

Indium Tin Oxide (ITO) Coatings Fabricated using Nanoparticle Slurry and Sol

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ABSTRACT

Indium tin oxide (ITO) coatings were made using an ITO slurry and an ITO sol. This was achieved by dispersing nanosized ITO powder in a mixed solvent without any dispersant and developing an adhesive ITO sol from indium acetate and tin tetrachloride in a mixture of DMF and n-butanol. Coating was carried out in one step by spin coating an ITO slurry, which was then followed by an ITO sol over it. Here, the sol penetrates into the nano ITO particle layers to make them adhere to each other as well as to a glass substrate. This is then followed by sintering at 500°C for 1 h to produce a uniform film consisting of ITO particles of about 50 nm and 10 nm. ITO films were obtained with sheet resistances from 450 to 1500 Ω/\square by varying spin speed and concentration. Transmittance is higher than 90% at 550 nm.

Key words : ITO film, ITO slurry, Sol-gel, Double-coating, Sheet resistance

1. Introduction

Indium tin oxide (ITO) is a transparent conductive material (TCO) which is used in transparent electrodes in solar cells, liquid crystal displays (LCDs), organic light-emitting diodes (OLEDs), antistatic coatings, EMI shieldings, electronic ink, etc. Low resistance is required for electrodes, which can be prepared by physical methods, such as sputtering, to give a sheet resistance of $\sim 20 \Omega/\square$ with a thickness of ~ 100 nm. The production of TCO coatings by wet process has not been established for industrial application yet. ITO coatings produced by a sol-gel process usually need a firing temperature not lower than 600°C for crystallization and post-annealing under a reducing atmosphere to obtain the resistance of a few $10^{-4} \Omega\cdot\text{cm}$.¹⁻³⁾ It is not practically possible to achieve a low sheet resistance of $\sim 20 \Omega/\square$ with reasonable thickness by wet process. However, it may be possible to obtain ITO films with a high sheet resistance of $> 500 \Omega/\square$ for touch panel applications, which is very difficult to obtain by sputtering. Commercial ITO touch panels are produced as 400~500 Ω/\square by sputtering.

There are a few reports on the preparation of ITO ($\text{In}_2\text{O}_3 : x\text{Sn}$) films using ITO nanoparticles. M. Toki and M. Aizawa⁴⁾ produced ITO thin films by dipping from an ITO sol containing ITO nanoparticles at concentrations between 20 and 50 wt%. They showed sheet resistance ranging from

43,000 to 38,000 Ω/\square at a thickness of ~ 100 nm. C. Goebert et al.^{5,6)} mechanically redispersed ITO powder in ethylene glycol with a carbon acid as a dispersant and diluted with water or ethanol. ITO coatings made on silica substrates by dipping showed resistivity of $1.5 \times 10^{-2} \Omega\cdot\text{cm}$ after sintering at 900°C and reduced to $3.4 \times 10^{-3} \Omega\cdot\text{cm}$ after annealing in N_2 atmosphere at 300°C. S.-J. Hong and J.-I. Han⁷⁾ reported that an ITO film of ~ 100 nm thickness was fabricated by spin coating an ITO sol including 0.6 wt% ITO nanoparticles (~ 5 nm, 117 m^2/g) and heating at 500°C. It showed sheet resistance of $7 \times 10^3 \Omega/\square$ and transmittance of 83%. This is attributed to poor dispersion of particles and poor crystalline state. N. Al-Dahoudi and M. A. Aegerter⁸⁾ prepared an ITO film of 500 nm thickness by dispersing ITO nanoparticles in ethanol and a spin-coating. It showed the specific resistance of $160 \times 10^{-4} \Omega\cdot\text{cm}$, which is equivalent to sheet resistance of 320 Ω/\square , by sintering at 550°C and post-annealing at 300°C. Its low resistance is simply attributed to the thick layer, which is of no use in practice. All these work do not provide ITO films with sheet resistance good enough for touch panels.

Here, we introduce a method to prepare an ITO film by producing a layer of ITO nanoparticles and applying an adhesive ITO sol over it, which is then followed by sintering at 500°C for 1 h.

2. Experimental

This process requires a well-dispersed nano ITO slurry and an adhesive ITO sol.

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2.1. Preparation of ITO slurry

ITO ($\text{In}_{0.9}\text{Sn}_{0.1}\text{O}_{3-x}$) powder (purity 99.99%, $d_{50} = 50$ nm) was purchased from L&F Co. in China. Dispersion was tried in a mixed solvent. Isopropyl alcohol and methyl alcohol are major components, and small amounts of ether, ketone, and amine without any dispersing agent. Optimal dispersion parameters were obtained by trial and error. The mixing ratios of the solvents and ball-milling time were varied. Dispersion was carried out using zirconia balls 1 or 0.5 mm in diameter in a polypropylene bottle by a painter shaker (Asada Co., Japan). Varying parameters were continued until the slurry could coat a slide glass transparently to the naked eye. Then, the coated glass was heated at 500°C for 30 min to see the transparency and adhesion.

