Effect of Surface-Modification of Indium Tin Oxide Particles on Their Electrical Conductivity

Y. Kobayashi, T. Kurosaka, K. Yamamura, T. Yonezawa, K. Yamasaki

Abstract—The present work reports an effect of surface-modification of indium tin oxide (ITO) particles with chemicals on their electronic conductivity properties. Examined chemicals were polyvinyl alcohol (nonionic polymer), poly(diallyl dimethyl ammonium chloride) (cationic polymer), poly(sodium 4-styrene-sulfonate) (anionic polymer), (2-aminopropyl) trimethoxy silane (APMS) (silane coupling agent with amino group), and (3-mercaptopropyl) trimethoxy silane (MPS) (silane coupling agent with thiol group). For all the examined chemicals, volume resistivities of surface-modified ITO particles did not increase much when they were aged in air at 80 ℃, compared to a volume resistivity of un-surface-modified ITO particles. Increases in volume resistivities of ITO particles surface-modified with the silane coupling agents were smaller than those with the polymers, since hydrolysis of the silane coupling agents and condensation of generated silanol and OH groups on ITO particles took place to provide efficient immobilization of them on particles. The APMS gave an increase in volume resistivity smaller than the MPS, since a larger solubility in water of APMS providing a larger amount of APMS immobilized on particles.

Keywords—Indium tin oxide, particles, surface-modification, volume resistivity.

I. INTRODUCTION

TIN-DOPED indium oxide, or indium tin oxide (ITO), is electro-conductive, and its film is transparent in the visible region. These properties are applicable to opto-electronic devices such as display, solar cell, and sensor [1]-[3]. The ITO faces at a problem: Electrical conductivity of ITO is reduced under exposure to air; that is, the ITO is unstable as for its electrical conductivity. According to Yu et al. [4], oxygen and moisture molecules adsorbed on ITO film surface diffuse into inside of the film, which controls the mobility of carriers. The control provides the reduction of electrical conductivity of ITO. Based on the mechanism of the reduction, the oxygen-adsorption should be controlled to stabilize the electrical conductivity. Covering of ITO surface with chemicals, or surface-modification might work for the stabilization since the covering chemicals prevent the ITO surface from contacting with air. In fabrication of metallic copper nanoparticles in aqueous solution, oxidation of the

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nanoparticles could be controlled with the presence of CTAB and citric acid in the aqueous solution [5], [6]. Adsorption of these chemicals on particle surface is considered to make the particle surface not contact with oxygen molecules in air. This result expects that use of chemicals acting on particle surface solves the problem on unstable electrical conductivity.

There are various chemical agents for surface-modification, in which representatives are the chemical agents such as cationic polymer, anionic polymer, non-ionic polymer and silane coupling agent. The present work examines various chemical agents for surface-modification to find chemical agents suitable to stabilization of electrical conductivity of ITO.

II. EXPERIMENTAL

A. Chemicals

ITO particles suspended in ethanol (25 wt.%) were supplied from Mitsubishi Materials Corporation. Their morphology is explained in a section of Results and Discussion. Polymers examined for surface-modification of ITO particles were polyvinyl alcohol (polymerization degree: 2000, Kanto Chemical) a nonionic polymer, poly (diallyl dimethyl ammonium chloride) (PDADMAC) (20 wt.% in H_2O, Mw: 100000-200000, Sigma-Aldrich) as a cationic polymer, and poly (sodium 4-styrene-sulfonate) (PSS) (Mw: ca. 70000, Sigma-Aldrich) as an anionic polymer. Silane coupling agents examined for the surface-modification were (2-aminopropyl) trimethoxy silane (APMS) (97%, Sigma-Aldrich) and (3-mercaptopropyl) trimethoxy silane (MPS) (95%, Sigma-Aldrich). Ethanol (99.5%, Kanto Chemical) was used as solvent for the examined chemicals. All the chemicals were used as received. Water that was ion-exchanged, distilled, sterilized with an ultra-violet lamp and filtrated with Advantec RFD270NC was used in all preparations.

