

Synthesis of InGaZnO₄ nanoparticles using low temperature multistep co-precipitation method



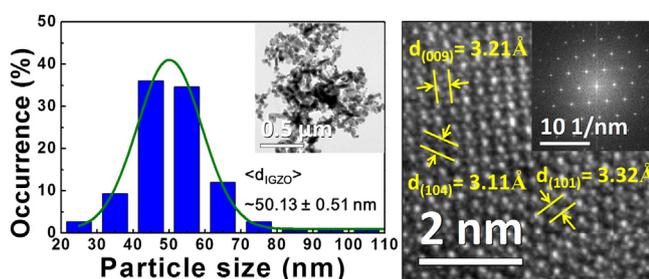
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HIGHLIGHTS

- InGaZnO₄ (IGZO) nanoparticle was synthesized by multistep co-precipitation method.
- The synthesis parameters were controlled precisely to prepare high quality powder.
- The relative density of highly crystalline IGZO tablet is as high as 97.30%.
- IGZO tablet exhibited highly crystalline structure and the large grain size.

GRAPHICAL ABSTRACT



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ABSTRACT

Indium gallium zinc oxide (InGaZnO₄, IGZO) has attracted explosive growth in investigations over the last decades as an important material in the thin-film transistor. In this study, the various nitrate precursors, including indium nitrate, gallium nitrate, and zinc nitrate, were prepared from the various metals dissolved in nitric acid. Then, we used these nitrate precursors to synthesize the IGZO precursor powder by the multistep co-precipitation method. The synthesis parameters of the co-precipitation method, such as reaction temperature, pH value and reaction time, were controlled precisely to prepare the high quality IGZO precursor powder. Finally, IGZO precursor powder was calcined at 900 °C. Then, the microstructure, the crystalline structure, the particle size distribution and specific surface area of calcined IGZO precursor powder were characterized by electron transmission microscopy, X-ray diffraction technique, dynamic light scattering method and the surface area and porosimetry analyzer, respectively. The relative density of IGZO tablet sintered at 1200 °C for 12 h is as high as 97.30%, and it showed highly InGaZnO₄ crystalline structure and the large grain size. The IGZO nanoparticles developed in our study has the potential for the high quality target materials used in the application of electronic devices.

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1. Introduction

Recently, there has been rapidly increasing interest in novel materials as a channel layer in thin-film transistors (TFT) used in

the TFT backplane of flat-panel displays (FPDs) [1–4]. Several of zinc based metal oxide-based materials, such as Cu·ZnO·ZnAl₂O₄, ZnAlSnO, InGaZnO₄, etc [5–7], have been widely studied for application as a channel layer in thin-film transistors. In particular, IGZO exhibits large bandgap and wide controllability of carrier concentrations [8–10], which make it very promising for transparent TFT applications [11–13]. In addition, IGZO can be deposited as a uniform amorphous phase and still exhibit the high carrier

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mobility. Amorphous IGZO could have subgap density of state and tail state originating from structure disorder and defects, which affect carrier transport properties and devices performances [14].

The solution-based process is one of the most promising strategies for obtaining IGZO thin films without the use of vacuum technology [15–19]. Chemical vapor deposition under atmospheric pressure is a unique technique among the usual solution-based methods [20,21]. The solution-based process is suitable for large area deposition and roll-to-roll processing, which represent important techniques with regard to mass and high-speed manufacturing. One of the major challenges in the research field of transparent conducting and semiconducting oxides concerns understanding the defect/doping mechanism responsible for carrier generation in these wide-bandgap materials.

In this study, we propose to introduce the IGZO synthesized by the low temperature multistep co-precipitation method, instead of the solid oxide reaction route that mixes various metal oxides directly. The low temperature multistep co-precipitation method will eliminate the impurity from the mechanical mixing process that uses a ball mill. The IGZO synthesized by the low temperature multistep co-precipitation method can obtain high relative density, high purity and single crystal structure InGaZnO_4 target materials when calcination temperature reached 1100 °C. Our method can reduce the formation temperature of single InGaZnO_4 phase around 200 °C compared with conventional solid state method [8]. The size and crystallinity of the IGZO precursor powders were examined as the function of temperature and synthesis parameters for applications as target. Therefore, the morphology, crystallinity and microstructure of IGZO precursor powders are studied. Here, we demonstrated the IGZO precursor powder that can be used as IGZO target for offering the possibility of the application of TFT backplane of FPDs.