2.2. Preparation of ITO sol

The following chemicals were used as purchased: indium (III) acetate (purity 99.99%, Aldrich Chemical Co., U.S.A.), tin (IV) chloride pentahydrate (purity 98%, Aldrich Chemical Co., U.S.A.), N,N-dimethylformamide (DMF, Aldrich Chemical Co., U.S.A.), 1-butanol (BuOH, Aldrich Chemical Co., U.S.A.), isopropyl alcohol (IPA) and ethanol (EtOH). The composition of ITO was chosen as $(\text{In}_{0.9}\text{Sn}_{0.1})\text{O}_{3-x}$.

Indium(III) acetate (6.85×10^{-3} mol) and tin (IV) chloride pentahydrate (7.7×10^{-4} mol) were placed in a mixture of DMF and BuOH. Adding 3N HNO_3 helped to dissolve them, and the mixture was then refluxed at 130°C for 30 min to obtain a clear solution. The optimal reaction condition was established by varying concentration, mixed ratio of solvents, and amount of acid, as well as reaction time and temperature.

2.3. Preparation of ITO films

Soda lime glass ($157 \times 117 \times 1$ mm) was cleaned with a detergent and deionized water, and was then dried in an oven at 100°C. Spin-coating was carried out at 110 to 300 rpm for ~40 sec by pouring an ITO slurry, which was followed by pouring an ITO sol over it and spinning for an additional ~40 sec. The coated glasses were dried in an oven at 100°C for 2 to 3 h. They were then heated to 350°C to 550°C at a heating rate of 5°C/min and maintained at that temperature for 30 min to 1 h, after which, they were cooled to room temperature.

2.4. 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 at various temperatures to see XRD pattern development. X-ray diffractometry was conducted by XRD (Model D-8 Advance, Bruker Co., Germany) using $\text{CuK}\alpha$ radiation at a scanning rate of $2\theta = 3^\circ/\text{min}$. The ITO films were subjected to an adhesion test with Scotch tape. Resistances were measured with a multimeter with Ag electrodes, and they were then converted to sheet resistances. The surfaces and cross-sections were analyzed using SEM (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) using a bare glass as a reference.

3. Results and Discussion

The strategy in preparing an ITO film is to fill intrinsic voids of layered nanoparticles with much smaller particles to create contacts among them and at the same time to provide their adhesion to the substrate. This can be accomplished by providing a uniform layer of ITO particles and making an adhesive sol infiltrated, which is then followed by sintering.

3.1. Preparation of ITO slurry

Dispersion of nanosized ITO particles was carried out by breaking agglomerates using small milling media, namely, zirconia balls of 0.1, 0.5, and 1 mm in diameter. Larger balls took much longer milling time than smaller ones. When balls of diameter of 0.1 mm diameter were used, dispersion progressed rapidly with changing color from yellow to deep green. However, washing the balls was very difficult and time consuming because the balls settled very slowly. Therefore, balls of 0.5 mm and 1 mm were chosen. The slurry concentration chosen was 20 wt%, and the weight of the balls was varied. The solvent was composed of mainly isopropanol and methanol and a small amount of an acid, a ketone, and an ether. The effects of milling media are compared in Table 1. A well-dispersed ITO slurry was obtained after 6 hour's milling with balls of 1 mm diameter, but milling time was reduced to 3 h when balls of 0.5 mm diameter were used. They gave a clear transparent coating which can be wiped off as expected because it is just a film of powder without any binder.

Table 1. Effects of Processing Parameters on Preparation of ITO Slurry

Sample	PD-A-1	PD-B-2		
Diameter of balls (mm)	1	0.5		
Weight of balls (g)	230.54	232.0		
Mixed solvent (g)	28.82	28.82		
ITO powder (g)	7.51	7.51		
Ball/ITO (wt%)	30.7	30.9		
ITO conc. (wt%)	20.67	20.67		
Physical properties versus milling time				
Milling time (h)	PD-A-1		PD-B-2	
	Slurry color	Film	Slurry color	Film
1	yellow	translucent	greenish yellow	translucent
2	greenish yellow	translucent	yellowish green	~transparent
3	greenish yellow	translucent	green	transparent
4	yellowish green	~transparent		
5	yellowish green	~transparent		
6	green	transparent		

