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RESEARCH ARTICLE

ANNEALING TEMPERATURE EFFECTS ON SURFACE MORPHOLOGY AND OPTICAL PROPERTIES OF IGZO THIN FILMS PRODUCED BY THERMAL EVAPORATION

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ABSTRACT

The use of Transparent Conductive Oxide (TCO) thin films in technology has increased in the last decades. These materials have good electrical conductivity visible light transmittance simultaneously. TCOs have many technology applications such as thin film transducers (TFTs), conductive electrodes, capacitors, sensors, electrochemical devices. Although indium tin oxide (ITO) is the most common semiconductor among these materials, studies on N-type indium-gallium-zinc oxide (IGZO) that better electrical properties (electron mobility μFE>10 cm^2 /V.s) cm^2 / Vs) have increased in recent years. In this study, IGZO thin films are produced which have a very homogeneous amorphous structure via using thermal evaporation system on glass substrates. Structural characterization was carried out by atomic force microscopy and scanning electron microscopy on IGZO thin films for various thickness and annealing temperatures. Transmittance and thickness measurements were performed using UV-VIS spectroscopy and profilometer *for the investigation of optical properties, respectively. It is seen that grain size grows and grain boundaries decreases when annealing temperature is increased. This results in reduced roughness and increased optical transmittance and energy gap (Eg).*

Keywords: *IGZO, AFM, Thin Film, Band Energy*.

Annealing Temperature Effects on Surface Morphology and Optical Properties of IGZO Thin Films Produced by Thermal Evaporation

TAVLAMA SICAKLIĞININ TERMAL BUHARLAŞTIRMA İLE ÜRETİLEN IGZO İNCE FİLMLERDE YÜZEY MORFOLOJİSİ VE OPTİK ÖZELLİKLERE ETKİSİ

ÖZ

Saydam İletken Oksit (TCO) ince filmlerin teknolojide kullanımı son yıllarda artmıştır. Bu malzemeler aynı anda iyi bir elektrik iletkenliğine ve görünür ışık geçirgenliğine sahiptir. TCO'lar, ince film dönüştürücüler (TFT'ler), iletken elektrotlar, kapasitörler, sensörler, elektrokimyasal cihazlar gibi birçok teknoloji uygulamasında kullanılmaktadırlar. İndiyum kalay oksit (ITO) bu malzemeler arasında en yaygın kullanılan malzeme olmasına rağmen, daha iyi elektriksel özelliklere (elektron hareketliliği $\mu FE>10\ cm^2/V.s$) cm^2 */ Vs) sahip olan N tipi indiyum-galyum-çinko oksit (IGZO) üzerinde yapılan çalışmalar günümüzde önem kazanmıştır. Bu çalışmada, cam alttaş üzerinde termal buharlaştırma sistemi kullanılarak yüksek vakum altında oda sıcaklığında çok homojen bir amorf yapıya sahip IGZO ince filmler üretilmiştir. Üretilen IGZO ince filmlerin yapısal karakterizasyonu ise Atomik kuvvet mikroskobu ve taramalı elektron mikroskobu kullanılarak çeşitli kalınlık ve tavlama sıcaklıkları için gerçekleştirilmiştir. Geçirgenlik ve kalınlık ölçümleri ise optik özelliklerin araştırılması için sırasıyla UV-VIS spektroskopisi ve profilometre kullanılarak yapılmıştır. Tavlama sıcaklığı arttıkça tanecik boyutunun büyüdüğü ve tane sınırlarının azaldığı görülmektedir. Bu durum, pürüzlülüğün azalmasına ve optik geçirgenliğin ve enerji boşluğunun* (E_g) *artmasına neden olmaktadır.*

