Physical Properties of Indium Reduced Materials for Transparent Conductive Electrodes

Seung-Hoon Kwak[1,2] · Min-Gi Kwak[1] · Sung-Jei Hong[1]* · Byeong-Kwon Ju[2] · Jeong In Han[3]*

[1]Display Components and Materials Research Center, Korea Electronics Technology Institute, Seongnam, 463-816, Korea
[2]School of Electrical Engineering, Korea University, Seoul 136-713, Korea
[3]Department of Chemical and Biochemical Engineering, Dongguk University-SEOUL Seoul 100-715, Korea

ABSTRACT: In this paper, indium reduced materials for transparent conductive electrodes (TCE) were fabricated and their physical properties were evaluated. Two of materials, indium-zinc-tin oxide (IZTO) and aluminum (Al) were selected as TCE materials. In case of IZTO nanoparticles, composition ratios of In, Zn and Sn is 8:1:1 were synthesized. Size of the synthesized IZTO nanoparticles were less than 10 nm, and specific surface areas were about 90 m^2/g indicating particle sizes are very fine. Also, the IZTO nanoparticles were well crystallized with (222) preferred orientation despite it was synthesized at the lowered temperature of 300°C. Composition ratios of In, Zn and Sn were very uniform in accordance with those as designed. Meanwhile, Al was deposited onto glass by sputtering in a vacuum chamber for mesh architecture. The Al was well deposited onto the glass, and no pore was observed from the Al surface. The sheet resistance of Al on glass was about 0.3 Ω/□ with small deviation of 0.025 Ω/□, and adhesion was good on the glass substrate since no pelt-off part of Al was observed by tape test. If the Al mesh is combined with ink coated layer which is consistent of IZTO nanoparticles, it is expected that the good and reliable metal mesh architecture for TCE will be formed.

Key words: Indium reduced, Transparent conductive electrode, Indium-zinc-tin oxide, Aluminum, Physical properties

1. Introduction

Transparent conductive electrode (TCE) is widely used for touch screen panel (TSP), flat panel display (FPD), and renewable energies such as solar cell and LED lighting, etc. As a material of the TCE, indium-tin-oxide (ITO) has been used for its unique characteristics of optical transparency and electrical conduction. ITO thin film is conventionally made by vacuum process such as sputtering or evaporation followed by photolithography and chemical etching. However, the exhaust of indium (In) has been a serious global issue, and the exhaust is accelerated with rapid market growth of the related industries. Thus, the price of the In increase in proportional to the market growth, and reduction of the In is extensively required. As one of the reduction, researches are being carried out to decrease the exhausted amount of In in the vacuum process, for example, to add Zn into the ITO[1], that is, indium-zinc-tin oxide (IZTO). Meanwhile, metallic mesh architecture is intensively considered as the TCE materials[2]. By using the mesh architecture, the conductivity is remarkably enhanced while optical transmittance is slightly decreased. Among the several metallic elements, aluminum was selected for its merits of highly electrical conductivity and low price. Therefore, two types of materials, IZTO and Al, were selected to apply for the TCE that the In is reduced. In this study, as a first step, their physical properties were investigated.

2. Experimentals

In case of IZTO nanoparticles, indium, zinc, and tin organic compounds were used as raw materials. Composition ratio of In, Zn and Sn were designed as 8:1:1 in weight. The raw materials were dissolved into alcohol solvent and the mixed solution was stirred to evaporate the solvent component. The precursors were heated at 300°C. The particle size, specific surface area, crystal structure, composition ratio of the synthesized IZTO nanoparticles were analyzed by means of high resolution transmission electron microscope (HRTEM, JEOL 300 kV), BET specific surface area analyzer, X-ray diffractometer (XRD, Rigaku Rotaflex D/MAX System) with monochromatic Cu target (λ=0.1541

*Corresponding author: hongsj@keti.re.kr, hanji@dongguk.edu
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nm), and energy dispersion spectrospcopy (EDS). Also, Al was deposited on glass substrate by using sputtering with condition of 300 W and 60 sccm of Ar. The Al surface was observed by microscope and sheet resistance was measured by 4 point probe.

3. Results and Discussion

Thermal behavior of the IZTO precursor is shown in Fig. 1. The weight of the precursor decreases to 50% at around 300°C. At similar temperature, the exothermic reaction is observed. This is attributed to thermal decomposition of the organic component out of the precursor. That is, the organic component is burnt out of the In, Zn and Sn above the temperature. From the thermal analysis, the heating temperature is expected as 300°C. Thus, the heating temperature of the IZTO precursor was determined as 300°C.