3.2. Preparation of ITO sol

DMF was selected to coordinate with In and Sn. The solution was stable but did not give a uniform film. Mixing the solution with n-butanol seemed promising for coating, so various reaction conditions were tried, and the proper amount of 3N nitric acid seemed to be 2 ml per 2 g of indium acetate, which gave transparent pale yellow ITO sols. Good adhesive transparent ITO films were obtained by spin-coating the ITO sol, and this was followed by heat treatment above 450°C. Analyzing the dried ITO sol by TG showed loss of ~28 wt% by 210°C, and then weight loss continued over 600°C as shown in Fig. 1, which meant that transformation was continuing. DSC analysis shows a strong exothermic peak at 209.3°C, which is attributed to SnO₂ as shown in Fig. 2. This indicates that ITO was formed by solid state reaction via SnO₂. Fig. 3 shows that SnO₂ is not consumed completely to form ITO even after heat treatment at 600°C for 1 h. This is consistent with many previous reports in which heat treatment was performed above 600°C. Formation of ITO seems to proceed

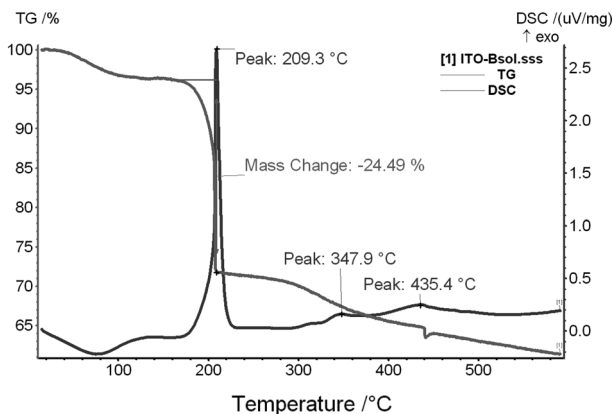


Fig. 1. TG/DSC curves of the dried ITO sol heated at 10°C/min under flowing air.

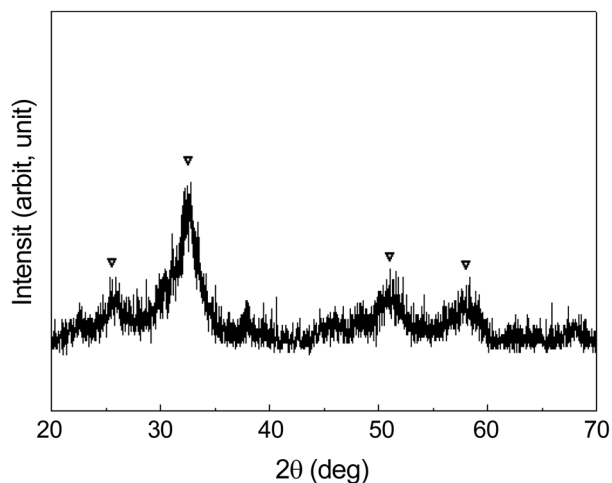


Fig. 2. XRD pattern of dried ITO sol heated to 210°C at a heating rate of 10°C/min in flowing air and then cooled rapidly (▽ : SnO₂, JCPDS 41-1445).

fast above 500°C; however, heat treatment was carried out at 500°C because of the soda lime glass employed.

3.3. Formation of ITO film

The spin-coated ITO film using the ITO sol shows a microstructure consisting of ~10 nm particles as shown in Fig. 4(a), while the spin-coated ITO slurry shows a microstructure consisting of layered ITO particles of about 40 to 60 nm with

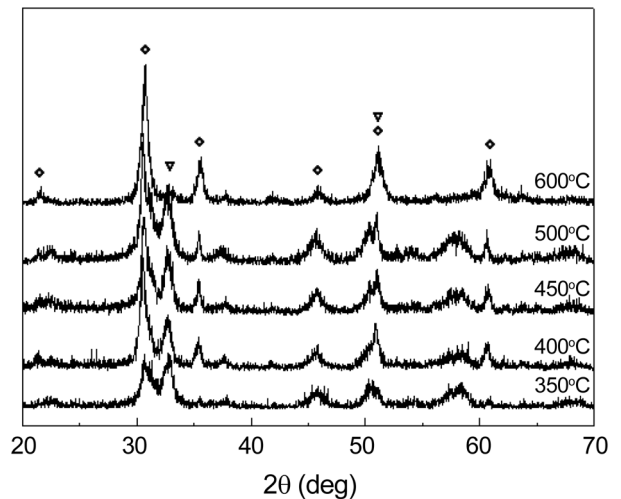


Fig. 3. Development of XRD patterns of dried ITO sol heated at various temperatures for 1 h (◇ : ITO (JCPDS : 88-0773), ▽ : SnO₂).