Anahtar Kelimeler: *IGZO, AFM, İnce Film, Band Enerjisi.*

1. INTRODUCTION

Transparent Conductive Oxides (TCO's) are materials that have good optical permeability and good electrical conductivity generally. They are mostly composed of special double or triple compounds and contain at least one metallic element. A good TCO has an optical transparency of around 80%, an energy band range of over 3 eV and a low resistivity value of 10-3 Ω.m. These properties can be improved by improving oxygen or by doping different metals to the pure TCO samples. Thus, we can obtain materials with a better optical transparency and electrical properties. As a sample of TCO, Zinc oxide (ZnO) thin films have high optical permeability, electrical conductivity, magnetic - piezo electricity and wide energy band gap (~ 3.4 eV) within this framework. These superior features allow ZnO thin films to be used in the areas of the LCDs, solar cells, thin film transistors and chemical gas sensors [1-8]. ZnO thin films can be produced by different methods such as magnetron sputter, spray pyrolysis and thermal evaporation, [9-15]. Studies on ZnO have shown an increase in the 1990's and its importance has increased with the presence of technological applications nowadays. Metal oxide materials, such as ZnO, have a wide band range of semiconductors in the II-VI semiconductor group, so they do not have sufficient electrical conductivity for technological applications alone. In order to maintain high optical permeability and to create materials with lower resistivity, it is necessary to create correct stoichiometric composition or doping.

Recently, researchers have made metal contributions to ZnO in order to improve electrical conductivity and optical permeability for the further development of technology applications of ZnO thin films. Aluminum-ZnO (AZO), Gallium-ZnO (GZO), Indium-ZnO (IZO) and Indium-Gallium-ZnO (IGZO) thin films are produced in this way. The most important reason for choosing materials such as indium, aluminum and gallium is that the Ionic diameters of these metals are close to the ion diameters of the zinc. Thus, Zn atoms can be replaced within the lattice matrix.

Although doping indium or gallium separately to the ZnO has investigated in the literature, the properties of doping of these two metals together to ZnO are still in the under the research. These type of materials are called

InGaZnO (IGZO). IGZO is a special material that attracts the most attention among the oxide semiconductor materials and also has semiconductor material properties [16-20]. Furthermore, there are technological application possibilities such as high electron mobility (> 10 cm^2 / V.s), reproducibility at room temperature and low temperature devices. Today, IGZO studies have begun to be published and are often focused on the device characteristics and atomic ratio and [19, 21-23]. In addition, in many articles, there are studies related to the annealing temperature of IGZO thin films [24].

In the technological applications of IGZO thin films, there are difficulties in the resistance of films and interfacial problems [22, 24-26].] In order to use these in technology more effectively, detailed investigation of the effects of preparation conditions such as chemical composition (dependence of the doping ratios) and annealing temperature on the samples is needed. One of the world's biggest technology company Sharp is produced crystal oxide semiconductor screen and they have started to use the first IGZO application on the screens in recent years. Smartphones, tablets and touch screens produced within the scope of these products have received awards from many parts of the world [27].

In this study, IGZO films were deposited on Si/SiO and glass substrates via thermal evaporation method [28] at various annealing temperatures. The effect of annealing temperatures on the structural, optical physical and opto-electrical properties of IGZO films was investigated.

2. MATERIALS AND METHOD

Semiconducting IGZO film samples were grown on Si/SiO and glass substrates by a thermal evaporation (Vaksis MİDASm PVD/2T) operating at a base pressure of 5 x 10^{-5} mbar. The typical deposition rates were kept constant at 0.5 nm/s for the samples. The IGZO thin films were prepared onto glass substrates using indium (In), gallium (Ga) and zinc (Zn) metals with the weight ratio of 1:1:1 wt% (In:Ga:Zn). In order to evaporate of metals, a tungsten boat was used for every metal. The glass substrates were cleaned by acetone, distilled water and ultrasonic cleaner. To prepare the IGZO thin film, the indium metal was firstly deposited, then gallium metal was deposited and finally zinc metal was deposited onto glass substrate under 10^{-5} mbar pressure. Five IGZO thin film samples were annealed for thermal oxidation at different temperatures for 1 hour in the program controller muffle furnace (Nabertherm L5 S27). One of the thin film called as deposited (IGZO-AD) which is without annealing, other four thin films were annealed at different temperatures, 475, 500, 550 and 600 °C. The samples were called according to their annealing temperatures as IGZO-475, IGZO-500, IGZO-550 and IGZO-600. profilometer.

Thickness of the thin film samples was checked with a KLA Tencor P6 profilometer. Thickness of IGZO thin films was around 221 nm IGZO-AD, 169 nm, 152 nm, and 149 nm and 134 nm as the annealing temperature of IGZO thin films was 475, 500, 550 and 600 °C, respectively.