2. Experimental details

The chemicals were used as received without further purification including indium slug (In, 99.995%, Ultimate Materials Technology Co., Ltd.), gallium metal (Ga, 99.99%, Ultimate Materials Technology Co., Ltd.), zinc pellet (Zn, 99.99%, Ultimate Materials Technology Co., Ltd.), nitric acid (HNO_3 , 65%, Panreac) and sodium hydroxide (NaOH , >97%, Fisher Chemical).

The various nitrate precursors, including indium nitrate ($\text{In}(\text{NO}_3)_3$), gallium nitrate ($\text{Ga}(\text{NO}_3)_3$), and zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), were prepared before the co-precipitation method. At first, In, Ga, and Zn were dissolved with 65.0 wt% HNO_3 . The concentrations of $\text{In}(\text{NO}_3)_3$, $\text{Ga}(\text{NO}_3)_3$, and $\text{Zn}(\text{NO}_3)_2$ used in our study were 2.30 M, 2.85 M, and 3.25 M respectively. 17.62 ml of $\text{In}(\text{NO}_3)_3$, 13.84 ml of $\text{Ga}(\text{NO}_3)_3$, and 12.45 ml of $\text{Zn}(\text{NO}_3)_2$ were transferred into a 250.0 ml three-necked flask to obtain an equal molar ratio of In, Ga, and Zn. Then, 5.0 M NaOH was added to the three-necked flask to precipitate the solution. The reaction temperature was kept below 10 °C during the precipitation process because the rate of nucleation and crystal growth can be reduced at a low temperature. At the same time, the reaction at low temperature can decrease the thermal motion of particles in solution [22,23]. The multistep co-precipitation method controlled the pH value in many steps according to the solubility product constant (K_{sp}) of each compound. In this study, we adopted three steps co-precipitation method to synthesize IGZO precursor powder due to the difference of K_{sp} , such as gallium hydroxide is $\sim 7.28 \times 10^{-36}$, indium hydroxide is $\sim 6.30 \times 10^{-34}$ and zinc hydroxide is $\sim 3.00 \times 10^{-17}$ [24]. In order to confirm the difference between the conventional method and our multistep co-precipitation method, we prepared a reference powder by the conventional method that controlled the pH value approaching to ~ 12.01 . For our multistep co-precipitation method,

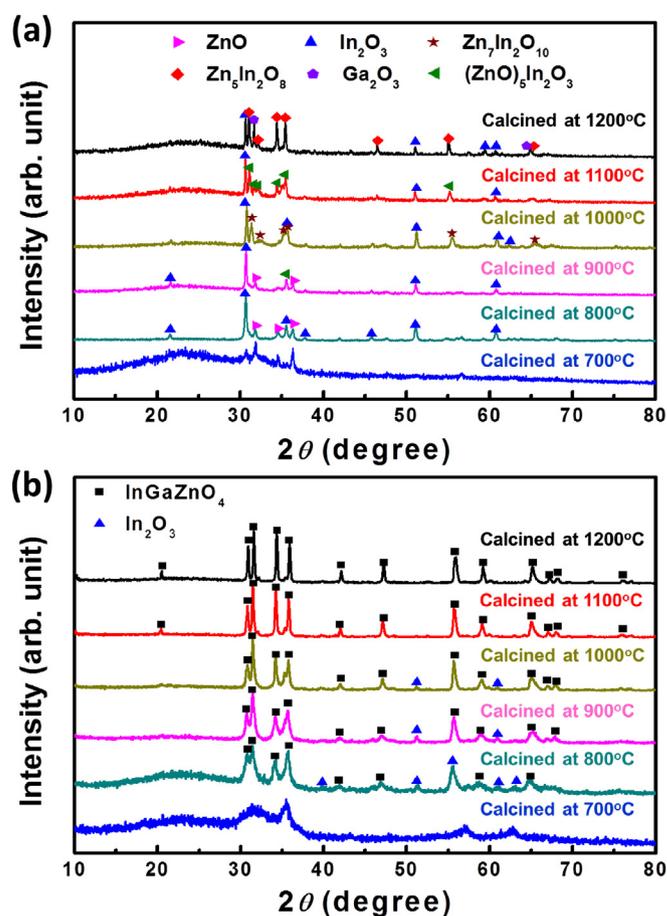


Fig. 1. X-ray diffraction patterns of various precursor powders synthesized in solutions at pH of (a) 12.01 and (b) 8.89, and then, they were calcined in the air at 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C for 1 h at a heating rate of 5 °C/min.

the IGZO precursor powder was carried out as follows. First, NaOH was added until pH value approached ~ 4.88 and was placed for 2 h in order to obtain $\text{Ga}(\text{OH})_3$. In the second step, NaOH was added until pH value reached at ~ 5.35 and was then placed for 2 h to obtain $\text{In}(\text{OH})_3$. Finally, NaOH was added until pH value located in the range from 8.34 to 9.99 and was placed for 2 h. After filtering IGZO precursor powder, it was washed again with deionized water until pH value was close to 7.0. Finally, the IGZO precursor powder was dried at 120 °C overnight.