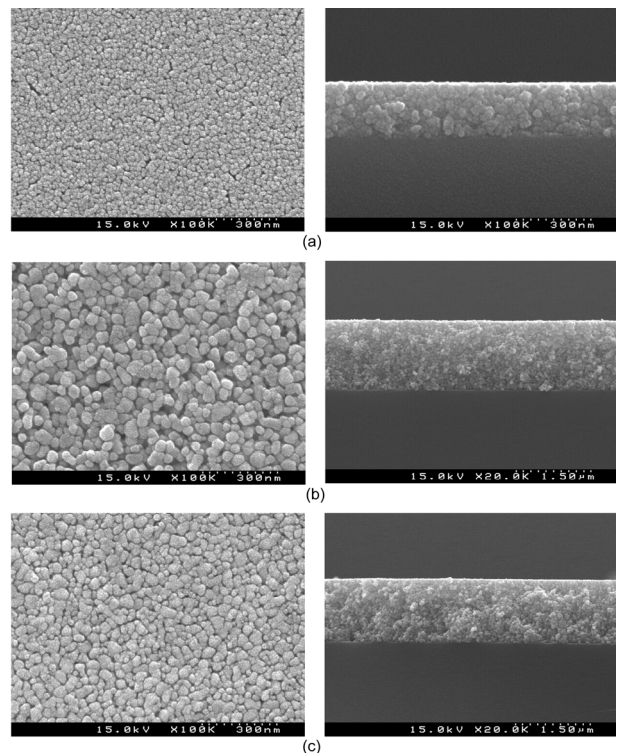


Fig. 4. SEM pictures of ITO films prepared by spin coating at 110 rpm using: (a) ITO sol, (b) ITO slurry, and (c) ITO slurry and followed by ITO sol.

Table 2. Characteristics of ITO Films Prepared with Slurry and Sol and Heat Treated at 500°C/1 h in Air

Sample	Conc. of ITO (wt%)		Spinning speed (rpm)	Thickness (nm)	Transmittance (%) at 550 nm	Sheet resistance (Ω/\square)
	Slurry	Sol				
1	2	0	200	n.a.	93	14k
2	2	2	200	225	92	450
3	1	2	110	175	95	670
4	1	2	200	125	95	840
5	1	2	300	75	96	1250
6	0.8	1.5	300	n.a.	95	1500
7	0	2	150	88	96	9100

some voids, which are not either uniform or flat as shown in Fig. 4(b). However, one prepared by our strategy shown in Fig. 4(c) shows a microstructure of layered large particles filled with ~ 10 nm particles from the ITO sol, resulting in a uniform and flat surface. The ITO sol of 2.0 wt% was used with the ITO slurry of 15 wt% for clarity. Their visible transmittances are $>90\%$ at 550 nm. This observation demonstrates the possibility to produce ITO films comparable to sputtered ITO films by a wet process with high sheet resistance. ITO films with various sheet resistance ranging from 450 to 1500 Ω/\square were obtained by varying concentrations of ITO slurry and sol, and varying the spinning speed from 110 to 300 rpm as shown in Table 2. The ITO film prepared from the ITO slurry showed a high sheet resistance of 14 k Ω/\square due to poor contact of particles because heat treatment temperature of 500°C was not high enough to induce sintering, but high transmittance proved good dispersion (Sample 1). The film from the ITO sol (Sample 7) also showed a high resistance of 9 k Ω/\square due to incomplete crystallization of ITO as shown in its XRD pattern of Fig. 3, but it also showed a high transmittance of 92%. This demonstrates that slurry or sol alone can not provide ITO film good enough for a substrate of soda lime glass. Using them in a proper way resulted in ITO films suitable for touch panels. The sheet resistance obtained in this work is much lower than any reported work using ITO slurry as described in the Introduction. This is mainly attributed to well-dispersed slurry and well-filled ITO particles derived from the sol.

4. Conclusion

Uniform, transparent, and adhesive ITO films were achieved by spin coating an ITO slurry followed by spin-coating an ITO sol over it. This successful approach is different from the reported process of making a slurry in ITO sol. Here, good adhesive sol penetrates into the nano ITO particle layers to make particles adhere to each other as well as to a glass substrate. Sintering at 500°C for 1 h resulted in films consisting of ITO particles of about 50 nm from the slurry and

about 10 nm from the sol. They were obtained with sheet resistances from 450 to 1500 Ω/\square and a transmittance of $>90\%$ by varying spin speed and concentration.

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