Surface nanostructures of IGZO samples were investigated by scanning electron microscope (Hitachi- SU1510). In order to investigate morphological properties of IGZO samples, atomic force microscopy (Nanosurf Flex-5) was used. These AFM images were obtained in the non-contact mode [29, 30]. [29, 30]. The scan was performed on the field of 25 μm with 1 line per second at a resonance frequency of about 160 kHz. Several fields were scanned on the sample surfaces. The optical properties of the ITO thin film samples were studied on the basis of transmittance and absorbance measurements, and these measurements in wavelength range from 300 to 1000 nm was carried out by a Shimadzu UV Mini-1240 Uv-Vis spectrophotometer. The optical band gap energy values and porosity of the films are calculated by this the transmittance spectra.

3. RESULTS AND DISCUSSION

Figure 1 (a) - (e) shows SEM images of the IGZO-AD, IGZO-475, IGZO-500, IGZO-550 and IGZO-600 thin films, respectively. Surfaces of the samples seem to be formed by grains and the grains have different shapes and sizes. The porous structures can also be seen from SEM images. After annealing, it was seen that the surface roughness decreases and the grains are larger in Figure 1 (b) and (c). Thanks to the annealing process, thin film samples have not only gained a transparent appearance, but have also shown a lower resistance and become more homogeneous due to the effect of oxygen. In Figure 1 (d), the grain sizes on the surface of the sample with an annealing temperature of 550 ^{o}C start to shrink again and become smaller. As the temperature increases, a more dense grained structure is formed. In Figure 2 (e), due to the high annealing temperature value, the particle structure on the surface of the sample has disappeared and a transition has started from amorphous structure to crystal structure [31]. Also, at this temperature, the transparency of the film was significantly reduced and its resistance increased significantly. The best transparency of the thin film samples was obtained at annealing temperature at 475 ° C.

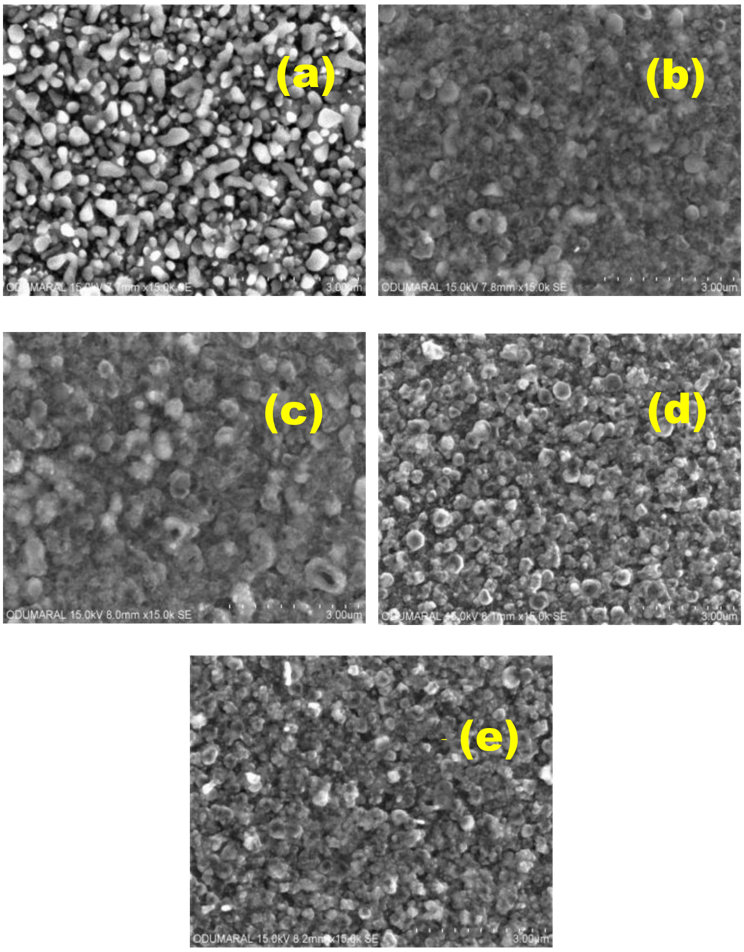

Figure 1. SEM images of (a) IGZO-AD; (b) IGZO-475; (c) IGZO-500; (d) IGZO-550; (e) IGZO-600.