The IGZO precursor powders synthesized at different pH value were calcined in the air by heating it to different temperature at 5 °C min^{-1} and then kept at the temperature for 1 h to obtain calcined precursor powder. After grinding and sieving, the particle size of the calcined IGZO precursor powders was determined by dynamic light scattering method (3000 HAS Zetasizer, Malvern Instrument), and the specific surface area of the calcined precursor powder is measured by the surface area and porosimetry analyzer (BET, Micromeritics ASAP2000). Moreover, Transmission Electron Microscope (TEM, JEOL, JEM-ARM200FTH, Japan) was used to observe the microstructures of the calcined IGZO precursor powders. Finally, the sintered IGZO tablets were fabricated from the IGZO precursor powders calcined at 900 °C for 1 h. For the tablets, 500 mg of calcined precursor powder was pressed into a disk of 13 mm in diameter under a uniaxial force of 150 kg cm^{-2} for 10 s, and then 350 kg cm^{-2} for 5 min. The IGZO tablets were sintered from 50 °C to various desired temperatures at 900 °C, 1000 °C, 1100 °C and 1200 °C. The temperature was increased at a rate of

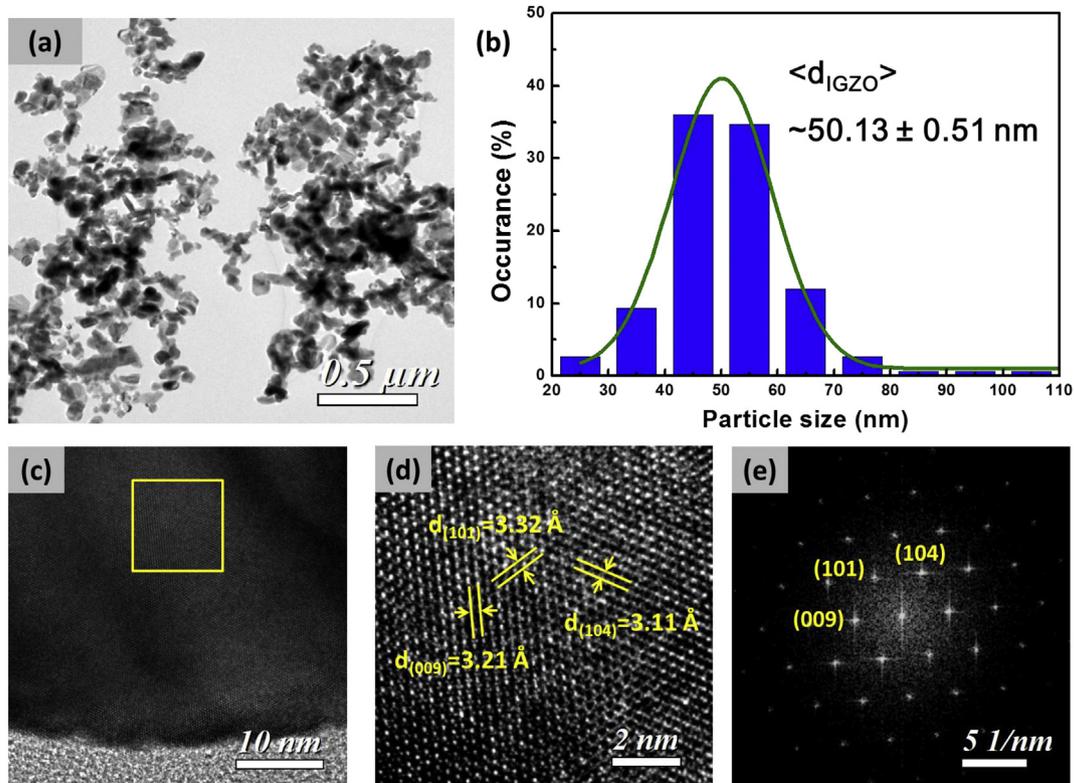


Fig. 2. TEM images of synthesized precursor powder calcined at 900 °C for 1 h at a heating rate of 5 °C/min. (a) The low magnification TEM image, (b) the particle size distribution, (c) the high-resolution TEM image, and (d) its high-magnification of the lattice with (e) the corresponding fast Fourier transformed pattern of this specimen.