B. Methods

For surface-modification using the polymers, ethanol and polymer/ethanol solution were added to the ITO suspension. The mixture was stirred at room temperature for 24 h. The concentrations of ITO and polymer in the mixture were 2.5 wt.% and 1 g/L, respectively. For surface-modification using the silicone alkoxides, silane coupling agent/ethanol solution, ethanol and water were added to the ITO suspension. The mixture was stirred at room temperature for 24 h. The concentrations of ITO and silane coupling agent in the mixture were 2.5 wt.% and 1 g/L, respectively. The H_2O concentration was adjusted to 0, 20, 40, 60 and 80 vol.% by varying the amounts of ethanol and water. The surface-modified ITO particles were washed by repeated centrifugation, supernatant

removal via decantation, ethanol addition and sonication. This procedure was repeated three times. To obtain a concentrated ITO particle colloid solution, the amount of added ethanol was reduced by 1/10, which resulted in an ITO concentration of 25 wt.% in the final colloid solution. The ITO particles surface-modified with PVA, PDADMAC, PSS, MPS and APMS are indicated as ITO/PVA, ITO/PDADMAC, ITO/PSS, ITO/MPS and ITO/APMS, respectively.
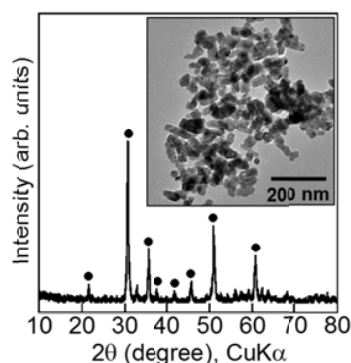

Fig. 1 XRD pattern of ITO nanoparticles. An inset shows their TEM image

The particles were characterized by using transmittance electron microscopy (TEM) and X-ray diffractometry (XRD). The TEM was performed by using a JEOL JEM-2000FX II microscope at 200 kV. The TEM samples were prepared by dropping and evaporating the particle suspensions onto a colloid-coated copper grid. The XRD patterns of the particle powder samples were obtained with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA with CuKα radiation (λ: 0.154056 nm).
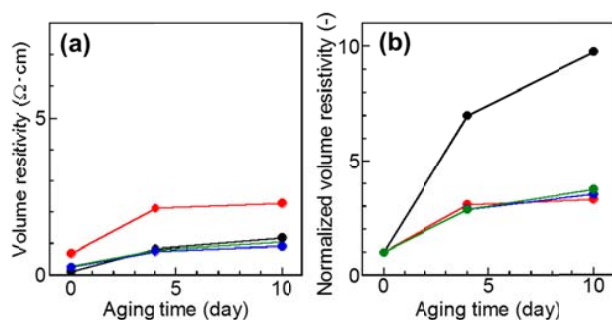

Fig. 2 Volume resistivities of various particle powders (a) and normalized volume resistivities (b) versus time after surface-modification. The volume resistivities were normalized with that for 0 day. Black plot: ITO (un-surface-modified). Red, blue and green plots: ITO surface-modified with PVA, PDADMAC and PSS, respectively

The volume resistivities of the particle powders were measured by using a 4-pin probe to determine the electrical resistivity of the particles. The concentrated ITO particle colloid solution was dropped on a substrate (polyethylene terephthalate (PET) (Toyobo: COSMOSHINE® A4100)) with

sizes of 5 cm×5 cm, spread by spin-coating with a Mikasa 1H-DS spinner at 1000 rpm for 30 s, and dried at room temperature. The ITO/PET film was covered with a polyimide film (Du Pont-Toray: Kapton®), and pressed with a Thank Metal 3t/hydraulic roll press at a linear pressure of 1000 kgf/cm and a rolling speed of 1.0 m/s. Film thicknesses were measured with an SFT-9400 SII X-ray fluorescent analysis thickness meter. The measurements of volume resistivities were performed by using a Mitsubishi Chemical Analytech MCP-T370 resistivity meter. The as-pressed ITO/PET film was aged at 80 °C in air with an As-One OFW-600B drying chamber.

III. RESULTS AND DISCUSSION

A. Morphology of ITO Nanoparticles

The inset of Fig. 1 shows a TEM image of the ITO particles. The ITO particles were quasi rod-shaped, and had longitudinal and lateral sizes of 40.6±15.0 and 25.7±7.7 nm, respectively. Fig. 1 shows an XRD pattern of the ITO particles. Several peaks were mainly recorded at 30.6, 35.5, 50.9 and 60.7 degrees. They were assigned to the (222), (400), (440) and (622) phases of cubic ITO according to references [7], [8] and the standard data (ICSD 01-089-4597). Their crystal size was calculated as 7.7 nm by applying Scherrer equation to the XRD line broadening of the 30.6° peak. The average particle size was larger than the crystal size. Accordingly, the ITO particles were polycrystallites of cubic ITO.

