Ultrafine ITO Nanoparticle for Ink Jet Printing

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Abstract

Ultrafine Indium tin oxide (ITO) nanoparticle was successfully fabricated by low temperature synthetic method (LTSM). Mean size of ITO nanoparticle is 5 nm, and uniformly dispersed with (222) orientated cubic structure. Using the nanoparticle, ITO thin film with good optical and electrical properties was fabricated by inkjet printing.

1. Introduction

Indium tin oxide (ITO) is widely used for transparent electrode of information display and other electronics. ITO electrode is made by sputtering followed by photolithography and chemical etching. Becuase In is being exhausted in earth, researches are being carried out to decrease the exhausted amount of ITO in the process [1,2]. As an alternative, inkjet printing is intensively paid attention [3]. Inkjet printing is to draw circuit electrode directly onto substrate and, therefore, the ITO material can be considerably saved. The ink is composed of ITO nanoparticle, solvent and additives. In order to achieve uniform thin film from the ink, the ultrafine sized ITO nanoparticle less than 10 nm has to be uniformly dispersed in the ink. However, current wet type synthetic method does not achieve the ultrafine nano-size less than 10 nm because the current process includes Cl and NO_3. High temperature of 700^{o}C is required for eliminating the elements, and size of the particle grows to 60 ~ 80 nm [4,5]. Therefore, lowering the temperature is demanded for the high quality ITO nanoparticle with the smaller size and uniform distribution.

In this work, ultrafine ITO nanoparticle was attempted to be synthesized using low temperature synthetic method (LTSM) to lowering the temperature from 700 to 300^{o}C by excluding the Cl and NO_3. Also, ITO ink was attempted to be formulated using the ultrafine ITO nanoparticle, and inkjet printing was attempted to fabricate ITO thin film.

2. Experimental

ITO nanoparticle was designed to dope 10 wt% SnO_2 onto In_2O_3 lattice, and precursor of ITO was synthesized using In and Sn organic compounds. The precursor was heated at 300^{o}C. Also, ITO nanoparticle was heated at higher temperature than 300^{o}C for comparison. The particle size and crystal structure of the ITO nanoparticle was analyzed by high resolution transmission electron microscope (HRTEM), and X-ray diffractometer (XRD). Also, degree of crystallization of the ITO nanoparticle was examined by the ratio of $I_{(222)}/I_{(622)}$. The $I_{(222)}$ and $I_{(622)}$ are the intensity of the X-ray peak at (222) and (622) direction. The highly crystallized ITO has (222) preferred orientation indicating the cubic structure. Also, in order to investigate the application to inkjet printing, the synthesized ITO nanoparticle was mixed with the solvent to formulate ITO ink. 20 wt% of ITO nanoparticle with small amount of additives was mixed with organic solvent. The formulated ITO ink was filtered with 0.2 μm sized filter, and printed onto glass substrate. After printing, the ITO thin film was evaluated by measuring the optical transmittance and electrical resistance.

3. Results and discussion

ITO nanoparticle synthesized at 300°C is shown in Fig. 1. Mean size of the ITO nanoparticle is 5 nm. The ultrafine size of the nanoparticle is attributed to suppress of particle growth by lowering the heating temperature. One of mechanisms to increase the nanoparticle size is owing to mainly particle surface migration [6]. According to the transformation kinetics;

$$D = \exp(-Q/kT) \qquad (1)$$

where D, Q, k and T are mean particle size, activation energy for particle surface migration, Boltzmann constant and temperature, respectively. When the activation energy for particle growth is decreases at constant particle size, the surface activity of ITO nanoparticle as a function of its temperature increases. Accordingly, the growth of nanopaticle can be suppressed by lowering the heating temperature.

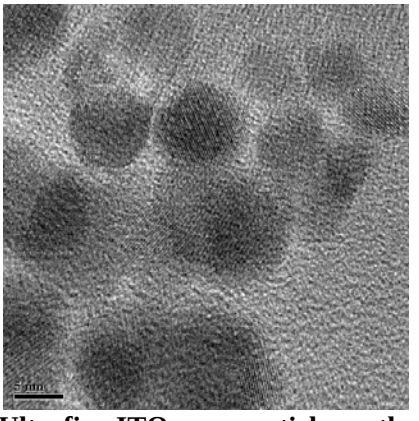

Fig. 1. Ultrafine ITO nanoparticle synthesized by LTSM (HRTEM observation).

Also, as shown in Fig. 2, X-ray diffracted peak of the nanoparticle was corresponding with that of crystallized ITO with three intensive peaks of <222>, <400>, <440>. 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. 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 [7]. Also, particle size was calculated using full width half maximum (FWHM) of the peak based on the Scherrer's equation [8]. From the X-ray diffraction peak, particle size can be calculated by using Scherrer's equation as

$$t = 0.9\,\lambda / B \cos\theta_B \qquad (2)$$

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. Calculation of the particle size from the equation (2) shows that size of the ultrafine ITO nanoparticle is also 5 nm.

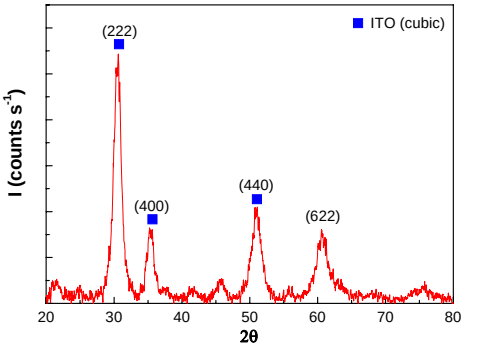

Fig. 2. X-ray diffracted pattern of ultrafine ITO nanoparticle synthesized at 300°C.

