Synthesis and Dispersion Stabilization of Indium Tin Oxide Nanopowders by Coprecipitation and Sol-Gel Method for Transparent and Conductive Films

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Abstract: Indium tin oxide (ITO) nanopowders were synthesized by coprecipitation and the sol-gel method to prepare a stable dispersion of ITO nano-colloid for antistatic coating of a display panel. The colloidal dispersions were prepared by attrition process with a vibratory milling apparatus using a suitable dispersant in organic solvent. The ITO coating solution was spin-coated on a glass panel followed by the deposition of partially hydrolyzed alkyl silicate as an over-coat layer. The double-layered coating films were characterized by measuring the sheet resistance and reflectance spectrum for antistatic and antireflective properties.

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1. INTRODUCTION

Transparent conductive oxides (TCOs) deposited on glass or flexible substrates are important materials in the field of optoelectric devices such as solar cells, liquid crystal displays, electroluminescence, and touch screen panels [1]. Among the various TCOs, tin-doped indium oxide (ITO) is widely used because it has the high figure of merit compared with the other n-type TCOs such as antimony-doped tin oxide (ATO) or fluorine doped tin oxide (FTO) [2].

One of the important applications of ITO is antistatic coating for shielding electromagnetic emissions. Though $10^8 \Omega/\square$ of sheet resistance is satisfactory for preventing the accumulation of charge on the display panel, it is necessary to form ITO film having a low resistivity not exceeding $10^6 \Omega/\square$, and preferably in the order of $10^2$ to $10^3 \Omega/\square$ is desired [3].

There are several methods to deposit ITO film on various substrates such as CVD, sputtering, vacuum deposition, and sol-gel process [4,5]. Among these versatile methods, the spin coating of ITO nano-colloid is now widely used for industrial purposes since this method is the most suitable for the mass production of coating layers as wet chemical process [6,7].

To prepare coating solution of ITO nanoparticles, ITO nanopowder should be first synthesized and redispersed as colloidal dispersion by using suitable dispersants with the aids of milling apparatuses. There have been developed various synthetic routes of ITO nanopowders such as coprecipitation, sol-gel, micro-emulsion technique, and hydrothermal process [8-14]. Among them, room temperature chemical synthetic methods in liquid phase are simple and economical ways, thus attracting the industrial fields for the production of the conductive nanopowders.

For coprecipitation method, different ions in solution phase are simultaneously precipitated after the mixing of precursors followed by the hydrolysis reaction. After the coprecipitation reaction, the resulting hydrolysis products can be transformed into desirable nanopowders via suitable heat treatment during calcination step. Similarly, metal alkoxide precursors can be used for the synthesis of nanopowders by sol-gel method, which enables the generation of solid particles through the hydrolysis and polycondensation reaction of the precursors. Micro-emulsions containing reaction precursors surrounded with suitable surfactants can be used as nanoreactors or reaction sites for the synthesis of nanoparticlecsl though the removal of

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surface active agents is essential step for the improvement of product purity. Hydrothermal method can be also adopted for the synthesis of nanopowders under the harsh reaction conditions such as high temperature for the increase of diffusion velocity of precursor molecules, thus accelerating the phase transformation speed, and high pressure to maintain the solution phase under increased reaction temperature.

In this study, to deposit redispersed ITO nano-colloid on glass panel, ITO nanopowders were synthesized by coprecipitation and sol-gel method, and coating solutions containing ITO nanoparticles were prepared by using titanate coupling agent as steric stabilizer during attrition process. The electrical and optical properties of the ITO coating films were examined using ITO nanoparticles prepared by both coprecipitation and sol-gel method for display coatings with ITO nano-colloids using spin coater, as shown in the work flow of Scheme 1.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Indium chloride (InCl$_3$, 99.999%) and tin chloride (SnCl$_4$, 99.995%) were used as metal precursors for coprecipitation reaction and obtained from Aldrich. Indium chloride tetrahydrate (InCl$_3$·4H$_2$O, Kanto Chemicals, 99.95%) and tin chloride pentahydrate (SnCl$_4$·5H$_2$O, Kanto Chemicals, 98%) were also used for coprecipitation method and as inorganic precursors and ammonium hydroxide (NH$_4$OH, Aldrich, NH$_3$ 28–30%) as a precipitating agent were utilized as received to prepare ITO nanopowder by coprecipitation method. Indium acetate (In(CH$_3$CO$_2$)$_3$, Aldrich, 99.99%) and tin acetate (Sn(CH$_3$CO$_2$)$_2$, Aldrich) as precursor materials and ammonium hydroxide as a basic catalyst were used as received to prepare ITO nanopowder by sol-gel method. Regenerated cellulose membrane (MWCO, molecular weight cut-off = 1000, Spectrum Laboratories Inc.) was used to remove organic residues from indium tin hydroxide solution by dialysis. The mixture of ethanol (Merck, 99.9%) and DMF (N,N-dimethylformamide, HCON(CH$_3$)$_2$, Duksan Pharmaceutical Co. Ltd., 99.9%) was used as a dispersion medium of ITO suspensions.

Tri(N-ethylenediamino)ethyl titanate as dispersion stabilizer for ITO suspension was purchased from Kenrich Petrochemicals. ZrO$_2$ beads with 0.3 mm in diameter were purchased from Toray (Japan) to comminute the ITO nanopowders during attrition and redispersion process.

2.2. The preparation of ITO nanopowder by coprecipitation method

In this article, ITO nanopowder was prepared by coprecipitation method. Coprecipitation reaction was performed by adding 0.45 to 0.73 M of aqueous NH$_4$OH solution into the precursor solutions. These reactions were performed overnight under vigorous agitation. The indium tin hydroxide nanoparticles obtained by the coprecipitation reaction were washed with distilled water to remove residual ions from the nanoparticle surfaces. During the washing process, centrifugal force (6,500 to 7,500 rpm for 5 to 10 minutes) was applied to the particulate suspensions. This washing and centrifugation process was performed 5 times. For the further purification, the aqueous indium tin hydroxide solution was put into dialysis membrane immersed in fresh water to remove residual ions. The distilled water outside of the membrane was changed several times to wash the indium tin hydroxide nanopowder.

The washed indium tin hydroxide nanopowder was collected and dried at 60 to 70°C overnight and crushed.