B. Volume Resistivities of Particles Surface-Modified with Polymers

Fig. 2 (a) shows the volume resistivities of particles surface-modified with various polymers as a function of aging time. A volume resistivity of ITO particles, or ITO particles that were not surface-modified, is also shown. The volume resistivity of ITO particles was 0.12 Ω·cm at an aging time of 0 day. The volume resistivity increased from 0.12 to 1.17 Ω·cm monotonously with an increase in aging time from 0 to 10 days, because of exposure to air. The volume resistivities of surface-modified particle powders at 0 day were larger than that for the ITO particle powder. The polymer molecules were immobilized through their adsorption on particle surface due to intermolecular force and/or electrostatic interaction to cover the particles. The covering prevented the particle surface from contacting directly with surface of other particles, which controlled electric conductivity of particles. The volume resistivities also increased monotonously with the increase in aging time. Fig. 2 (b) shows normalized volume resistivities of the surface-modified particles as a function of aging time. A normalized volume resistivity of the ITO particles increased from 1 to 9.8 with the increase in aging time from 0 to 10 days. For all the surface-modified ITO particles examined, them normalized volume resistivities also increased with increasing the aging time. The normalized volume resistivities were around 3.5 at the aging time of 10 days. These values were smaller than that of the ITO particles at 10 days, which indicated that the surface-modification with polymer controlled

the increase in volume resistivity. Accordingly, the surface-modification was confirmed to have an ability to protect the ITO particles and to make the particles stable as for electric resistivity.
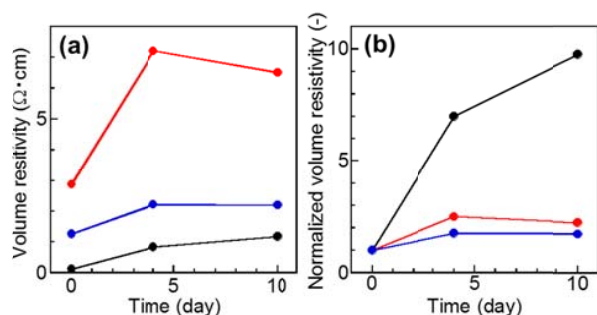

Fig. 3 Volume resistivities of various particle powders (a) and normailzed volume resitivities (b) versus time after surface-modification. The volume resitivities were normalized with that for 0 day. Black plot: ITO particles (un-surface-modified). Red and blue plots: ITO particles surface-modified with MPS and APMS, respectively. H_2O concentrations in surface-modification were 20 and 80 vol% for MPS and APMS, respectively

C. Volume Resistivities of Particles Surface-Modified with Silane Coupling Agents

Fig. 3 (a) shows volume resistivities of the particles surface-modified with different silane coupling agents as a function of aging time. The volume resistivity of ITO particles that were not surface-modified is also shown, which is the same as in Fig. 2 (a). The volume resistivities of surface-modified particle powders at 0 day were also larger than that for the ITO particle powder, due to effect of the covering of the ITO particles with the silane coupling agents on electric conductivity of particles. Volume resistivities increased remarkably with an increase in aging time to 4 days due to exposure to air. Over 4 days, the volume resistivities tended to level off. Fig. 3 (b) shows normalized volume resistivities of the surface-modified particles as a function of aging time. For the surface-modified ITO particles examined, their normalized volume resistivities were 2.3 for ITO/MPS and 1.7 for ITO/APMS at the aging time of 10 days. These values were smaller than those for the polymers: the surface-modification using silane coupling agents controlled electric conductivity of ITO particles more dominantly. The silane coupling agent was hydrolyzed to form silanol groups. The silanol groups acted on hydroxide groups on particle surface. The groups were condensed to form chemical bond like Si-O-Sn and Si-O-In, and then the silane coupling agent molecules were immobilized on particle surface. The formation of chemical bonds was considered to immobilize the surface-modifying agents more efficiently than the adsorption in the case of polymers. Thus, the efficient immobilization for silane coupling agents controlled interaction between particle surface and air, and kept the electric conductivities of ITO particles.
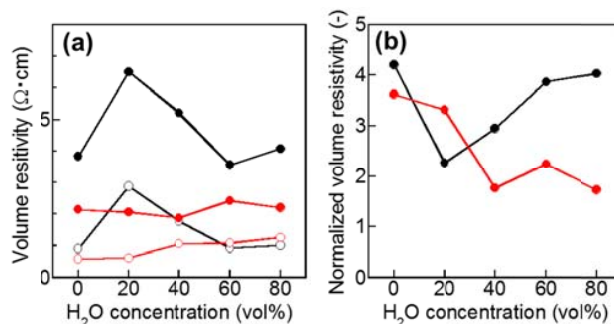