3 °C min⁻¹. When the desired temperature was reached, the IGZO tablets were kept at that temperature for various amount of time. At the end of sintering process, the furnace was switched off and the sintered disk was naturally cooled inside the furnace. Finally, the sintered IGZO tablets were examined to obtain their crystal structure, microstructure, theoretical density and chemical composition.

The densities of various sintered IGZO tablets were measured using the Archimedes' method. The crystal structures of various

sintered InGaZnO₄ tablets were determined by X-ray Diffraction Spectrometry (XRD, Bruker, D2 phaser with Xflash 430) using Cu K_α radiation at 50.0 kV and 300.0 mA. XRD patterns were collected from 2θ between 10 and 80 with a 0.005° step at 5° min⁻¹. The surface microstructures of sintered InGaZnO₄ tablets were studied by Scanning Electron Microscope (SEM, SEC SNE-4500M). The molar ratio of In:Ga:Zn in the sintered InGaZnO₄ tablets was estimated by Energy Dispersive X-Ray Spectrometer (EDS, Bruker Quantax EDS with SEM XFlash Detector 410-M). The IGZO tablets sintered at 1200 °C were also identified by Fourier-Transform Infrared Spectrometer (FTIR, Bruker Tensor27). For Raman scattering spectra of the sintered IGZO tablets, the specimens were positioned on a high-resolution piezoelectric stage of Confocal Raman Microscope (WiTec, Alpha300S) and excited by a He–Ne laser of 632.8 nm wavelength (25 mW).

3. Results and discussion

The pH control for the multistep co-precipitation method played an important role. In order to prepare the high-purity IGZO nanoparticles, two kinds of precursor powder were co-precipitated from solutions at different pH of 12.01 and 8.89 respectively. These powders were calcined at 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C, respectively. The calcined powders were investigated with XRD as shown in Fig. 1. For the precursor powder synthesized at pH of 12.01 (Fig. 1(a)), many phases formed with increasing calcination temperatures from 700 °C to 1200 °C [25], including ZnO, In₂O₃, Ga₂O₃, Zn₇In₂O₁₀, (ZnO)₅In₂O₃, Zn₅In₂O₈ and IGZO. The formation of many phases during the calcination process made it difficult to produce the single phase of IGZO. When the pH of co-precipitation was over 9.99, the Zn(OH)₂ could be re-dissolved in the solution and reacted with indium ion. Then, it produced a

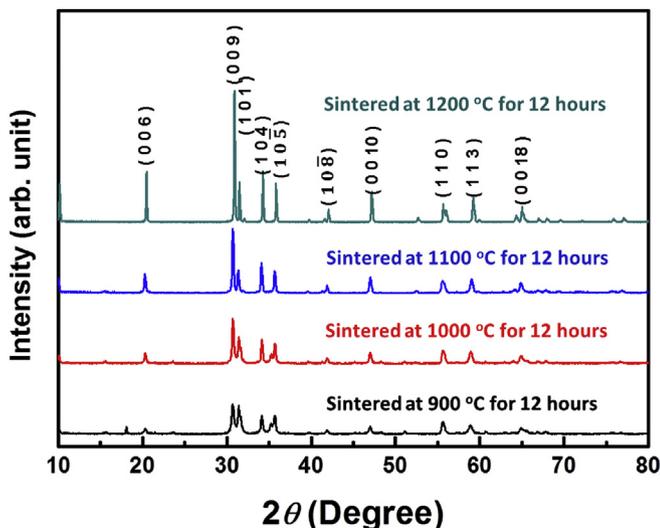


Fig. 3. X-ray diffraction patterns of IGZO tablets sintered at 900 °C, 1000 °C, 1100 °C and 1200 °C for 12 h at a heating rate of 3 °C/min in the air.

Table 1The calculated InGaZnO_4 crystallite size sintered at different temperature and time calculated by Scherrer formula.

Calculated crystalline size (nm)												
Sintering temp. (°C)	900			1000			1100			1200		
Sintering time (hour)	4	6	12	4	6	12	4	6	12	4	6	12
Plane												
(101)	18.1	19.7	20.6	22.1	22.8	28.5	38.8	45.9	46.9	59.4	59.4	60.7
(104)	26.6	27.2	29.1	30.9	33.3	36.5	36.3	44.5	44.9	52.9	53.6	54.0
(009)	18.9	19.8	20.0	25.5	26.3	28.0	37.0	41.8	45.0	52.5	53.0	55.0

precipitate consisting of zinc indium complexes. For the precursor powder synthesized at pH of 8.89 (Fig. 1(b)), IGZO and In_2O_3 were observed with increasing calcination temperatures from 800 °C to 1000 °C. At 1000 °C, a major phase of IGZO combined with a secondary phase of In_2O_3 was found. Finally, the single phase of IGZO was formed when the calcination temperature reached 1100 °C. All reflections can be indexed as the rhombohedral symmetry structure [JCPDS No. 38–1104] [26].