AFM images of the surfaces of thin films produced at different annealing temperatures are shown in figure 2 (a) - (e).The AFM roughness results are summarized in Table 1. As seen from the table 1 , the IGZO-475 sample has the lowest surface, roughness as 32.964 nm among the films while IGZO-AD found to be the highest roughness values, without annealing, as 74.713 nm. In addition to this, the different surface roughness values can be interpreted as the lack of the oxygen [32, 33].

Table 1. Summary of AFM roughness results.

Sample	**Average roughness (Sa) (nm)**	**RMS roughness (Sq) (nm)**
IGZO-AD	74.713	92.781
IGZO-475	32.964	46.013
IGZO-500	59.503	97.182
IGZO-550	42.221	61.269
IGZO-600	68.754	85.05

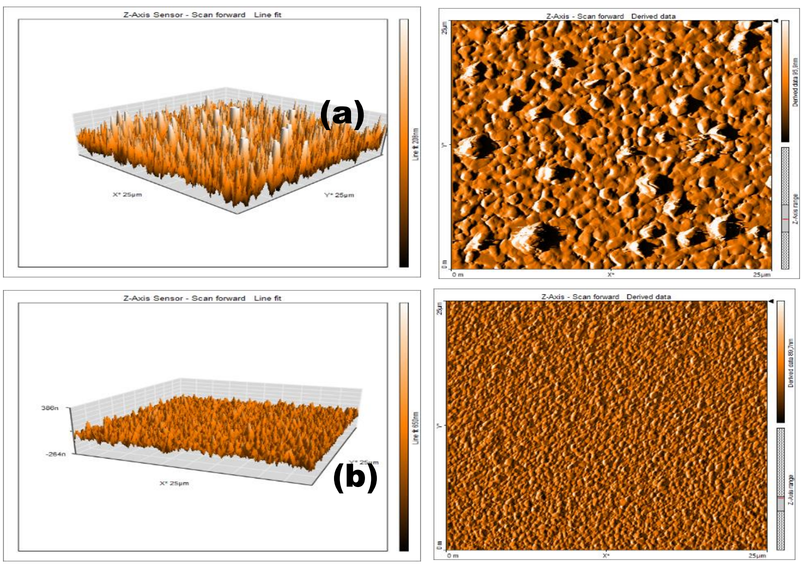

Figure 2. Atomic force microscopy (AFM) images of the IGZO films annealed at (a) as deposited; (b) 475 °C;

