Indium Tin Oxide (ITO) Coatings Fabricated Using Mixed ITO Sols

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ABSTRACT

ITO films were achieved by sintering at 500–550°C. This was possible by inducing a seeding effect on an ITO sol by producing crystalline ITO nanoparticles in situ during heat treatment. Two kinds of ITO sols (named ITO-A and ITO-B) were prepared at 2.0 wt% from indium acetate and tin(IV) chloride in different mixed solvents. The ITO-A sol showed a high degree of crystallinity of ITO without any detectable SnO₂ on XRD at 350°C/1 h, but the ITO-B sol showed a small amount of SnO₂ even after annealing at 600°C/1 h. The 10 wt% ITO-A/ITO-B showed the sheet resistance of 3600Ω/□, while the ITO-B sol alone showed 5200Ω/□ by sintering at 550°C for 30 min. Processing parameters were studied by TG/DSC, XRD, SEM, sheet resistance, and visible transmittance.

Key words: ITO thin film, Sol-gel coating, Solvent effect, In situ seeding, Mixed sol

1. Introduction

Indium tin oxide (ITO) is a typical transparent conductive oxide which is widely used as transparent electrodes in a wide range of optoelectronic applications. The optical and electronic properties of ITO thin films are strongly influenced by the density of defects created by disturbed stoichiometry, as well as the nature of ITO sols and processing parameters. The sputtering process is commonly used for the production of ITO films. Continuous efforts have been made to develop preparation methods of ITO films comparable to the sputtered and this is still an active area of research.

Properties of ITO films are strongly dependent on the source of reactants and annealing conditions. US patent 6,235,260 disclosed the method for producing In₂O₃-SnO₂ precursor sol from alkoxides. ITO sols were prepared by acid hydrolysis and condensation of indium alkoxide and tin alkoxide as common process for other sols such as silica, alumina, titania, and magnesium sol. However, here water has to be added at low temperature, below −20°C. If added at room temperature, it forms gel or precipitate whose crystallization temperature lies above 400°C while those of the ITO sols lies in the range of 250 and 280°C. Considering the ITO sols crystallize in the range of 250 and 280°C, this crystallization temperature is substantially high and undesirable. The ITO film with a thickness of 80 nm showed sheet resistance of 7.4 × 10⁴Ω/□ and specific resistance of 5.92 × 10⁷ Ω cm by 500°C. Efficient sols are obtained in this way but there are some disadvantages such as the need for expensive chemicals and a cautious process. Therefore, studies have focused on the preparation of ITO sols from inorganic salts, such as chlorides, nitrates, acetate, etc. H. Tomanaga et al. prepared an ITO sol by reacting indium nitrate with tin oxalate in a mixture of ethylene glycol and 2,4-pentanedione at 60°C and then diluting the sol with a mixture of propylene glycol monomethyl ether and methanol. The mixture was spin-coated on alkali-free glass and heated to 700°C to give rise to an ITO film with a thickness of ~60 nm and resistance of 2.8 × 10⁷ Ω cm. The resistance was reduced to 6.2 × 10⁶ Ω cm by annealing under a reduced atmosphere, which is comparable to that of the sputtered. J. Zhang et al. prepared an ITO sol with 10 wt% Sn by mixing the anhydrous indium trichloride in acetylacetonate and tin (IV) chloride in ethanol. Poly(ethylene glycol) (PEG) was added as an additive at 30 wt%. Films were then coated four times to obtain ~100 nm in thickness. A crack-free, uniform and compact ITO thin film was observed with some microscale porosity, and the longer annealing duration leads to finer particle size and lower porosity by SEM analysis. The film annealed at 450°C showed ~35 kΩ/□ and ~19 kΩ/□ at 600°C. A-C. Dippel et al. prepared an ITO sol by a chemical solution deposition route based on a pot reaction of indium acetate, tin tetrachloride and propionic acid. The dried gel showed an exothermic peak at 334°C on a DSC curve attributed to the crystallization of the amorphous indium tin oxide. Spin-coating was performed at 2500 rpm or 4000 rpm on polished oxidized silicon wafers or conventional quartz glass substrates. XRD analysis showed that
heat-treatment at 300°C yielded mainly amorphous films and crystallization set in when the annealing was carried out at 350°C. It is interesting that solutions concentrated as low as 0.1 mol/L yielded films with a rather columnar structure. Higher molealities of the coating solutions resulted in granular films. The columnar ITO film with a thickness of 60 nm obtained by annealing at 500°C for 60 min showed 1.1 × 10^8 Ω cm, and 2.5 × 10^7 Ω cm after annealing under a flow of 10% H2/N2. The granular ITO film of thickness of 80 nm obtained by sintering at 600°C showed 5.8 × 10^7 Ω cm, and 1.2 × 10^6 Ω cm after annealing. E. Shigeno et al. achieved ITO film by dissolving indium dipropionate monohydrate and tin tetrachloride in propionic acid. Low resistivity (3.1 × 10^7 Ω cm) was obtained by annealing at 600°C in a N2-0.1% H2 atmosphere. A. Beaurain et al. prepared an ITO sol using indium chloride and stannous chloride with acetylaceton. Resistivities lower than 5 × 10^7 Ω cm were obtained by annealing at 550°C under N2/H2 atmosphere and the surfaces were rough. S. Seki et al. prepared an ITO sol by dissolving indium diacetate monohydrate and tin dichloride in ethanol and 2-aminoethanol. Highly conductive (5.8 × 10^6 Ω cm) ITO film was obtained by annealing at 600°C under nitrogen.