Fig. 4 Volume resistivities of various particle powders versus H_2O concentration in surface-modification (a graph (a)). Open and closed circles: ITO particles for 0 and 10 days after surface-modification, respectively. A graph (b) shows normalized volume resistivities versus H_2O concentration. The volume resistivities were normalized with that for 0 day. Black and red plots: ITO particles surface-modified with MPS and APMS, respectively

D. Effect of Water Concentration in Surface-Modification Using Silane Coupling Agent on Volume Resistivity

Figs. 4 (a) and (b) show volume resistivities and normalized volume resistivities of particles surface-modified with different silane coupling agents as a function of H_2O concentration in surface-modification, respectively. For ITO/MPS, a volume resistivity at an H_2O concentration of 0 vol.% was 0.91 $\Omega\cdot$cm for the 0 day-film. The volume resistivity was a maximum of 2.88 $\Omega\cdot$cm at 20 vol.%. This result implied that the MPS was immobilized on particle surface most efficiently at 20 vol.% among the H_2O concentrations examined, because of the maximum volume resistivity. Over 20 vol.%, the volume resistivity decreased with increasing the H_2O concentration. Because MPS is organic compound, the amount of MPS in the ethanol/water solution is expected to be small at the high water concentrations. Accordingly, the particle surface was not covered with MPS well at the high water concentrations because of loss of undissolved MPS, so that the volume resistivities were low compared to at the concentration as low as 20 vol.%. The aging for 10 days increased the volume resistivity for all the H_2O concentrations. A normalized volume resistivity was a minimum of 2.3 at 20 vol.% among all the H_2O concentrations. The amount of MPS on particles was the largest at 20 vol.%, according to the implication on efficient immobilization at 20 vol.%. The covering with the large amount of MPS controlled the contact of ITO particle surface with air. As a result, the change in volume resistivity was the smallest at 20 vol.%.

For ITO/APMS, a volume resistivity at an H_2O concentration of 0 vol.% was 0.59 $\Omega\cdot$cm for the 0 day-film. The volume resistivity increased with increasing the H_2O concentration, and reached 1.26 $\Omega\cdot$cm at 80 vol.%, which was the largest among the H_2O concentrations examined. This result implied that the APMS was immobilized on particle surface the most efficiently at the water concentration as high as 80 vol.% because of the maximum volume resistivity. It is known that amino organofunctional trialkoxysilanes are readily soluble in water to give solutions of unlimited solubility [9]. Accordingly, many APMS molecules were considered to be dissolved in water, and

be consumed for the immobilization, which provided efficient covering of particle surface. Consequently, the largest volume resistivity was recorded at the high water concentration. The volume resistivity increased with the aging for 10 days for all the H_2O concentrations as well as the ITO/MPS. A normalized volume resistivity tended to decrease with the increase in H_2O concentration, and was the smallest value of 1.7 at 80 vol.%. The largest amount of APMS was present on particle surface at 80 vol.%, which was implied from the result on the largest volume resistivity at 80 vol.%. The covering with the large amount of APMS controlled the contact of ITO particle surface with air. As a result, the change in volume resistivity was the smallest at 80 vol.%. The normalized volume resistivity of 1.7 for ITO/APMS at 80 vol.% was smaller than 2.3 for ITO/MPS at 20 vol.%. The results on the volume registivities implied that the amount of APMS on particle surface was larger than that of MPS. This indicated that the smaller volume resistivity was attained with smaller amount of silane coupling agent for ITO/APMS. Accordingly, it was demonstrated that the APMS was suitable to control the resistivity of ITO particles, compared to MPS, although a mechanism on the different abilities to control the resistivity is still unclear.

IV. CONCLUSIONS

The ITO particles were surface-modified with various chemicals such as polymers (PVA as the nonionic polymer, PDADAMC as the cationic polymer and PSS as the anionic polymer) and silane coupling agents (MPS as the silane coupling agent with thiol group and APMS as the silane coupling agent with thiol group). Volume resistivities of particles increased with aging in air at 80 °C. Any chemicals examined had the ability to reduce the increase in volume resistivity of ITO particles, due to covering their surfaces with the chemicals. Increases in volume resistivities of ITO particles were controlled dominantly for the surface-modifications with the silane coupling agent, since the silane coupling agents were efficiently immobilized on the ITO particle surface through hydrolysis of the silane coupling agents and condensation of generated silanol and OH groups on ITO particles. In particular, the surface-modification using APMS was more effective against the increase in volume resistivity than MPS, since the APMS was more soluble in water, and more APMS molecules were immobilized on particles.

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