After heat-treatment, crystal structure of the IZTO nanoparticles was observed with X-ray diffraction method. As seen in Fig. 2, the detected peaks of the IZTO nanoparticles were corresponded with that of crystallized ITO. That is, in spite of reduction of In,

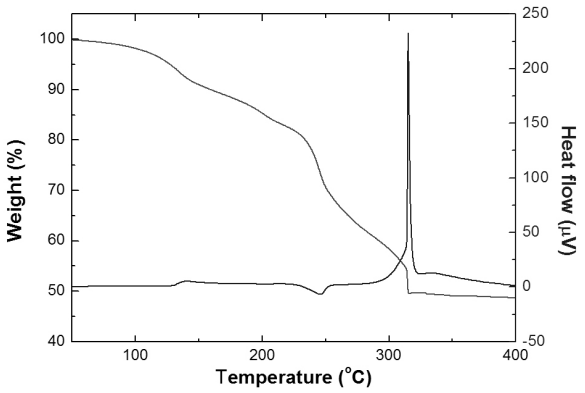

Fig. 1. Thermal analysis of IZTO precursor

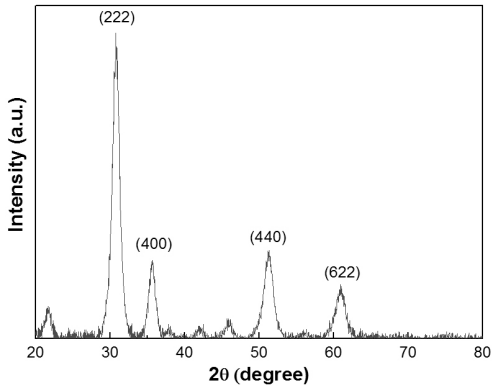

Fig. 2. X-ray diffracted patterns of IZTO nanoparticles after heat-treatment at 300°C

the crystal structure was rarely affected.

From the figure, very intense peak was found at the three most important peaks of In_2O_3 namely <222>, <400>, <440> reflections. In case of (811) sample, the main peaks due to ZnO at 35.6° 2θ and SnO_2 at 26.5° were absent in the observed pattern, indicating complete miscibility of In, Zn and Sn in the proposed composition[3]. That is, in ITO material, Sn is tetravalent, each Sn^{4+} replacing In^{3+}, thereby, donating a free electron for the conductivity in the process[4]. Similarly, it is assumed that each of Zn^{2+} and Sn^{4+} substituted In^{3+} in the lattice structure. In contrary, in case (622) sample, peaks of ZnO and SnO_2 are slightly observed as well as the main peaks of IZTO. It is attributed to precipitation of secondary phases from the crystalline IZTO nanoparticle as the solid contents are over the solubility limit[4]. Also, full width half maximum (FWHM) of the peak was increased as the heating temperature is lowered. It means that the size of the IZTO nanoparticle heated at lower temperature was decreased according to the Scherrer's equation[5]. From the X-ray diffraction peak, particle size can be calculated by using Scherrer's formula as;

$$t = 0.9\lambda / B \cos \theta_B \quad (1)$$

where t, λ, B, and θ_B are particle size, wavelength (0.1542 nm for CuK_α radiation), FWHM of a peak in radians and diffracted angle, respectively. In equation (1), the intensity peak increases along with a reduction in the peak half width indicating the growth of IZTO particles. So, as the FWHM is widened, the size of the particle is smaller. In case of specific surface area (SSA), the SSA of the IZTO nanoparticles after heat-treatment at 300°C are about 90 m^2/g. The particle size is calculated from the SSA as follows;

$$D = 6 / \rho \cdot d \quad (2)$$

where D, ρ and d are particle size, SSA and density, respectively. The calculated average particle size after heat-treatment at 300°C is 9.3 nm. It is guessed that the growth of nanoparticle was suppressed at low temperature. That is, the low SSA is attributed to particle growth with the heating temperature. One of mechanisms to increase the nanoparticle size is owing to mainly particle surface migration[6]. According to the transformation kinetics;

$$D = \exp(-Q/kT) \quad (3)$$

where D, Q, k and T are particle size, activation energy for particle surface migration, Boltzmann constant and heating temperature, respectively. As the activation energy for particle growth becomes high at constant particle size, the surface activity of IZTO nanoparticle as a function of its temperature becomes low. Therefore, it is confirmed that the lower temperature is required in order to synthesize a smaller sized nanoparticle. For certifying the size of ITO nanoparticle synthesized at 300°C, the particle was observed with HRTEM. As a result, seen in Fig. 3, the size of the IZTO nanoparticles was around 10 nm.

Also, the composition ratio of In, Zn and Sn, analyzed by using EDS, selecting five points of the particles for investigating the distributed state of Zn^{2+} and Sn^{4+} in the IZTO nanoparticle. Uniform distribution is very important since, in nanocrystalline systems, the additives should be exactly distributed in the matrix particles different from bulk state. If segregated distribution occurs, the In_2O_3, Zn^{2+} and Sn^{4+} particles are separated, and the characteristics of IZTO as transparent conductive oxide will be degraded. As a result of analysis, shown in Fig. 4, the distributions of Zn^{2+} and Sn^{4+} in the IZTO nanoparticle were within 8.0 ~ 8.8 and 12.0 ~ 13.2 wt%, respectively. That is, uniformly distribution of the maximum deviation between 2.1 wt% was achieved. Such distribution is owing to uniform mixing of the precursor among the elements, That is, all the elements were uniformly mixed when the IZTO precursors are synthesized followed by heat-treatment at 300°C. It is guessed that the uniform distribution was kept until heat-treatment without migration as though heat-treated at the low temperature. Accordingly, well-crystallized ultrafine IZTO nanoparticle with good uniformity could be synthesized at 300°C.