In this study, we chose the synthesized precursor powder calcined at 900 °C to further study because it started to produce single InGaZnO_4 phase and the particle size is smaller than the other precursor powders with higher calcination temperature (>900 °C). TEM images of the synthesized precursor powder calcined at 900 °C are shown in Fig. 2(a), and its particle size is about 50.13 ± 0.51 nm (Fig. 2(b)). Moreover, the particle size distribution of the precursor powders measured by the dynamic light scattering method is about 52.9 nm, which is consistent with the TEM data. In addition, the specific surface area of the calcined IGZO precursor powder is $20.82 \text{ m}^2/\text{g}$ measured by Surface Area and Porosimetry Analyzer. The high-magnification images of the lattice shows that the synthesis parameters and calcination processes were sufficient to form a highly crystalline structure as shown in Fig. 2(c,d), and the corresponding fast Fourier transformed pattern as shown in Fig. 2(e). The (009), (101) and (104) planes are visible with d-spacings of 3.31, 3.32 and 3.11 Å, respectively. From TEM data, it suggests that the multistep co-precipitation method plus

calcination thermal treatment at 900 °C is sufficient to form the highly-crystalline IGZO precursor powder.

In order to prepare the high density and highly crystalline IGZO tablets, a quick screening was carried out to find the optimal sintering temperature. The synthesized precursor powder calcined at 900 °C was pressed to form the tablets and then sintered at various temperatures and for various amounts of time. The relative densities of various IGZO tablets were measured as shown in Fig. S1. The densities of IGZO tablets increased as the sintering temperature and sintering time increased. The IGZO tablets prepared at 1200 °C for 12 h shows the highest relative density and can even reach to 97.30%. It is indicated that the tablets is suitable for future application as sputtering target. The relative density of IGZO disk was calculated based on the theoretical density of 6.38 g cm^{-3} by assuming a rhombohedral symmetry structure with lattice parameters of $a = b = 3.30 \text{ \AA}$, $c = 26.07 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ [26,27].

The crystal structure of IGZO tablets sintered at different temperatures for 12 h in the air was measured by XRD as shown in Fig. 3. The intensity of reflections increased as the sintering temperature increased, indicating better ordering of the lattice of IGZO. With sintering temperature rising up to 1200 °C, single phase of IGZO with a rhombohedral symmetry structure was the only product formed. All reflections can be perfectly indexed as the rhombohedral symmetry structure [JCPDS No. 38–1104] with its lattice parameters of $a = b = 3.35 \text{ \AA}$, $c = 25.62 \text{ \AA}$, $\alpha = \beta = 90^\circ$,

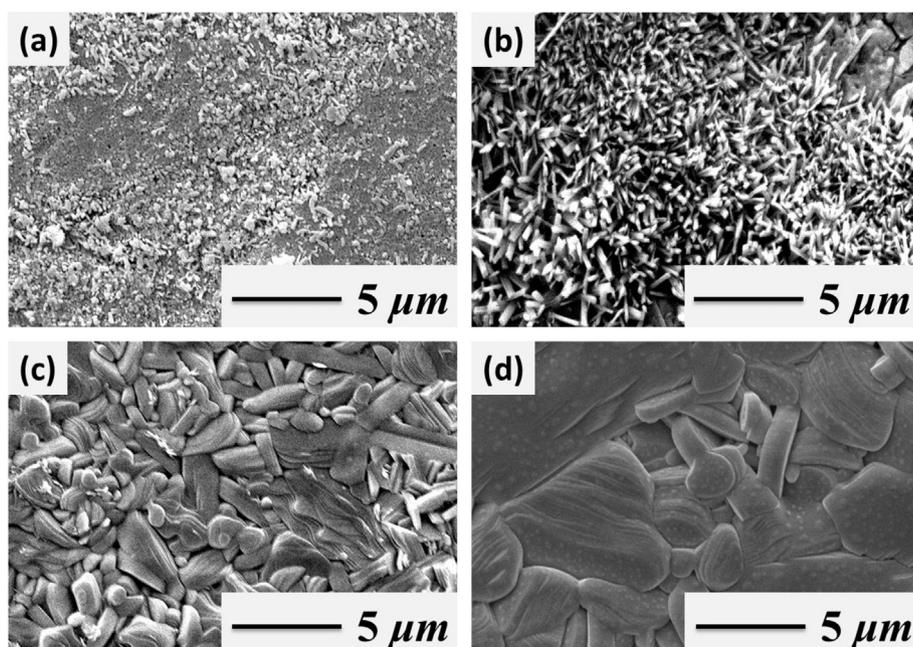


Fig. 4. SEM images of InGaZnO_4 tablets sintered at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C for 12 h at a heating rate of 3 °C/min in the air.