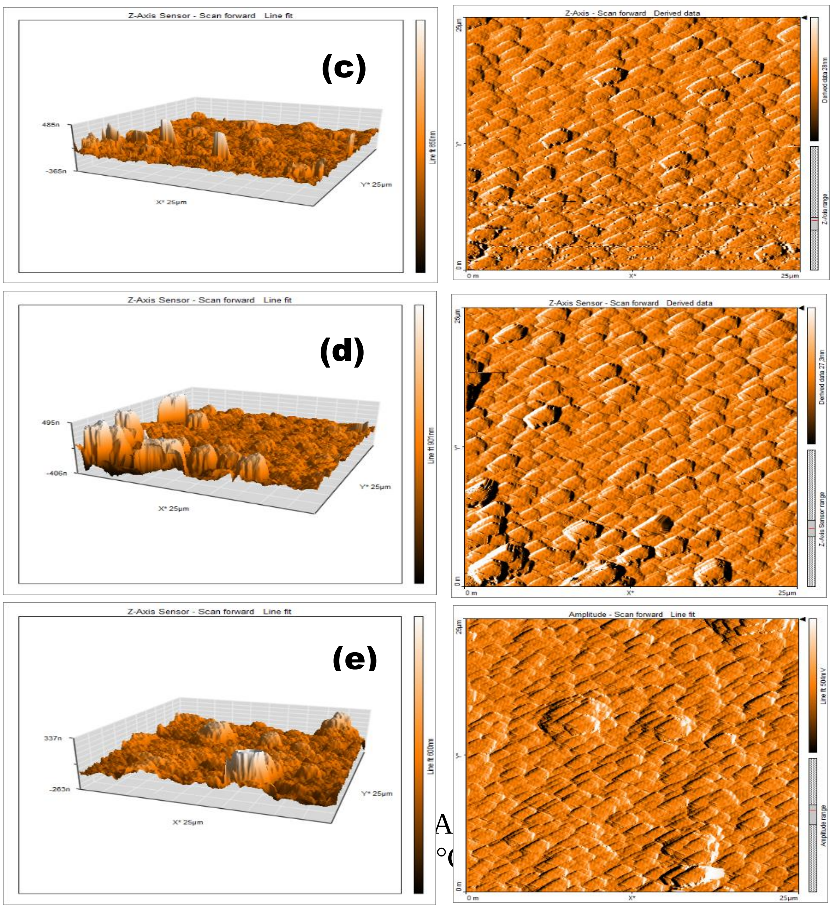

Figure 2. Atomic force microscopy (AFM) images of the IGZO films annealed at (c) 500 °C; (d) 550°C; and (e) 600 °C.

Figure 3 shows the transmittance spectra of the IGZO films as a function of wavelength in the range of 300 to 900 nm. The average transmittance ratio of IGZO thin films was 14%, 33%, 27 %, 28.5 % and 25 %, respectively. The decrease in the optical transmittance value is due to the formation of oxygen vacancies [34, 35] and large grains [36], which is supported by AFM results.

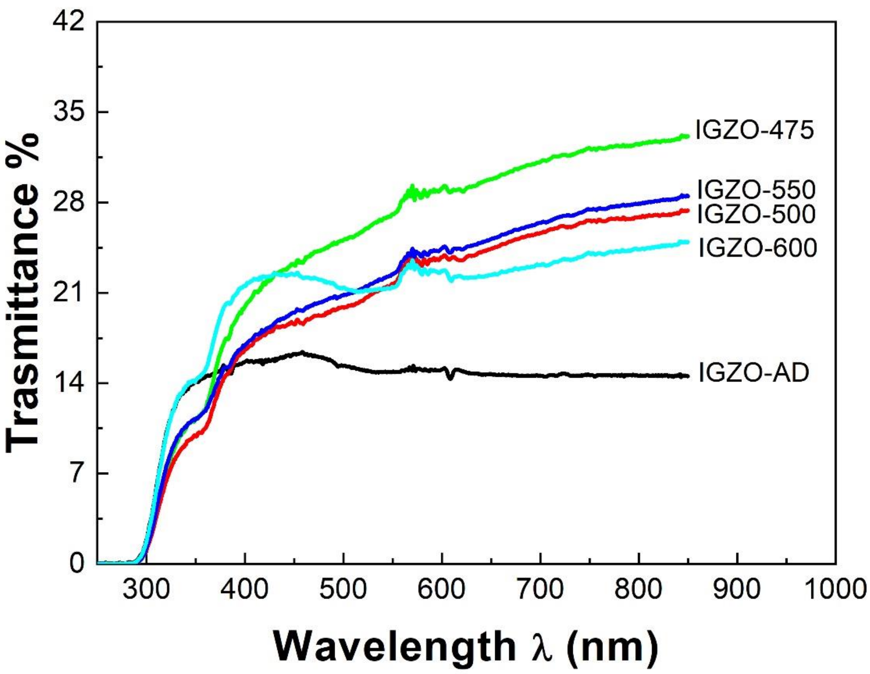

Figure 3. Optical transmittance spectra in visible region of the IGZO Samples.

There are several methods to calculate optical band gap energy (Eg) of the materials in the literature. In this study, to determine the energy gap of the samples the absorption coefficient α of the thin films were evaluated using the optical transmittance spectra and the absorption coefficient was calculated using Equation (1) [36]

$$\alpha = \frac{\left[\ln\left(\frac{1}{T}\right)\right]}{d} \quad (1)$$

where T is transmittance, d is the film thickness. In addition, the dependence of the absorption coefficient on the incident photon energy is given by [38]

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \quad (2)$$

where B characteristic parameter, E_g denotes the energy bandgap, $h\nu$ is the photon energy. Thus extrapolation of the straight-line portion of the plot of $(\alpha h\gamma)^2$ versus photon energy ($h\nu$) to zero absorption (α=0) gives the direct band gap of the films.

