Indium Tin Oxide (ITO) Thin Film Fabricated by Indium-Tin-Organic sol with ITO Nanoparticle at Low Temperture

Sung-Jei Hong, Sang-Gweon Chang, and Jeong-In Han*
Information Display Research Center, Korea Electronics Technology Institute,
68 Yatap, Bundang, Seongnam, Gyeonggi, Korea
***Epixon Co., Ltd., 111-7 Guon, Gweonseon, Suwon, Gyeonggi, Korea**
Phone: +82-31-789-7260, E-mail: hanji@keti.re.kr

Abstract
In this work, indium tin oxide (ITO) thin film was fabricated by indium-tin-organic sol including ITO nanoparticle. ITO nanoparticle showed ultrafine size about 5 nm and (222) preferred crystal structure. Also, ITO sol-gel thin film showed good optical transmittance over 83% and electrical resistance less than $7 \times 10^3\ \Omega$.

1. Introduction
Indium tin oxide (ITO) thin film has attracted interest because of its characteristics of high optical transmittance over the visible wavelength region, and excellent adhesion to the substrate. Among several coating methods of the ITO film such as sputtering, electron beam evaporation, thermal evaporation, chemical vapor deposition, sol-gel coating method attracts recently [1]. The sol-gel coating method has advantages of low cost process, easy control of composition ratio, etc. However, electrical properties of the sol-gel thin film are not good. In order to solve this disadvantage, M. Toki et al. [2] suggested a dip coating method of ITO film by sol-gel including ITO particle. The role of the ITO particle is to promote the crystallization of the amorphous ITO gel. However, the particle size of 34 nm in their work is very large because it was synthesized at the high temperature above 600^{o}C, which is required to remove the chloride of the raw materials. Moreover, sol solutions including chloride component requires heat-treatment with higher temperature above 700^{o}C to remove the chloride [3]. The glass substrate is damaged by the high temperature while heat-treating the sol-gel thin film.

So, in order to lower the heat-treating temperature, ITO sol including organic component instead of chloride was attempted to synthesize. Also, ultrafine ITO nanoparticle of which size is smaller than 10 nm was made into the ITO sol-gel thin film. The process temperature does not exceed 300^{o}C by the exclusion of chloride ions from the synthetic materials. The ITO sol-gel thin film was fabricated on the glass substrate, and the optical transmittance and electrical resistance was characterized.

2. Experimentals
ITO nanoparticles were designed to dope 10wt% SnO_2 onto In_2O_3, and synthesized under 300^{o}C. The particle size, composition ratio, specific surface area, and crystal structure of the synthesized ITO particles were analyzed by means of BET surface analyzer and X-ray diffractometer, respectively. The ITO nanoparticles were included into ITO sol in order to coat ITO sol-gel thin film by spin coating. The ITO sol was made using organic solution in which indium and tin acetic reagents were dissolved. The mixture of ITO sol and nanoparticle was spin coated on glass substrate of which area and thickness were 7×7 cm and 0.1 mm, respectively. After coating, the ITO thin film was characterized by measuring the optical transmittance and electrical resistance.

3. Results and Discussion
ITO precursor was synthesized by using the acetic raw material, and it was heat-treated at 300^{o}C. Also, for comparison, the precursor was heat-treated at higher temperature of 400^{o}C, 500^{o}C, and 600^{o}C, respectively. The specific surface areas (SSA) of the samples were measured, and the results are shown in Fig. 1. The SSA of ITO nanoparticle heat-treated at 300^{o}C is 117 m^2/g. However, in cases of the samples heat-treated at higher temperature of 400^{o}C, 500^{o}C, and 600^{o}C, SSA is decreased to 82 m^2/g, 50 m^2/g, and 23 m^2/g. The decrease of SSA means the particle growth. The particle heat-treated at 600^{o}C is

coarsened to 5 times of that heat-treated at 300°C. It is owing to grain boundary migration based on diffusion. The lower temperature is required in order to synthesize a smaller sized nanoparticle, and 300°C seems to be an appropriate temperature for the nanoparticle.

