JMSAE
Journal of Materials Science and Applied Energy

A study of annealing temperatures on electrical conductivity and optical properties of nanostructure ITO film as deposited by ion assisted e-beam evaporation

Peerapong Nuchuay[a, *], Chinoros Laongwan[a], Wimol Promcham[a],
Athorn Vora-ud[b], Saksorn Limwichean[c], Mati Horprathum[c]

[a] Program of Industrial Electrical conductivity Technology, Faculty of Science and Technology, Suratthani Rajabhat University, Mueang, Surat Thani, 84100 Thailand
[b] Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Mueang, Sakon Nakhon, 47000 Thailand
[c] National Electronics and Computer Technology Center, Pathum Thani, 12120 Thailand

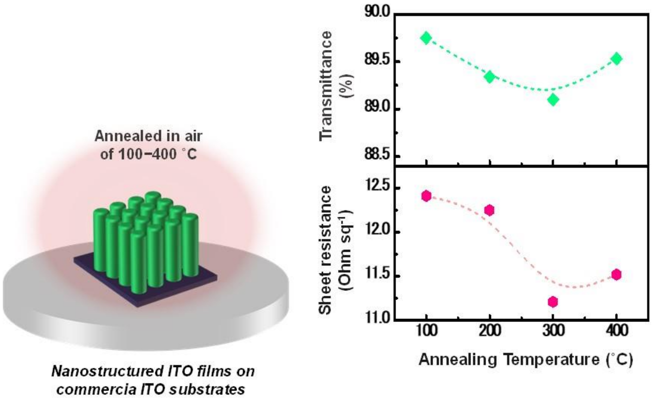
***Corresponding Author:** peerapong.nuc@sru.ac.th

https://doi.org/10.55674/jmsae.v11i2.244615

Received: 18 June 18 2021 | **Revised:** 12 July 2021 | **Accepted:** 27 April 2022 | **Available online:** 1 May 2022

Abstract

In this research, the electrical and optical properties of nanostructured Indium Tin Oxide (ITO) films were investigated. The ITO films were deposited by ion assisted e-beam evaporation with the glancing angle deposition (GLAD) technique on commercial ITO substrates, followed by annealing treatment. The results of crystal structure showed that the nanostructured ITO films are polycrystalline and cubic bixbyite structure (222). The sheet resistance and average transmission at the visible region were 12.17 Ω sq^{-1} and 89 %, respectively. The films presented the lowest resistivity and good transparency, where the sheet resistance and an average transmittance were 11.21 Ω sq^{-1} and 91% after annealing. The omnidirectional characteristics for a wide range of incident angle (0 − 80°) of nanostructured ITO film which was annealed at 300 °C had higher optical transmission than films without annealing. This work eventually proved that the plasma treatments have effectively promoted the performance of the dye-sensitized solar cells and confirmed their potentials in the real-world applications.



Keywords : Nanostructured ITO; Anneal treatment; Ion assisted E-Beam evaporation

© 2022 Center of Excellence on Alternative Energy reserved

Introduction

Transparent conducting oxides (TCO) are the most widely used as front optoelectronic devices such as solar cells, flat panel displays, and light-emitting devices[1 – 6]. Most commonly used TCO films are aluminum-doped zinc oxide (AZO), fluorine-doped tin oxide (FTO), and indium tin oxide (ITO). Among them, ITO film is one of the most widely used materials for TCO film because of its unique properties such as highly degenerate n-type material with an optical bandgap of 3.50 − 4.30 eV, good electrical conductivity, high optical transparency, and long-term stability [8 − 10]. In addition, the nanostructure ITO films properties showed high optical absorption, enhance antireflection, and low reflective index due to the increasing of randomly diffused light of surface-to-volume ratios [10 – 12]. However, the way of increasing electrical conductivity and optical transparency of ITO film was applied by depositing seed layer indium tin oxide grown, followed by growing ITO films to obtain preferred (222) crystalline orientation in mixed argon and oxygen gas [13]. Additionally, post-deposition annealing treatment of the films was practically used [12]. After post-deposition annealing of ITO film at temperatures higher than 200 °C was effective on the grain size of crystallinity [14], resulting in increasing crystallinity of ITO film. The improvement of the optical and electrical conductivity properties by annealing have been involved with the local ordering of the structure during crystallization and oxygen vacancies creation/annihilation that depends on the atmosphere of annealing systems.