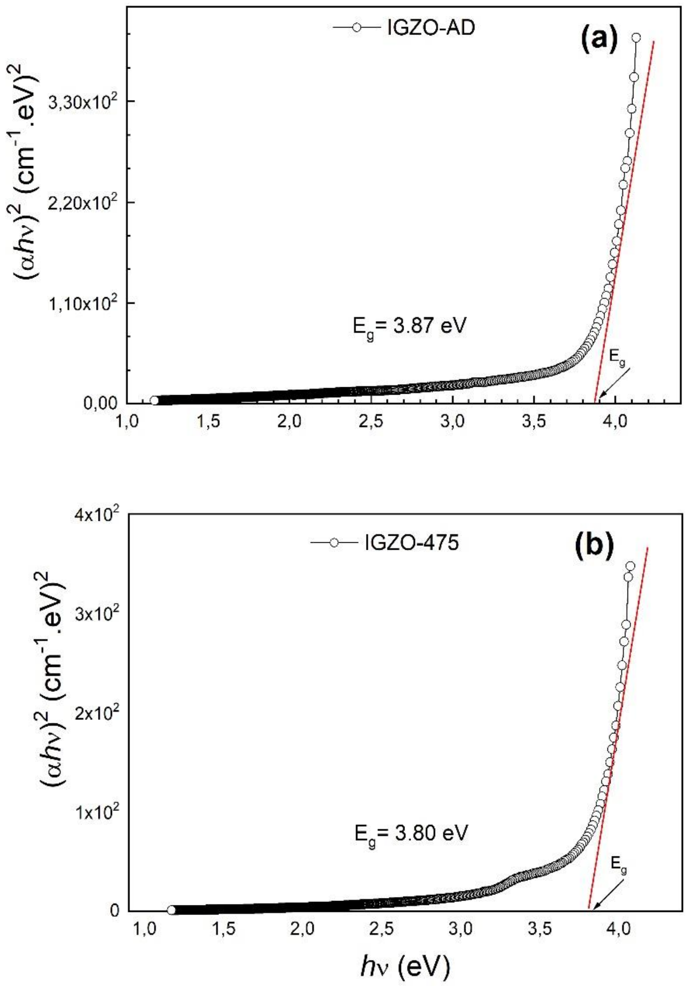

Figure 4. Variation of the optical band gap of IGZO thin films: (a) as deposited (without annealing); (b) 475˚C.

