resultant hydroxide species, the hydrous gel obtained was subsequently washed with water and ethanol. Before the washing procedure, the precipitate was not left to age which is a significant difference as compared with our previously reported synthesis [10].



Figure 1 (a) TG and (b) DTG curves of ITO-NA xerogel dried at 50 °C.

As we presented earlier, the electric resistance of ITO films can be decreased by the addition of PVP to the ITH sol [10]. After the washing procedure, therefore the gel was dispersed ultrasonically in ethanol, and PVP was added to the sol in final concentration of 0.1 w/v%. The solid con- tent of the sol was 3.5 w/v%. To obtain ITH xerogel powder, the ethanol was evaporated from the sol at 50°C. The thermogravimetric (TG) curve of the ITH-NA xerogel obtained is presented in Fig. 1, curve a. The total mass loss in the range 25–1000°C was 25.2%. The differential thermogravimetric (DTG) curve (Fig. 1, curve b) exhibited minima at 50, 150, 280, 350 and 480°C. Two main processes can be distinguished; the first ($25-215^{\circ}$ C) is due to dehydration, while the mass loss above 215°C is assigned to the dehydroxylation of ITH and the decomposition of PVP. In the interval 550–1000°C, the xerogel lost its residual OH groups, which caused only a minor mass loss (0.7%). Since total mass loss of the xerogel without PVP was 19.9%, the PVP content of the ITO-NA xerogel was 5.3%. It should be noted that the total mass loss of the previously synthesized aged ITH xerogel [10] was slightly lower, which may be due to the higher drying temperature (80° C) applied prior to the TG analysis. The XRD patterns of the ITH-NA powder both before and after calcination are displayed in Fig. 2. The XRD pattern of the sample dried at 50°C (Fig. 2, curve a) did not contain any peaks, which indicates that the ITH-NA was amorphous. However, the ITH-A sample was nanocrystalline, as reported previously [10]. In contrast with ITH-NA, the ITH-A xerogels consisted of cubic $In(OH)_3$ and orthorhombic InOOH crystal phases. It should be noted that the nature of the medium during the aging process is of crucial importance for the crystal phase evolution. When the as- prepared precipitate (hydrous gel) was subsequently washed with ethanol, the ITH did not become crystalline even after several months of storage. We therefore conclude that the aging of the gel in an aqueous medium favors the formation of nanocrystalline ITH.



Figure 2 XRD patterns of (**a**) ITH-NA and (**b**) ITO-NA powders. The characteristic reflections of In2 O3 with cubic and rhombohedral structures are indexed.

In the XRD pattern of the calcined ITH-NA at 550°C (hereafter designated ITO-NA), cubic (JCPDS No. 06-0416) and rhombohedral (JCPDS No. 22-0336) In₂O₃ can be identified (Fig. 2, curve b). Other crystal phases (e.g. SnO and SnO_2) could not be detected, indicating a homogeneous distribution of Sn^{4+} in the In₂O₃ host. The broadened XRD lines revealed that the ITO-NA was nanocrystalline. Due to this broadening, several reflections of the two crystal phases overlapped. The predominant crystal phase was cubic; the (104) reflection of the rhombohedral phase appeared only as a shoulder on the wide-angle side of the (222) peak. To determine the average crystallite size, the broad peak in the range $29-32^{\circ}$ was deconvoluted in accordance with the positions of (222) and (104) reflections. From the FWHM of the (222) and (110) reflections, the average sizes (determined via the Scherrer equation) were 19.5 and 11.6 nm for the cubic and rhombohedral crystallites, respectively. From a comparison of the line broadening it is clearly seen that the calcined ITH-A at 550°C (hereafter designated ITO-A) consisted of smaller crystallites than those of ITO-NA. For ITO-A, the sizes were 8.3 and 9.4 nm for the cubic and rhombohedral crystallites, respectively. The XRD patterns also revealed that the ratio of the cubic and rhombohedral phases was influenced by the aging. For ITO-NA, the intensities of the lines relating to the rhombohedral phase were significantly lower. Consequently, the aging of ITH favors the formation of rhombohedral ITO crystallites. However, it should be noted that the phase evolution may also depend on the pH during aging. Kim et al. [22] reported that lower pH (8) promotes the formation of rhombohedral ITO. TEM picture of the ITH-NA (Fig. 3a,b) indicated an amorphous structure confirming the XRD results. The ITO-NA sample (Fig. 3c) was composed of round particles with a diameter of 8– 26 nm. The estimated average particle size was 17 nm, although the precise particle size distribution could not be given because of the sintering, which caused the particles to assemble into large aggregates. The electron diffraction pattern of ITO-NA (inset in Fig. 3c) confirmed the presence of both cubic and rhombohedral phases. As may be seen from the TEM picture of ITO-A (Fig. 3d), the rectangular morphology remained after calcination; the cubes and columns were still present and only a minor coarsening of the round particles could be observed. It is clear from the TEM image of ITO-A that the large rectangular particles were composed of primary particles 5-10 nm in size, in accordance with the value (8.3 nm) calculated via the Scherrer equation.

ITH-NA thin films with different layer numbers were pre- pared on photosensitive glass from ITH-NA sol by a spin-coating technique. To obtain crystalline and conductive ITO films, the

as-deposited ITH layers were calcined at 550°C. No heat treatment was applied between the film deposition steps. The surface morphology of the ITO-NA films obtained is presented in Fig. 4a. The SEM picture revealed that ITO-NA consisted of fine particles with uniform round-shaped morphology, resulting in lower surface roughness as compared with ITO-A. The SEM picture also revealed that the film was significantly porous. The cross-sectional view (Fig. 4b) of ITO- NA film made up of 3 layers showed a uniform thickness of 360 nm.