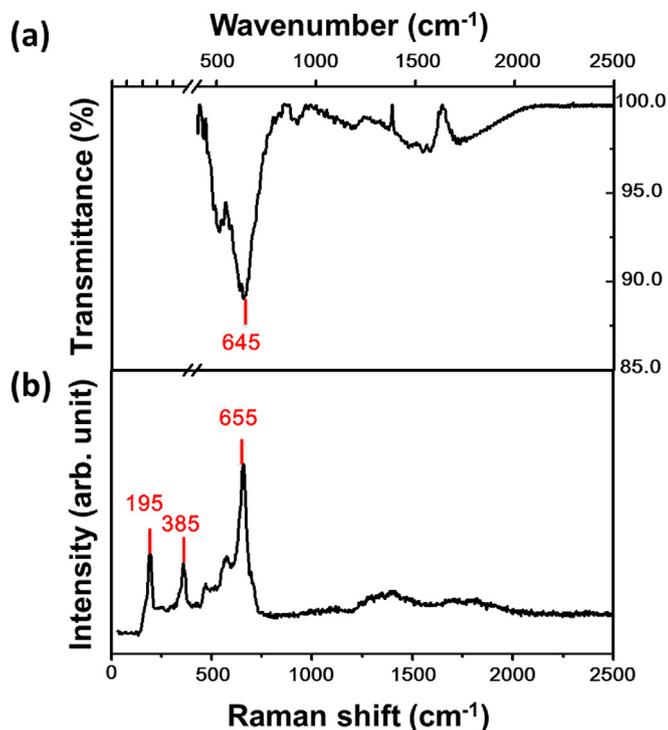


Fig. 5. (a) Fourier transform infrared spectroscopy spectra and (b) Raman spectra of IGZO tablets sintered in the air at 1200 °C for 12 h at a heating rate of 3 °C/min.

$\gamma = 120^\circ$ [26]. Moreover, Scherrer equation is a formula that relates the size of particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern as shown in equation (1),

$$\tau = \frac{K\lambda}{\beta \cos(\theta)} \quad (1)$$

λ is 1.54 Å of the wavelength of X-ray, β is the full width at half maximum of the diffraction peak and K is a constant related to crystallite shape, normally taken as 0.9. The average InGaZnO₄ crystallite size sintered at different temperature and time calculated by Scherrer formula as shown in Table 1. From the results, we can observe InGaZnO₄ crystallite size increased as the sintering temperature and time increased. However, when sintering temperature was up to 1200 °C the sintering time effect became more slightly. Eventually the crystallite size can reach up to 56.54 nm while sintered at 1200 °C for 12 h and the result also reflected the relative density of tablet sintered at the same condition was the highest.

The surface microstructures of IGZO tablets sintered at various temperatures in the air were observed by SEM as shown in Fig. 4. For IGZO tablets sintered at 900 °C, it showed many small IGZO grains. When sintering temperature was at 1000 °C, many submicro-scale rods started to form on the surface of IGZO tablets. For IGZO tablets sintered at 1100 °C, it showed long IGZO grains with size of 1–2 μm. The grain size of IGZO tablets sintered at 1200 °C for 12 h with a heating rate of 3 °C/min in the air is about 3–5 μm. The results indicated that as the sintering temperature increased, the grain size of IGZO tablets were increased and the porosity was decreased. Moreover, the elemental analysis of various IGZO tablets was obtained by Energy Dispersive X-ray Spectrometer, and the elemental analysis for Ga/In and Zn/In of IGZO tablets sintered at various temperatures and for various amounts of time were shown in Table S1. The result indicated that

the chemical composition of IGZO can be controlled by the multi-step co-precipitation method. In addition, energy dispersive X-ray spectrum of InGaZnO₄ tablet sintered at 1200 °C for 12 h is shown in Fig. S2, and it showed no impurity in IGZO tablets.