This work introduces a way to lower the annealing temperature of ITO film by mixing two ITO sols where one sol transforms to crystalline ITO at low temperature and plays the role of a seed to enhance the other sol’s crystallization.

2. Experimental

2.1. Preparation of ITO sols

Chemicals were used as received: indium(III) acetate (purity 99.99%, Aldrich Chemical Co., U.S.A.), tin(IV) chloride pentahydrate (purity 98%, Aldrich Chemical Co., U.S.A.), propionic acid (99.5%, Aldrich Chemical Co., U.S.A.), N,N-dimethylformide (DMF, 99%, Aldrich Chemical Co., U.S.A.) and 1-butanol (BuOH, 99.0%, Junsei, U.S.A.), N,N-dimethylformide (DMF, 99%, Aldrich Chemical Co., U.S.A.), tin(IV) chloride (purity 99.99%, Aldrich Chemical Co., U.S.A.).

Indium(III) acetate (6.85 × 10^−3 mol) and tin(IV) chloride pentahydrate (7.7 × 10^−4 mol) were mixed in a mixed solvent of propionic acid and 1-butanol (BuOH) heated at 50°C for 15 min with stirring to give rise to an ITO sol and was assigned as ITO-A sol. ITO-B sol was prepared by heating a mixture of indium(III) acetate (6.85 × 10^−3 mol) and Tin(IV) chloride pentahydrate (7.7 × 10^−4 mol) in a mixed solvent of DMF and 1-butanol at 130°C for 25 min. The solution turned yellow. Mixed sols were prepared by mixing ITO-A sol with ITO-B sol at ratios of 5, 10, and 20 wt% and designated as 5, 10, and 20 wt% A/B, respectively.

2.2. Preparation of ITO films

Soda lime glass (357 × 117 × 1 mm) was cleaned with detergent and water, and dried at 100°C in an oven. Spin-coating was carried out at 1500−3000 rpm for ~1 min. Coated glasses were dried at 100°C oven for 2−3 h, heated to 400°C−550°C at a heating rate of 5°C/min and maintained at that temperature for 1 h or 30 min, and then cooled to room temperature.

2.3. Characterization

The ITO sol was dried and subjected to TG/DSC analysis. Samples of ~30 mg were placed in an alumina crucible and heated to 600°C at a heating rate of 10°C/min under flowing air by using TG/DSC (Model STA 409C, Netzsch Co., Germany). Dried ITO precursors were heated to various temperatures to see XRD pattern development. X-ray diffractometry was conducted by XRD (Model D8 Advance, Bruker Co., Germany) using CuKα radiation at scanning rate of 2θ=3/2/min.

ITO films were subjected to an adhesion test with Scotch tape. The resistance measurement was performed by a multimeter with Ag electrodes and then converted to sheet resistance. Surface and cross-section have been analyzed using a SEM (Model S-3000H, Hitachi Co., Japan). Transmittance was measured in the wavelength range from 400 to 800 nm using a UV-VIS spectrometer (Model UV-1650PC, Shimadzu Co., Japan).

3. Results and Discussion

ITO coatings by the wet process have not yet to enter commercial production since they usually require annealing temperatures not lower than 600°C. Therefore, efforts were focused to lower sintering temperature below 550°C via a seeding effect. Here seeds produced in situ are preferred, so we attempted to develop a sol of lower crystallizing temperature which can provide crystalline ITO nanoparticles during heat treatment.