In this report, nanostructured ITO films which were fabricated on commercial ITO (ITO Commercial 11.50 Ω sq^{-1}) and annealing treatment at different temperatures. Therefore, quality of nanostructured ITO films, surface morphology, electrical conductivity, and optical properties have been investigated.

Materials and Methods

Nanostructured ITO films were fabricated on Si wafer (100) and commercial ITO substrates by ion assisted e-beam evaporation with the GLAD technique at range of incident angle of 85° with respect to the substrate normal angle. The commercial substrates coating by ITO were used for characterization of the optical properties. These were chemically cleaned by acetone, isopropyl alcohol and deionized water in an ultrasonic cleaning system. Then, substrates were dried in nitrogen flow. The nanostructured ITO films on Si wafer were used for crystallinity and morphological characterization. Inside the chamber for deposition, the base pressure was 8×10^{-7} Torr, and the working gas oxygen flow rate of 8 sccm was fixed at operated pressure of 1×10^{-5} Torr during deposition to produce low energy oxygen ions. The ion gun current and voltage were fixed at 1 A and controlled at 120 V, respectively. After the deposition, all the prepared samples in the same conditions were separately annealed in the furnace in ambient for about 2 h at temperatures 200, 300 and 400 °C. The film thickness of all samples was fixed as 80 nm by controlling the deposition time. The XRD results of nanostructured ITO films were determined by grazing-incidence X-ray diffraction (KTTRAXIII, Rigaku). The morphological structures were studied by field-emission scanning electron microscope (SU8030, Hitachi). The electrical properties were measured by Four-point-probe (Jandel RM3). Additionally, the optical transmission was conducted using a UV-Vis-NIR spectrophotometer (Cary 7000, Agilent). The light source was performed at a normal incident angle from the film surfaces in the wavelength range from 200 − 2,000 nm for direct transmission measurements. Angle-dependent transmission was measured between 0 − 80° for scattered transmission measurements.

Results and Discussion

The surface and cross section images of nanostructured ITO films on Si wafer are shown in Fig. 1(a) and Fig. 1(b). Fig. 1(a) indicated the surface of the sample (as-deposited: ASD) with increasing annealed temperature at 100, 200, 300 and 400 °C, respectively. The surface morphologies before and after annealing were nearly identical. The results from FE-SEM indicated that the temperature annealing had no

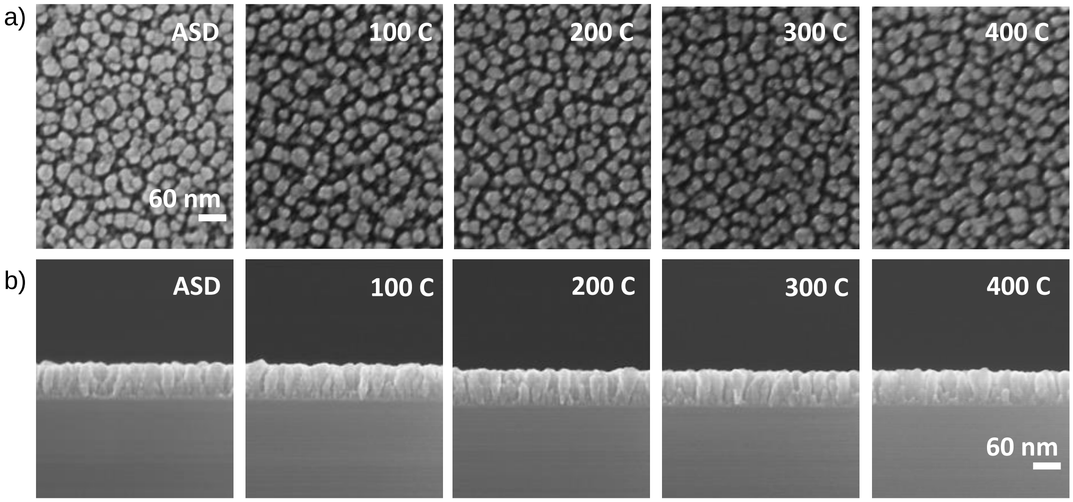


Fig. 1 (a) surface and (b) cross section images of nanostructured ITO films with various annealed temperature in the range of 100, 200, 300 and 400 °C.

effect on ITO nanostructure films. Our results are similar to those reported in literatures [15]. The cross sectional exhibiting a nanostructure of ITO films growth because of the shadowing effect.