When the sintered temperature rose above 1200 °C, the crystal phase transformed to InGaZnO₄ completely. The IGZO tablets sintered at 1200 °C were also identified by Fourier-Transform Infrared Spectrometer (FT-IR) and Confocal Raman Microscope equipped with a 632.8 nm He–Ne laser (25 mW). FT-IR spectrum presented major bonding, such as (In, Ga, Zn)–O, that was located at around 645 cm⁻¹ as shown in Fig. 5(a) [28]. Raman spectrum also presented several major Raman bands of M–O vibrations that were located at 195 cm⁻¹, 385 cm⁻¹, and 655 cm⁻¹ as shown in Fig. 5(b) [29]. Raman spectrum and FT-IR spectrum are consistent with the results of XRD data (Fig. 3). In addition, the chemical composition of IGZO tablets was studied by Energy Dispersive X-Ray spectrometer. The molar ratio of In:Ga:Zn in our IGZO tablets sintered at 1200 °C for 12 h is ~1.00:0.92:0.86. The elemental analysis using Energy Dispersive X-Ray Spectrometer is usually biased toward the heavier element. The results indicated that the stoichiometry ratio had no apparent change after thermal treatment at 1200 °C for 12 h. Finally, we have successfully demonstrated the low cost and convenient method to prepare IGZO materials which has potential application as the high quality target materials for the application of TFT backplane of FPDs.

4. Conclusion

In summary, we adopted various nitrate precursors to synthesize the IGZO. These precursors were prepared from metals being dissolved in nitric acid followed by the low temperature multistep co-precipitation method. The uniform IGZO precursor powder calcined at 900 °C for 1 h was prepared successfully and the size of the particles is about 50 nm. After sintering IGZO tablet at 1200 °C for 12 h, the relative density can reach as high as 97.30%. Moreover, from microstructure observation and X-ray diffraction study, it showed the IGZO grain were large and had a high purity. The IGZO materials developed in our study has a potential of the high quality target materials for electronic device application.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.matchemphys.2015.06.003>.

References

- [1] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors, *Nature* 432 (2004) 488–492.
- [2] H. Yabuta, M. Sano, K. Abe, T. Aiba, T. Den, H. Kumomi, K. Nomura, T. Kamiya, H. Hosono, High-mobility thin-film transistor with amorphous InGaZnO₄ channel fabricated by room temperature rf-magnetron sputtering, *Appl. Phys. Lett.* 89 (2006) 112123.
- [3] J.H. Shin, D.K. Choi, Amorphous in-Ga-Zn-O transparent thin-film transistors, *J. Korean Phys. Soc.* 4 (2008) 2019–2023.
- [4] J.C. Moon, Y.S. Shin, G. Lee, Y.C. Leem, H. Ju, S.H. Kim, C.W. Park, Effect of