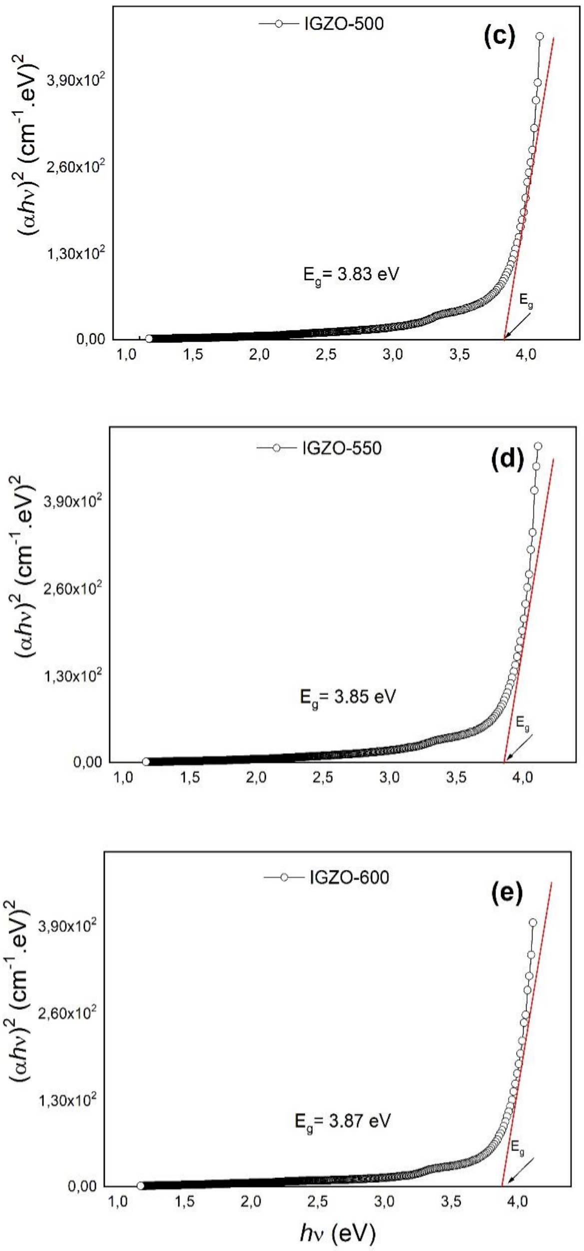

Figure 4. Variation of the optical band gap of IGZO thin films: (c) 500; (d) 550˚C and (e) 600˚C.

Figure 4 (a)-(e) shows the calculated values of the band gap energies (E_g) of IGZO thin films were 3.87 eV, 3.80 eV, 3.83 eV, 3.85 eV and 3.87 eV as the annealing temperatures were As-deposited, 475, 500, 550 and 600 °C, respectively. While increasing the annealing temperature the bandgap energy decreases then it reaches its previous value with the increase of annealing temperatures further.

Generally, higher band gap value causes low optical absorption. Observing low absorption in the visible range is a main characteristic of metal oxide semiconductors (MOS), having a band gap energy of above 3 eV.

4. CONCLUSION

In this study, polycrystalline IGZO thin films were deposited on glass and Si/SiO substrates by thermal evaporation technique at room temperature. it is investigated that how the annealing temperature affects the microstructural and optical properties of the IGZO thin films. Characterization of the samples was conducted by atomic force microscopy, scanning electron microscopy, UV-VIS spectroscopy. The results showed that Structural, optical, morphological properties of the thin films are strongly dependent on annealing temperature. The grain size is increased by temperature. Without annealing sample (IGZO-AD) has the highest Average roughness (74.713 nm) while IGZO-475 has the smallest roughness 32.964 nm. The maximum transmittance is observed to be 33 % for the IGZO-475 sample while the minimum transmittance is observed to be 14 % for the IGZO-AD film as a result of the different grain sizes and roughness. While the maximum energy gap has the 3.87 eV for the IGZO-600 sample the minimum band gap energy value is 3.80 eV for IZGO-475 sample. This is of the opinion that it is related to the structural disorder existing at the grain boundaries.

5. ACKNOWLEDGEMENTS

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REFERENCES

[1] Zhang, M. L., Jin, F., Zheng, M. L., Liu, J., Zhao, Z. S., & Duan, X. M. (2014). High efficiency solar cell based on ZnO nanowire array prepared by different growth methods, Rsc Advances, 4(21), pp. 10462-10466.

[2] Choi, Y. S., Kang, J. W., Hwang, D. K., & Park, S. J. (2009). Recent advances in ZnO-based light-emitting diodes, IEEE Transactions on electron devices, 57(1), pp. 26-41.

[3] T. P. H. Sidiropoulos, R. Roder, S. Geburt, O. Hess, S. A. Maier, C. Ronning, and R. F. Oulton, (2014). Ultrafast plasmonic nanowire lasers near the surface plasmon frequency, Nat Phys, 10, p. 870.

[4] Yun, D. J., & Rhee, S. W. (2009). Deposition of Al-doped ZnO thin-films with radio frequency magnetron sputtering for a source/drain electrode for pentacene thin-film transistor, Thin Solid Films, 517(16), pp. 4644-4649.

[5] Kumar, R., Al-Dossary, O., Kumar, G., & Umar, A. (2015). Zinc oxide nanostructures for NO 2 gas–sensor applications: A review, Nano-Micro Letters, 7(2), pp. 97-120.

[6] Cai, A., Du, L., Wang, Q., Chang, Y., Wang, X., & Guo, X. (2016). Kelp-inspired N–I-doped ZnO photocatalysts with highly efficient catalytic activity, Materials Science in Semiconductor Processing, 43, pp. 25-33.

[7] Cao, X., Li, X., Gao, X., Liu, X., Yang, C., Yang, R., & Jin, P. (2011). All-ZnO-based transparent resistance random access memory device fully fabricated at room temperature, Journal of Physics D: Applied Physics, 44(25), p. 255104.