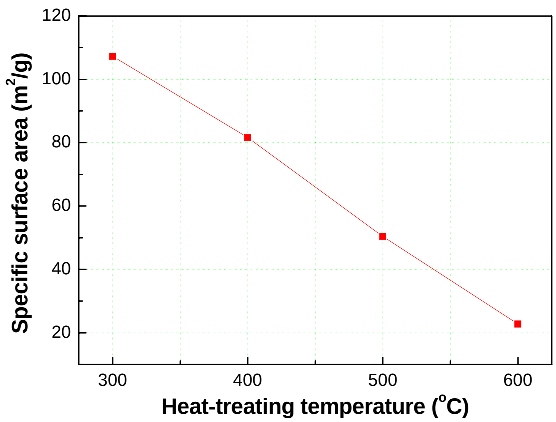
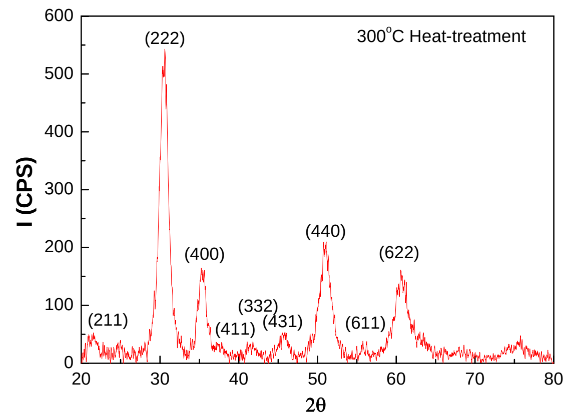
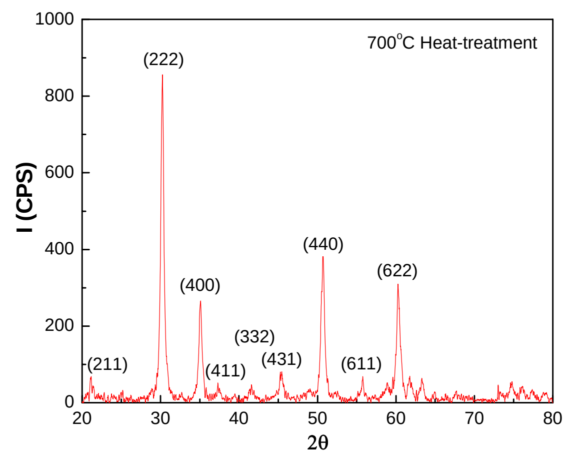


Fig. 1. Specific surface area of ITO nanoparticle according to heat-treating temperature

Then, the crystal structure of the ITO nanoparticle heat-treated at 300°C was analyzed with X-ray diffraction method. Also, for comparison, the ITO sample heat-treated at 700°C was analyzed in the same way. As seen in Fig. 2 (a), the detected peak of the nanoparticle was corresponding with that of crystallized ITO. That is, very intense peak was found at the three most important peaks of In_2O_3 namely <222>, <400>, <440> reflections. The peaks do not deviate from the PDF intensities, implying random non-oriented arrangement of the ITO particles. The major peaks due to SnO_2 at 26.5° and SnO at 33.2° 2θ were absent in the observed pattern, indicating complete miscibility of In and Sn in the proposed composition [4]. It is known that in ITO material, Sn is tetravalent, each Sn^{4+} replacing In^{3+} substitutionally, thereby, donating a free electron for the conductivity in the process. So, the ITO materials retain the cubic In_2O_3 structure up to the solid solubility limit of the SnO_2 in In_2O_3 [5]. Also, compared to ITO particle heat-treated at 700°C (Fig. 2 (b)), full width half maximum (FWHM) of the peak was wider than that of the commercialized ITO particle. It means that the size of the ITO particle heat-treated at lower temperature is ultrafine nanocrystal according to the Scherrer's equation [6]. In the equation, the intensity peak increases significantly along with a reduction in the peak half width indicating the growth of ITO particles. So, as the FWHM is widened, the size of the particle is smaller. Calculation from the FWHM of the XRD peak using the Scherrer's equation shows that size of the ITO nanoparticle heat-treated at 300°C is about 5 nm.



(a) Heat-treated at 300°C



(b) Heat-treated at 700°C

Fig. 2. X-ray diffracted pattern of ITO nanoparticles

Also, we compared the ratio of <622> peak of the orthorhombic structure to <222> peak of cubic structure. The lower ratio means the higher cubic structured nanocrystal. The ratios of 300°C and 700°C heat-treated ITO particle are 0.220 and 0.362, respectively. As mentioned, the ITO particle heat-treated at 300°C shows closer to cubic structure than that heat-treated at 700°C. From the results of XRD and BET surface area, the highly qualified ITO nanoparticle was successfully synthesized by the low temperature synthetic method.