As well, as seen in Fig. 3, degree of crystallization decreased as the heating temperature increased up to 500°C. The degree of crystallization slightly increased from 500°C to 600°C. Therefore, the ultrafine ITO nanoparticle heated at 300°C showed the highest degree of crystallization.

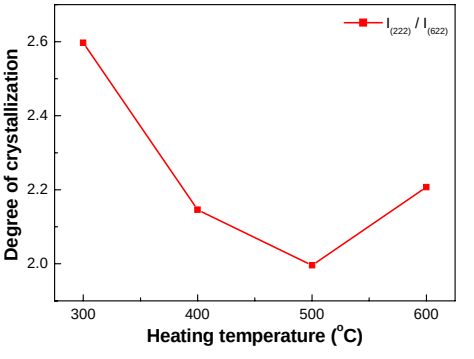

Fig. 3. Degree of crystallization of ITO nanoparticles according to heating temperature.

In order to investigate the feasibility of ITO nanoparticle as a solid material for ink jet printing, ink was attempted to formulate using the ultrafine ITO nanoparticle. As a result, the ITO ink was well formulated. As shown in Fig. 4, the ultrafine ITO nanoparticle was uniformly dispersed in the ink solvent, and the ITO ink was very stable for long time.

Fig. 4. ITO ink formulated using ultrafine ITO nanoparticle.

Then, ink jet printing of ITO thin film was attempted on glass substrate applying the ink material. For ink jet printing, optical transmittance and electrical resistance of the ITO pattern have to be considered carefully for good transparent electrode. Long-term stability of the properties has to be considered. So, as an accelerated evaluation, the inkjet printed ITO thin film was heated at the range of 400°C to 600°C. As a result, ITO thin film was well fabricated by inkjet printing as seen in Fig. 5. The dimension of line is in accordance with the design (0.1 × 1.0 mm). As well, despite of the repeated ink drop for increase of thickness, the sharp line pattern was made without spread of linewidth.

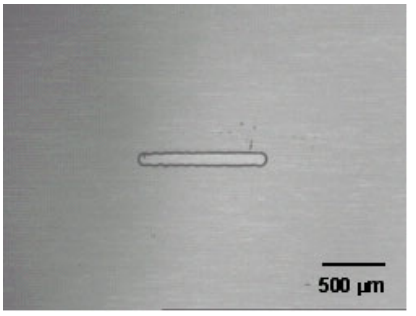

Fig. 5. ITO thin film fabricated by inkjet printing.

After fabrication of the ITO thin films, optical transmittance and electrical resistance 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. 6. All the ITO thin films showed transmittance over 85% at 600 nm, the central wavelength of the visible range. Moreover, despite of increase of heating temperature, the optical transmittance was rarely changed. This is attributed to stability of the physical properties of the printed thin film. That is, particle size and crystal structure of the ITO thin film are so stable that the optical transmittance are rarely changed. Accordingly, optical transmittance of the ITO thin film was turned out to be stable.

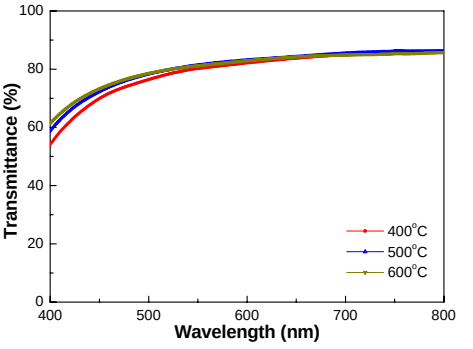

Fig. 6. Optical transmittance of ITO thin film according to heating temperature.

Then, electrical resistance of the ITO thin film was measured. As a result, shown in Fig. 7, the resistance of the ITO thin film was also rarely changed in spite of increase of the heating temperature. That is, all the resistances of the printed ITO thin films were very stable within very narrow range of 4 and 6×10^3 Ω. This is also attributed to stability of the physical properties of the printed thin film. That is, particle size and crystal structure of the ITO thin film are so stable that the electrical resistance are rarely changed. Accordingly, as well as optical transmittance, electrical resistance of the ITO thin film was turned out to be stable. Base on the stability, the electrical resistance of the ITO thin film by inkjet

printing is expected to lower by increasing the concentration of ITO nanoparticle in the ink.

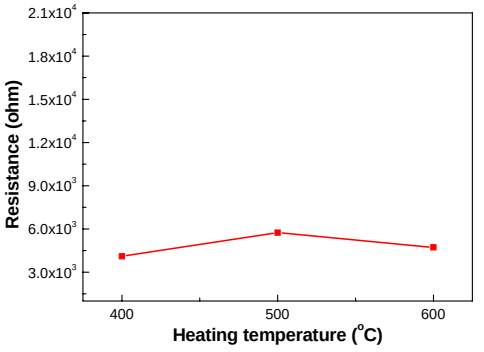

Fig. 7. Resistance of ITO thin film according to heating temperature.

4. Summary

In this work, ultrafine ITO nanoparticle for inkjet printing was successfully fabricated by LTSM. Mean size of ITO nanoparticle is 5 nm and uniformly dispersed. The crystal structure is cubic with (222) preferred orientation. Also, ITO thin film by inkjet printing was successfully made using the ultrafine ITO nanoparticle. ITO thin film was uniformly printed with ultrafine nanoparticle. Such a well-coated thin film reflected the good optical and electrical properties. Therefore, ultrafine ITO nanoparticle for inkjet printing was successfully fabricated using the LTSM.

5. References

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