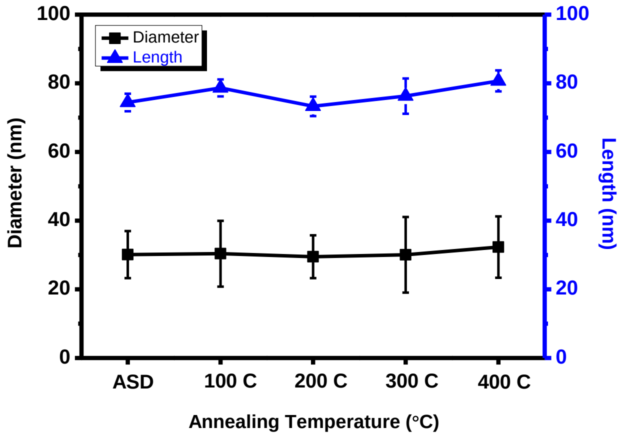


Fig. 2 Diameter and length of nanostructured ASD ITO films and annealed at different temperature in vacuum.

Fig. 2 shows the diameter and length of the nanostructured ITO films. The diameter of nanostructured ITO films annealing at 100, 200, 300, and 400 °C were 30.38, 29.90, 30.06 and 32.28 nm and length were 78.62, 75.29, 76.27 and 80.12 nm, respectively. Both of parameter exhibited a gradual change.

The XRD peaks of the nanostructured ITO films on Si wafer fabricated ASD and annealed at different temperature were shown in Fig. 3 The nanostructured ITO films deposited ASD and annealing at 100 − 200 °C were determined to be amorphous. The annealing at 300 °C, the nanostructured ITO film has revealed the XRD peaks which can be assigned to (211), (222), (400), (440) and (622) planes at 2θ degree of 21.13°, 30.70°, 35.60°, 51.30° and 60.63° respectively, indicating polycrystallinity with a cubic bixbyite structure (JCPDS 01089-4198). The nanostructured ITO films which were annealed at 300 and 400 °C showed a prominently strong (222) peak due to the preferable orientation of the structure at high temperature [13,15]. Moreover, it was observed that the crystallinity of nanostructured ITO film continuously increased with the increased temperature of the annealing temperature [16].

The sheet resistance of samples using four-point probe measurements, as shown in Fig. 4. The as-deposited ITO film was compared to the ITO film followed by annealing of nanostructured ITO films, indicating the sheet resistance of 12.17 Ω sq^{-1} and annealed ITO films were 12.41, 12.25, 11.21 and 11.52 Ω sq^{-1} of annealing temperature at 100, 200, 300 and 400 °C, respectively. The lowest resistivity of 11.21 Ω sq^{-1} was obtained from the film that was annealed at 300 °C, indicating that all annealed samples were acceptable to use as the TCO material for optoelectronic applications.

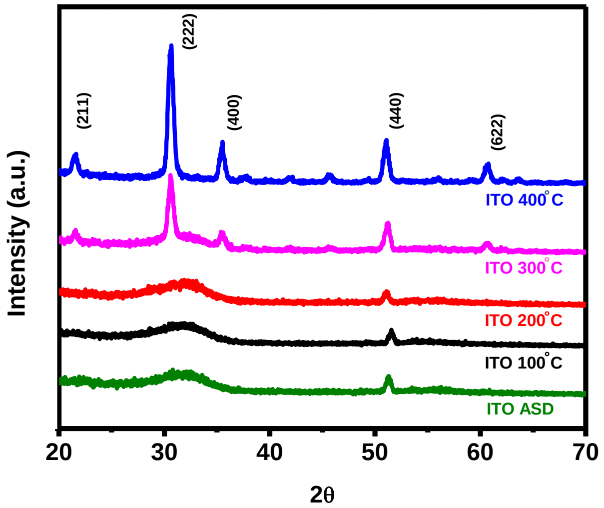


Fig 3. XRD peaks of the different nanostructured ITO films.

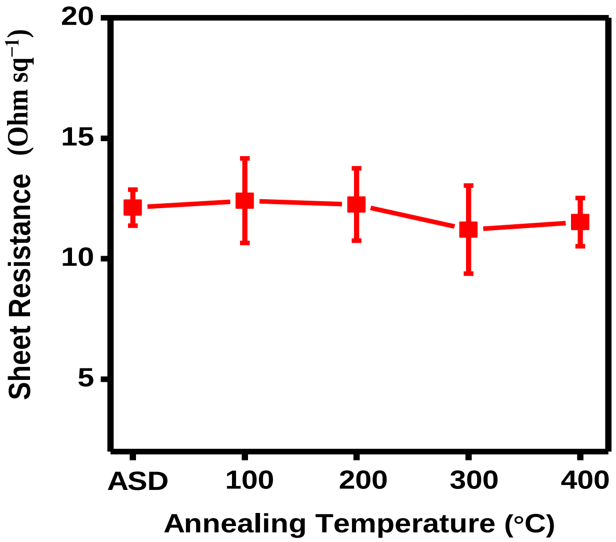


Fig. 4 Sheet resistance of ITO nanostructured films that was measured by four-point probes.