XPS measurements on the ITO-NA film yielded the high- resolution spectra of In 3d, Sn 3d and O 1s regions depicted in Fig. 5. Both the In 3d and the Sn 3d spectra were symmetric, indicating a single chemical state and the O–In–O



Figure 3 TEM images of (a) ITH-NA, (b) ITH-A, (c) ITO-NA and (d) ITO-A samples. *The inset* in (c) shows the corresponding electron diffraction pattern.

and O–Sn–O chemical environments. The In $3d_{5/2}$ and Sn $3d_{5/2}$ peaks were located at 444.3 and 486.6 eV, respectively. These binding energies reveal In and Sn oxidation states of 3 and 4, respectively [16, 23]. Table 1 lists the binding energies of In, Sn and O components in various ITO samples prepared by different synthesis methods.

Our XPS results are in good agreement with those re- ported for ITO films elsewhere [24, 25]. Quantitative analysis using the atomic sensitivity factors (ASF) of In (ASF 4.51) and Sn (ASF 4.89) resulted in an In:Sn atomic ratio of 3.73, a value slightly lower than the estimated theoretical atomic ratio In:Sn 10. While the In 3*d* and Sn 3*d* spectra are symmetrical, reflecting one chemical state, the O 1*s* spectrum has a shoulder on the high binding energy side at 531.6 eV, due to surface OH groups. Similar asymmetric O 1*s* spectra were observed for other OH-containing metal oxides (SnO₂ and TiO₂) [23, 26]. The main component of the O 1*s* spectrum is at 530 eV, which corresponds to the lattice oxygen. The atomic ratio (In Sn):O wat found to be 0.664.

3.2 Optical and electrical properties

The UV-Vis transmittance spectra of ITO-NA films are presented in Fig. 6a. It is clearly seen that in the visible wave- length range the uncoated photosensitive glass has a lower transmittance (T) than that of the ITO-NA-coated substrate (Fig. 6a, inset). This phenomenon is due to the ITO layers on the substrate acting as an antireflection coating. After de- position of an ITO-NA monolayer, T increased from 91.6 to 95% throughout the whole visible wavelength range. In the UV range, T decreased slightly with increasing number of layers. The T spectra of the ITO-NA multilayers exhibited interference fringes, and hence the T values depended on the wavelength of the incident light. It should be noted that the ITH-NA layers

also exhibited higher transparency than that of the uncoated substrate. The *T* values of all ITO-A-coated Foturan glasses also exceeded the *T* of the uncoated substrate (Fig. <u>6</u>b, inset). For ITO-A films, the transparency increased with increasing layer number in the whole UV-Vis range. The highest *T* was 96% after three deposited ITO-A layers.



Figure 4 SEM images of (**a**) surface morphology and (**b**) cross-sectional view of ITO-NA thin film made up of 3 layers on Foturan glass.



Figure 5 High-resolution XP spectra of In 3d , Sn 3d and O 1s regions for ITO-NA thin film Calcined at 550 \circ



Figure 6 UV-Vis transmittance spectra of (a) ITO-NA and (b) ITO-A thin films composed of different numbers of layers on Foturan glass.

For the ellipsometric measurements, the wavelength range of high T (400–800 nm, see Fig. 6) was used because this allows application of a simple polynomial dispersion function for the refractive index [27] (in a broader range, complex oscillator models must be used [28]). The spectra could be fitted by using a linearly graded depth profile of the refractive index in the range 3–8% (graded models have also been described for RF sputtered ITO films [27]). Figure 8 shows the better fit with the graded model relative to non-graded one. We note that the application of a sur- face nano-roughness model did not improve the fit, which indicates that the thin films were of high surface quality, in agreement with the above SEM results. For the ITO-A samples, the thickness varied from 26 to 72 nm. The lower film thickness of ITO-A is due to the lower concentration of the ITH-A sol. The refractive indices at the He–Ne laser wavelength of 633 nm were in the range 1.3–1.4 and 1.1–1.3 for the ITO-NA and ITO-A samples, respectively. This is lower than the published values for evaporated and sputtered ITO films (in the range 1.7–2.0 [28, 29]), which is in agreement with the porous structure revealed by SEM (Fig. 3).

The measured sheet resistance (Rs) of ITO-NA films de- creased significantly with increasing layer number. For film thickness of 166, 254 and 328 nm, Rs was 13.72 0.04, 5.96 0.05 and 4.02 0.02 kQ/sq, respectively, i.e. lower than the values measured earlier [10] for ITO-A at similar layer thickness. The differences may be due to the lower surface roughness and better particle-to-particle contacts in ITO-NA films.

4. CONCLUSIONS

ITO thin films were successfully prepared on photosensitive glass substrates by the combination of sol–gel and spin- coating techniques. For film deposition, an amorphous ITH sol in ethanol medium was used. Whereas the as-deposited films were amorphous, nanocrystalline ITO was formed after calcination at 550°C. These ITO nanoparticles displayed spherical morphology and high crystallinity. It was established that the aging process in aqueous medium promotes the crystallization of ITH and favors the formation of large (40–70 nm) particles with rectangular morphology. With- out the application of aging, a lower surface roughness is achieved and the resulting ITO film on photosensitive glass acts as an antireflection coating. After deposition of an ITO monolayer, the transmittance in the visible wavelength range increased from 91.6 to 95%. As the thickness increased from

166 to 328 nm, the sheet resistance decreased from 13.7 to

4.0 kQ/sq.

We believe that the developed ITO films, especially their successful processing on photosensitive glass, can find ap- plications in diverse areas of micro- and nano-technology, such as the development of conductive and highly transparent 3D structures for microreactor applications.

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