Finally, Al deposited on glass substrate by sputtering is shown in Fig. 5. Al was uniformly deposited on the glass substrate. Defect such as pore is not found. The adhesion was also good. That is, after tape test, no pelt-off part was observed. As well, seen in Fig. 6, sheet resistance was very uniform. The average of

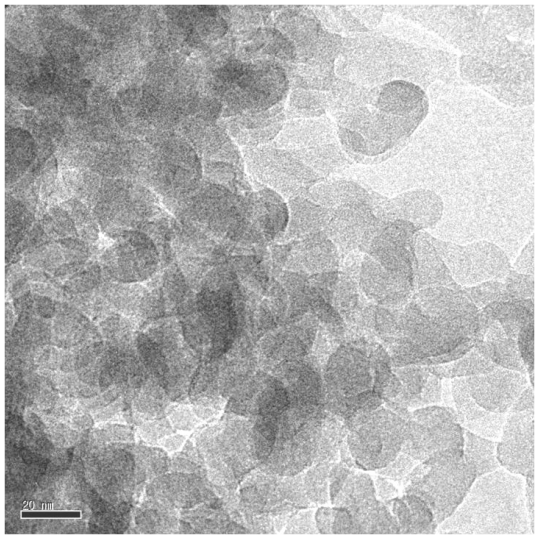

Fig. 3. HRTEM observation of IZTO nanoparticles

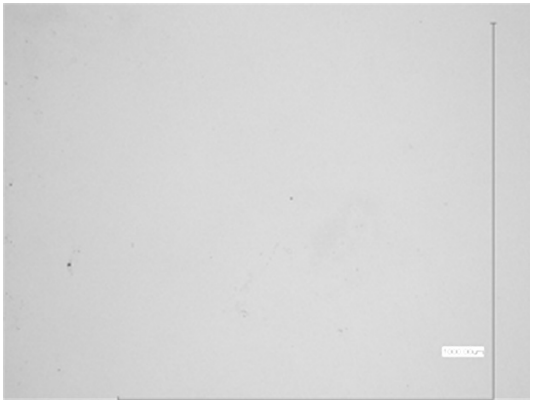

Fig. 5. Al surface deposited on glass substrate (observed by using microscope)

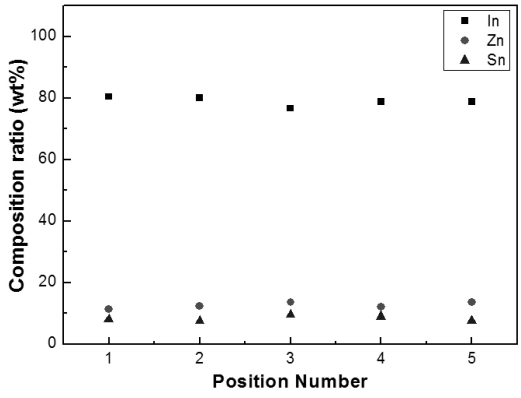

Fig. 4. Composition ratio of IZTO nanoparticles

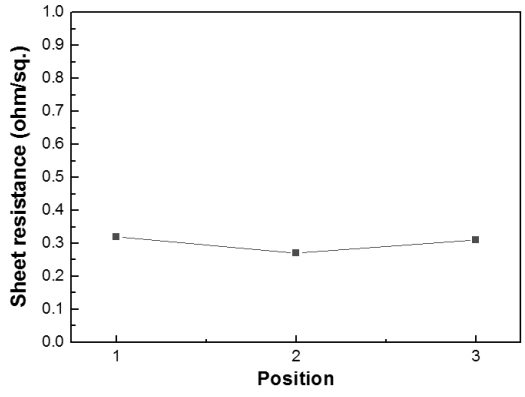

Fig. 6. Sheet resistance of Al layer at different position

sheet resistance was 0.3 Ω/□. Also, the deviation of the sheet resistance was only 0.025 Ω/□.

Those results are attributed to good pre-treatment of glass substrate followed by good sputtering of Al onto the pre-treated surface area. Thus, it is expected that mesh will be patterned well, and good architecture of Al mesh will be formed with good optical properties. Also, if the mesh is combined with ink coated layer which is consistent of IZTO nanoparticle, the reliability of the mesh will be enhanced.

4. Conclusions

In this paper, indium reduced materials for TCE, IZTO and Al, were fabricated. Size of the synthesized IZTO nanoparticles were less than 10 nm, and specific surface areas were about 90 m^2/g. Also, the IZTO nanoparticles were well crystallized with (222) preferred orientation despite it was synthesized at the low temperature of 300°C. Composition ratios of In, Zn and Sn were very uniform in accordance with those as designed. In case of metal for mesh architecture, Al was deposited well onto glass by sputtering. No pore was observed from the Al surface, and adhesion of the Al layer on the glass was well without any peel off by tape test. The sheet resistance of Al on glass was about 0.3 Ω/□ with small deviation of 0.025 Ω/□.

Acknowledgments

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