So, including the synthesized ITO nanoparticles into ITO sol, we fabricated ITO thin film on glass substrate by spin coating and heat-treatment at 500°C. The ITO sol was fabricated by dissolving and mixing the calculated amount of organic In and Sn compounds in the solvent. After the fabrication, ITO nanoparticle was added to the sol at room temperature. We attempted spin coating as a fabrication method in this work since currently used dip coating has a disadvantage that the thin film is formed on both sides of the substrate and removal process of the ITO thin film on one side is inevitably added resulting in raise of manufacturing cost. Thickness of the ITO thin film was controlled with spin speed ranging from 500 rpm to 5000 rpm. The ITO sol was spin coated after 1 minute of dispense on the substrate, heat-treated, and ITO thin films with the thickness of 100, 450, and 600 nm were fabricated. The ITO nanoparticle was included with the concentration of 0.2 wt%, 0.4 wt%, and 0.6 wt%, respectively. After fabrication, optical transmittance and electrical properties of the ITO thin film according to the film thickness were characterized. In case of optical transmittance, the wavelength was ranged from 400 nm to 800 nm, the visible range, and the air was regarded as reference. The transmittances of the ITO thin films are seen in Fig. 3. As the film thickness was thinner, the transmittance was raised.

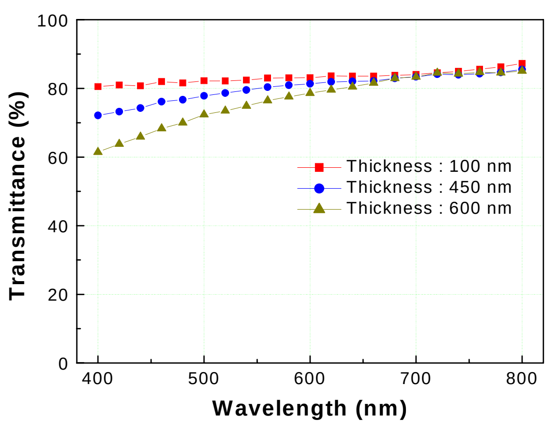


Fig. 3. Optical transmittance of the ITO sol-gel thin film including ITO nanoparticle

The transmittance should exceed 80% in the visible range for good optical properties [7]. As shown in Fig. 4, ITO thin films of which thickness is 100, 450, and 600 nm started to exceed 80% at the wavelengths of 400, 560 and 640 nm, respectively. Since the visible wavelength starts from 400 nm, the 100 nm thick ITO film showed good optical transmittance.

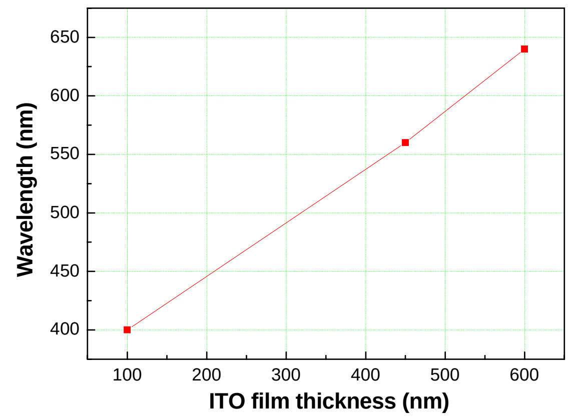


Fig. 4. Wavelength over 80% transmittance according to thickness of ITO sol-gel thin film including ITO nanoparticle

Also, at 600 nm, the central wavelength of the visible range, the 100 nm thick ITO films showed good transmittance. In Fig. 5, 600 nm thick ITO films showed transmittance of 78.6% at 600 nm wavelength. The transmittance rose as the film thickness was lowered at the same wavelength, and good transmittance of 83.1% could be achieved from the 100 nm thick ITO thin film.

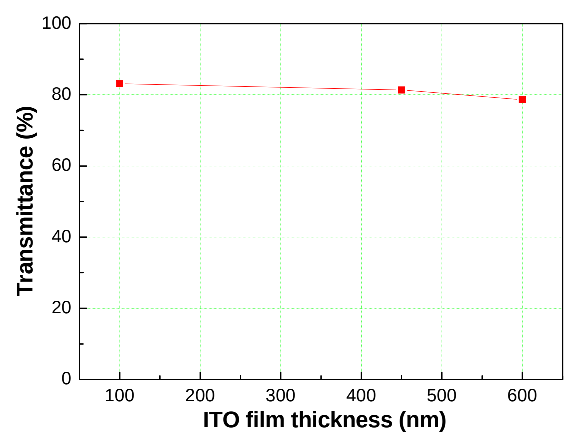


Fig. 5. Transmittance at 600 nm wavelength transmittance according to thickness of ITO sol-gel thin film including ITO nanoparticle

Accordingly, optical transmittance of the ITO sol-gel thin film including ITO nanoparticle could be optimized, and the ITO sol-gel thin film with the thickness of 100 nm was fabricated in order to optimize the electrical properties. Firstly, in order to investigate of heat-treating temperature on the electrical properties, ITO sol-gel thin film without ITO nanoparticle was spin-coated, dried, and heat-treated at 500^{o}C, 700^{o}C, and 900^{o}C, respectively. Then, electrical resistance was measured with 4-point probe method. As a result, shown in Fig. 6, the resistance of the sol-gel thin film was intensively affected by the heat-treating temperature. The resistance of sample heat-treated at 500^{o}C is 7.8 × 10^4 Ω, very high value. As the heat-treating temperature is increased to 700^{o}C, the resistance is decreased to 3.6 × 10^4 Ω. The resistance continues to be lowered to 2.0 × 10^4 Ω when it is heat-treated at 900^{o}C. However, the 700^{o}C and 900^{o}C were so high temperatures that glass substrates were deformed.