Fig. 5 (a) shows UV-visible light transmittance of nanostructured ITO films on commercial substrates, which were 89.75, 89.34, 89.10 and 89.53% of annealed

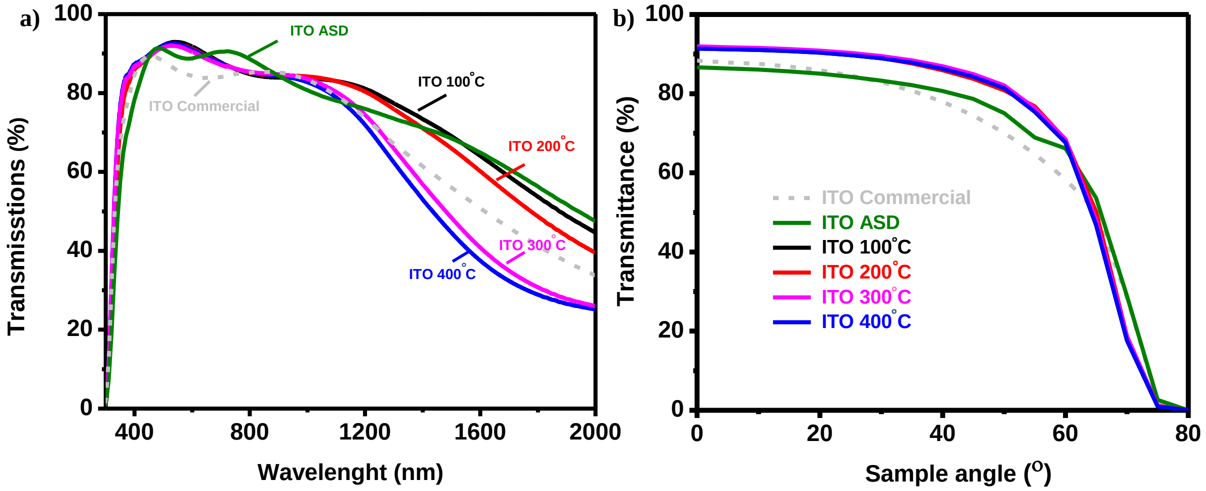


Fig. 5 (a) Optical properties and (b) the omnidirectional anti-reflection characteristics of nanostructured ITO films.

temperature from 100 – 400 °C, respectively. It was found that ITO films showed an average optical transmittance in the visible region (380 − 780 nm) which was higher than commercial ITO.

The omnidirectional anti-reflection characteristics of nanostructured ITO films were shown in Fig. 5(b), at specific wavelength range at 500 nm. The result was similar to those reported in literatures [16], which was a wide range of incident angle (0 − 80°). The graph showing the nanostructured ITO films of annealed temperature from 100 − 400 °C had omnidirectional transmission higher than the commercial ITO reference at all incidence angles due to the performance of the samples were sensitive to the incident angle and the Fresnel reflections from the rear sides [12]. Thus, nanostructured ITO films were applied to antireflection coatings of TCO applications.

Conclusion

Nanostructured ITO films were deposited by ion assisted e-beam evaporation with different temperature of annealing treatment. The crystal structure of nanostructured ITO films was mostly polycrystalline with the cubic bixbyite structure (222). The lowest resistivity of 11.21 Ω sq^{-1}, was obtained from the film that was annealed at 300 °C. The average optical transmittance of 89.75 % in the visible region could be obtained when the optimum temperature of annealing treatment was used. The nanostructured ITO films were found to have better optical properties than commercial ITO. Thus, the annealing treatments effectively promoted the performance of nanostructured ITO film and improved potential of optoelectronic applications.

Acknowledgement

The work was supported by National Electronics and Computer Technology Center (NECTEC) and National Metal and Materials Technology Center, National Science and Technology Development Agency (NSTDA). The authors gratefully acknowledge.