- oxygen on the optical and the electrical properties of amorphous InGaZnO thin films prepared by RF magnetron sputtering, *J. Korean Phys. Soc.* 53 (2008) 2029–2032.
- [5] M.A. Subhan, T. Ahmed, R. Awal, R. Makioka, H. Nakata, T.T. Pakkanen, M. Suvanto, B.M. Kim, Synthesis, structure, luminescence and photophysical properties of nano CuO·ZnO·ZnAl₂O₄ multi metal oxide, *J. Lumin.* 146 (2014) 123–127.
- [6] Q.J. Jiang, L.S. Feng, C.J. Wu, R.J. Sun, X.F. Li, B. Lu, Z.Z. Ye, J.G. Lu, Amorphous ZnAlSnO thin-film transistors by a combustion solution process for future displays, *Appl. Phys. Lett.* 106 (2015) 053503.
- [7] N. Fukuda, Y. Watanabe, S. Uemura, Y. Yoshida, T. Nakamura, H. Ushijima, In-Ga-Zn oxide nanoparticles acting as an oxide semiconductor material synthesized via a coprecipitation-based method, *J. Mater. Chem. C* 2 (2014) 2448–2454.
- [8] Y.-S. Lee, Z.-M. Dai, C.-I. Lin, H.-C. Lin, Relationships between the crystalline phase of an IGZO target and electrical properties of a-IGZO channel film, *Ceram. Int.* 38 (2012) 595–599.
- [9] A. Takagi, K. Nomura, H. Ohta, H. Yanagi, T. Kamiya, M. Hirano, H. Hosono, Carrier transport and electronic structure in amorphous oxide semiconductor, a-InGaZnO₄, *Thin Solid Films* 486 (2005) 38–41.
- [10] A. Murat, A.U. Adler, T.O. Mason, J.E. Medvedeva, Carrier generation in multicomponent wide-bandgap oxides: InGaZnO₄, *J. Am. Chem. Soc.* 135 (2013) 5685–5692.
- [11] W. Lim, E.A. Douglas, D.P. Norton, S.J. Pearton, F. Ren, Y.-W. Heo, S.Y. Son, J.H. Yuh, Low-voltage indium gallium zinc oxide thin film transistors on paper substrates, *Appl. Phys. Lett.* 96 (2010) 053510.
- [12] Y.S. Rim, H.S. Lim, H.J. Kim, Low-temperature metal-oxide thin-film transistors formed by directly photopatternable and combustible solution synthesis, *Appl. Mater. Interfaces* 5 (2013) 3565–3571.
- [13] Y.H. Kang, T.I. Lee, K.-J. Moon, J. Moon, K. Hong, J.-H. Cho, W. Lee, J.-M. Myoung, Observation of conductive filaments in a resistive switching nonvolatile memory device based on amorphous InGaZnO thin films, *Mater. Chem. Phys.* 138 (2013) 623–627.
- [14] K. Nomura, T. Kamiya, H. Yanagi, E. Ikenaga, K. Yang, K. Kobayashi, M. Hirano, H. Hosono, Subgap states in transparent amorphous oxide semiconductor, In-Ga-Zn-O, observed by bulk sensitive X-ray photoelectron spectroscopy, *Appl. Phys. Lett.* 9 (2008) 202117.
- [15] C.-Y. Tsay, T.-T. Huang, Improvement of physical properties of IGZO thin films prepared by excimer laser annealing of sol-gel derived precursor films, *Mater. Chem. Phys.* 140 (2013) 365–372.
- [16] E. Luévano-Hipólito, A.M. Cruz, E.L. Cuéllar, Synthesis, characterization, and photocatalytic properties of γ -Bi₂MoO₆ prepared by co-precipitation assisted with ultrasound irradiation, *J. Taiwan Inst. Chem. E.* 45 (2014) 2749–2754.
- [17] Z.L. Luo, M.L. Lu, J. Bao, W.H. Liu, C. Gao, Co-precipitation synthesis of gadolinium gallium garnet powders using ammonium hydrogen carbonate as the precipitant, *Mater. Lett.* 59 (2005) 1188–1191.
- [18] C. Jung, M.S. Choi, K.H. Choi, D.H. Yoon, Controllable crystallinity of synthesized In-Ga-Zn-O nano-powder by using a pulp precursor for printing processes, *Phys. Status Solidi A* 207 (2010) 1680–1683.
- [19] C.-Y. Tsay, T.-T. Huang, Improvement of properties of IGZO thin film prepared by excimer laser annealing of sol-gel precursor thin film, *Mater. Chem. Phys.* 140 (2013) 365–372.
- [20] D.H. Kim, D.H. Lee, S.B. Yoon, J.N. Jang, M.P. Hong, Low-temperature fabrication (<150°C) of amorphous IGZO TFTs via high density CVD and superimposed rf/dc magnetron sputtering, *Curr. Appl. Phys.* 12 (2012) 48–51.
- [21] S. Kwon, J.H. Noh, J. Noh, P.D. Rack, Quantitative calculation of oxygen incorporation in sputtered IGZO films and the impact on transistor properties, *J. Electrochem. Soc.* 158 (2011) H289–H293.
- [22] F. Schüth, M. Hesse, K.K. Unger, *Handbook of Heterogeneous Catalyst*, 2008, pp. 100–109.
- [23] W.D. Callister, D.G. Rethwisch, *Material Science and Engineering*, ninth ed., 2014, pp. 385–426 (Asia).
- [24] J.G. Speight, *Lange's Handbook of Chemistry 70th Anniversary Edition*, 8.7–8.17, 2005.
- [25] T. Moriga, D.D. Edwards, T.O. Mason, Phase relationships and physical properties of homologous compounds in the zinc oxide-indium oxide system, *J. Am. Ceram. Soc.* 81 (1998) 1310–1316.
- [26] C. Chen, K.-C. Cheng, E. Chagarov, J. Kanicki, Crystalline in-Ga-Zn-O density of states and energy band structure calculation using density function theory, *Jpn. J. Appl. Phys.* 50 (2011) 091102.
- [27] Z.C. . Feng, *Handbook of Zinc Oxide and Related Materials*, vol. 2, CRC Press, Boca Raton, 2013, pp. 500–504.
- [28] K. Nomura, T. Kamiya, H. Hosono, Effects of diffusion of hydrogen and oxygen on electrical properties of amorphous oxide semiconductor, in-Ga-Zn-O, *J. Solid State Sci. Technol.* 2 (2013) 5–8.
- [29] Q.-L. Chen, L.-J. Qi, J.-Z. Chen, Raman spectrum study on turquoise, *Spectrosc. Spect. Anal.* 29 (2009), 406–409(4).