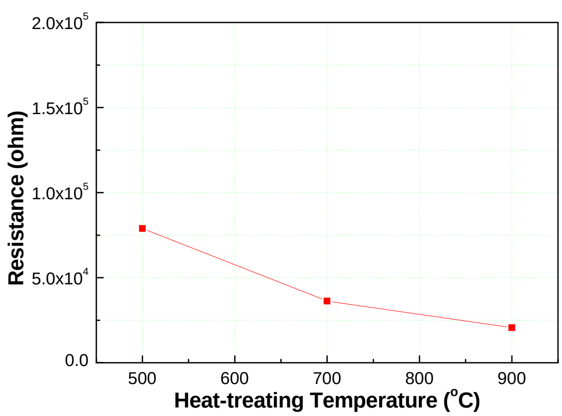


Fig. 6. Resistance of ITO sol-gel thin film according to heat-treating temperature

Therefore, it is important to decrease the resistance with lowered heat-treating temperature, 500^{o}C. So, ITO nanoparticle synthesized at 300^{o}C was included into the ITO sol, and thin film was fabricated at 500^{o}C and characterized in the same way. The ITO nanoparticle was included with concentration of 0.2 wt%, 0.4 wt%, and 0.6 wt%, respectively. As a result, seen in Fig. 7, the resistance of the ITO thin film was decreased as the concentration of ITO nanoparticle was increased. The ITO thin film including 0.2 wt% shows resistance value of 1.8 × 10^5 Ω. It is higher value than that of the ITO thin film without ITO nanoparticle. It is reported that the ITO nanoparticle decrease the resistance of the ITO sol-gel thin film by linking the conductive elements with it [2]. The assumption requires optimal concentration of the particles. If the concentration is either higher or lower than the optimal point, the particle acts as a barrier to inhibit the electrical conduction. Based on the assumption, the concentration of the ITO nanoparticle was increasingly added. As a result, the resistance was lowered. When 0.4 wt% ITO nanoparticle was included, the resistance is decreased to 1 × 10^5 Ω. Moreover, the resistance of the ITO sol-gel thin film including 0.6 wt% ITO nanoparticle showed 7 × 10^3 Ω. The optical transmittance of this film condition shows high value over 83%. It is lower value than that of pure ITO sol-gel thin film heat-treated at 900^{o}C. These phenomena are in accordance with the assumption. That is, as the concentration of the ITO nanoaprticle increased to 0.6 wt%, the conductive elements were linked via ITO nanoparticle. For more obvious mechanism, the more specific analysis should be followed. When the concentration of the ITO nanoparticle was increased, however, the electrical resistance was increased, and optical transmittance was decreased. So, the electrical properties of the ITO sol-gel thin film could be optimized by including 0.6 wt% ITO nanoparticle into the sol.

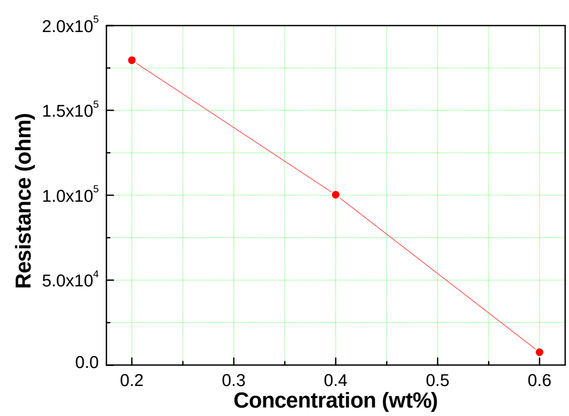


Fig. 7. Resistance of ITO sol-gel thin film with ITO nanoparticle according to concentration of the particle

4. Conclusion

In this work, ITO sol-gel thin film was attempted to fabricate at the low temperature of 500^{o}C by including the ITO nanoparticle into the organic sol. ITO nanoparticle was synthesized at 300^{o}C in order to make ultrafine sized particle. As a result, the ITO nanoparticle with 5 nm, 117 m^2/g, (222), and preferred cubic structure could be synthesized. Also, using the indium-tin-organic sol, highly transparent and conductive ITO thin film could be fabricated with over 83% transmittance and less than 7×10^3 Ω by including the 0.6 wt% ITO nanoparticle into the ITO sol.

5. References

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