References

[1] J. Du, X. liang Chen, C. chi Liu, J. Ni, G. fu Hou, Y. Zhao, X. dan Zhang, Highly transparent and conductive indium tin oxide thin films for solar cells grown by reactive thermal evaporation at low temperature, Appl. Phys. A Mater. Sci. Process. 117 (2014) 815 – 822.

[2] A. Valla, P. Carroy, F. Ozanne, D. Muñoz, Understanding the role of mobility of ITO films for silicon heterojunction solar cell applications, Sol. Energy Mater. Sol. Cells. 157 (2016) 874 – 880.

[3] S.K. Park, J.I. Han, W.K. Kim, M.G. Kwak, Deposition of indium-tin-oxide films on polymer substrates for application in plastic-based flat panel displays, Thin Solid Films. 397 (2001) 49 – 55.

[4] J. Hotovy, J. Hüpkes, W. Böttler, E. Marins, L. Spiess, T. Kups, V. Smirnov, I. Hotovy, J. Kováč, Sputtered ITO for application in thin-film silicon solar cells:

Relationship between structural and electrical properties, Appl. Surf. Sci. 269 (2013) 81 – 87.

[5] Y. Gil, H. Kim, Hybrid ITO transparent conductive electrodes embedded with Pt nanoclusters for enhanced output efficiency of GaN-based light-emitting diodes, Thin Solid Films. 603 (2016) 307 – 312.

[6] W. Wang, H. Peng, S. Chen, Highly transparent quantum-dot light-emitting diodes with sputtered indium-tin-oxide electrodes, J. Mater. Chem. C. 4 (2016) 1838 – 1841.

[7] C.J.M. Emmott, A. Urbina, J. Nelson, Environmental and economic assessment of ITO-free electrodes for organic solar cells, Sol. Energy Mater. Sol. Cells. 97 (2012) 14 – 21.

[8] Y.S. Park, E. Kim, B. Hong, J. Lee, Characteristics of ITO films with oxygen plasma treatment for thin film solar cell applications, Mater. Res. Bull. 48 (2013) 5115 – 5120.

[9] M. Ismail, A.M. Rana, I. Talib, T.L. Tsai, U. Chand, E. Ahmed, M.Y. Nadeem, A. Aziz, N.A. Shah, M. Hussain, Room-temperature fabricated, fully transparent resistive memory based on ITO/CeO_2/ITO structure for RRAM applications, Solid State Commun. 202 (2015) 28 – 34.

[10] S. Xu, Y. Shi, Low temperature high sensor response nano gas sensor using ITO nanofibers, Sens. Actuators B Chem. 143 (2009) 71 – 75.

[11] X. Li, G.M. Kale, Influence of thickness of ITO sensing electrode film on sensing performance of planar mixed potential CO sensor, Sens. Actuators B Chem. 120 (2006) 150 – 155.

[12] P. Nuchuay, T. Chaikeeree, M. Horprathum, N. Mungkung, N. Kasayapanand, C. Oros, S. Limwichean, N. Nuntawong, C. Chananonnawathorn, V. Patthanasettakul, P. Muthitamongkol, B. Samransuksamer, S. Denchitcharoen, A. Klamchuen, C. Thanachayanont, P. Eiamchai, Engineered omnidirectional antireflection ITO nanorod films with super hydrophobic surface via glancing-angle ion-assisted electron-beam evaporation deposition, Curr. Appl. Phys. 17 (2017) 222 – 229.

[13] D.P. Pham, B.T. Phan, V.D. Hoang, H.T. Nguyen, T.K.H. Ta, S. Maenosono, C.V. Tran, Control of preferred (222) crystalline orientation of sputtered indium tin oxide thin films, Thin Solid Films. 570 (2014) 16 – 19.

[14] P. Canhola, N. Martins, L. Raniero, S. Pereira, E. Fortunato, I. Ferreira, R. Martins, Role of annealing environment on the performances of large area ITO films produced by rf magnetron sputtering, Thin Solid Films. 487 (2005) 271 – 276.

[15] N.M. Ahmed, F.A. Sabah, H.I. Abdulgafour, A. Alsadig, A. Sulieman, M. Alkhoaryef, The effect of post annealing temperature on grain size of indium-tin-oxide for optical and electrical properties improvement, Results Phys. 13 (2019) 102159.

[16] N. Manavizadeh, A. Khodayari, E. Asl Soleimani, S. Bagherzadeh, M.H. Maleki, Structural properties of post annealed ITO thin films at different temperatures, Iran. J. Chem. Chem. Eng. 28 (2009) 57 – 61.