3.1. TG-DSC analysis of ITO sols

The dried ITO-A sol showed ~45 wt% loss by 350°C and the ITO-B sol ~30 wt% loss by 200°C. However, the mixed sol of 10 wt% A/B shows two-step weight loss at ~210°C and ~330°C amounted to 53% by 330°C. The weight losses were continued slowly over 500°C for all the sols as shown in Fig. 1, which implies that the transformation is continuing. DSC analysis shows a strong exothermic peak at 350°C for the
DSC peaks were assigned by the analysis of XRD patterns of heated samples up to the peak temperatures and then cooled rapidly. The peak at 350°C is assigned as ITO according to the XRD patterns shown in Fig. 3. The peak at 200°C is for SnO₂ as shown in Fig. 4. It seems that the two sols form ITO via different pathways. The ITO-A sol forms crystalline ITO without going through SnO₂, but the ITO-B sol goes through crystalline SnO₂. The mixed sol shows two exothermic peaks at 210°C and 340°C, which seem to be the shifted peaks of the ITO sols. Therefore, two more mixed sols were prepared as 5 and 20 wt% of the ITO-A sol in the ITO-B sol, and their DSC curves are shown in Fig. 5.

The mixed sols were dried and subjected to DSC analysis. The peak at 200°C is shifted to higher temperatures of 210°C, 220°C, and 230°C for 5, 10, and 20 wt%, respectively. The appearance of the exothermic peak at 340°C is noticeable and assigned to crystalline ITO, which is clear for the mixed sols of 10 and 20 wt%. The peak temperature of 340°C is lower than that of the ITO-A sol by 10°C, which demonstrates that the seeding effect of the ITO-A sol takes place in the crystallization of the ITO-B sol and 5 wt% of the ITO-A sol seemed to be enough to induce the seeding effect.

Both ITO films prepared from the ITO-A sol and the ITO-B sol were transparent, however, the one from the ITO-A sol came off completely but that of the ITO-B sol showed excellent adhesion. Films from the mixed sol of 5 wt% and 10 wt% showed strong adhesion but the one from the 20 wt% showed poor adhesion. Therefore, the 10 wt% A/B was chosen for fur-
The seeding effect was also proved by the XRD analysis of the dried mixed sols heated at various temperatures that are shown in Figs. 6 and 7. The ITO-A sol shows almost the same degree of crystallinity by the heat treatment through 350°C to 500°C, while the ITO-B sol still shows the presence of SnO₂ after the heat-treatment at 600°C. However, the mixed sol shows enhanced crystallization; a small amount of SnO₂ is formed by heat treatment at 350°C but the complete formation of crystalline ITO occurs at 400°C, and the crystallinity increases as the temperature is increased. The seeding effects were also observed at a low heat treatment temperature of 300°C for 24 h, and the 20 wt% A/B sol almost transformed to crystalline ITO while the ITO-B sol showed strong SnO₂ peaks with medium ITO peaks. These findings may provide a possibility to coat fiber with ITO as the reported ITO coating of Kevlar fiber.

Differences in the solvent system made a marked difference in the microstructure of ITO films as shown in Fig. 8. The ITO-A film shows a homogeneous microstructure of grains of ~30 nm, and the ITO-B film consists of poor crystalline grains of ~20 nm but the 10 wt% A/B film grains of ~20 nm with clear boundaries when heat treated at 500°C for 1 h. The difference in morphology became obvious at 550°C, as the ITO-A film becomes inhomogeneous with rapidly grown grains of >100 nm and sustained grains of ~30 nm, while almost the same microstructure is maintained for the ITO-B film. But the 10 wt% A/B film shows well grown grains of ~20 nm ascribed to the seeding effect. Their visible transmittances shown in Table 1 were ~86% at 550 nm due to the high porosity resulting from a single coating and were improved to >90% by a second coating. Mixed sols provided ITO films with lower sheet resistance of 3600 Ω/□ than the ITO-B sol alone (5200 Ω/□) as shown in Table 1.

### 4. Conclusion

ITO thin films are generally prepared by multi-coating and heat-treatment not lower than 600°C; therefore, a sol-gel process has not been established for ITO thin films. However, developing an ITO sol which transforms into nanosize crystalline ITO at ~350°C creates the possibility of reducing the sintering temperature of ITO film substantially via a seeding effect. ITO films were prepared by spin-coating mixed ITO sols on soda glass and followed by heat treatment at 500~550°C in air. Single coating provided ~110 nm thickness with excellent adhesion, transmittance of ~86% at 550 nm, and ~3600 Ω/□. Sheet resistances are expected to be lowered to a large extent when post annealed in a reduced atmosphere. This approach can be expanded to various thin films by the sol-gel process.
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REFERENCES