[8] Struk, P., Pustelny, T., Gut, K., Golaszewska, K., Kaminska, E., Ekielski, M., & Piotrowska, A. (2009). Planar optical waveguides based on thin ZnO layers. Acta Physica Polonica-Series A General Physics, 116(3), p. 414.

[9] Jayaraman, V. K., Kuwabara, Y. M., & Álvarez, A. M. (2016). Importance of substrate rotation speed on the growth of homogeneous ZnO thin films by reactive sputtering, Materials Letters, 169, pp. 1-4.

[10] Tsoutsouva, M. G., Panagopoulos, C. N., Papadimitriou, D., Fasaki, I., & Kompitsas, M. (2011). ZnO thin films prepared by pulsed laser deposition, Materials Science and Engineering: B, 176(6), pp. 480-483.

[11] Hasim, S. N. F., Hamid, M. A. A., Shamsudin, R., & Jalar, A. (2009). Synthesis and characterization of ZnO thin films by thermal evaporation, Journal of Physics and Chemistry of Solids, 70(12), pp. 1501-1504.

[12] Duan, L., Zhao, X., Zhang, Y., Shen, H., & Liu, R. (2016). Fabrication of flexible Al-doped ZnO films via sol–gel method, Materials Letters, 162, pp. 199-202.

[13] Ergin, B., Ketenci, E., & Atay, F. (2009). Characterization of ZnO films obtained by ultrasonic spray pyrolysis technique, International journal of hydrogen energy, 34(12), pp. 5249-5254.

[14] Ali, M. M. (2011). Characterization of ZnO thin films grown by chemical bath deposition, Journal of Basrah Researches (Sciences), 37(3A), pp. 49-56.

[15] Huang, Y., Sarkar, D. K., & Chen, X. G. (2015). Superhydrophobic nanostructured ZnO thin films on aluminum alloy substrates by electrophoretic deposition process, Applied Surface Science, 327, pp. 327-334.

[16] Nomura, K., Ohta, H., Takagi, A., Kamiya, T., Hirano, M., & Hosono, H. (2004). Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors, nature, 432(7016), pp. 488-492.

[17] Leppänen, K., Saarela, J., Myllylä, R., & Fabritius, T. (2013). Electrical heating synchronized with IR imaging to determine thin film defects, Optics express, 21(26), pp. 32358-32370.

[18] Kim, S., Jeon, Y. W., Kim, Y., Kong, D., Jung, H. K., Bae, M. K., & Park, J. (2011). Impact of oxygen flow rate on the instability under positive bias stresses in DC-sputtered amorphous InGaZnO thin-film transistors, IEEE Electron Device Letters, 33(1), pp. 62-64.

[19] Kikuchi, Y., Nomura, K., Yanagi, H., Kamiya, T., Hirano, M., & Hosono, H. (2010). Device characteristics improvement of a-In–Ga–Zn–O TFTs by low-temperature annealing, Thin Solid Films, 518(11), pp. 3017-3021.

[20] Matsuo, T., Mori, S., Ban, A., & Imaya, A. (2014, June). 8.3: Invited paper: advantages of IGZO oxide semiconductor, In SID Symposium Digest of Technical Papers (Vol. 45, No. 1, pp. 83-86).

[21] Nakata, M., Takechi, K., Eguchi, T., Tokumitsu, E., Yamaguchi, H., & Kaneko, S. (2009). Flexible high-performance amorphous InGaZnO4 thin-film transistors utilizing excimer laser annealing, Japanese Journal of Applied Physics, 48(8R), 081607.

[22] Gosain, D. P., & Tanaka, T. (2009). Instability of amorphous indium gallium zinc oxide thin film transistors under light illumination, Japanese Journal of Applied Physics, 48(3S2), 03B018.

[23] Ohara, H., Sasaki, T., Noda, K., Ito, S., Sasaki, M., Endo, Y.,& Yamazaki, S. (2010). 4.0-inch active-matrix organic light-emitting diode display integrated with driver circuits using amorphous In–Ga–Zn-Oxide thin-film transistors with suppressed variation, Japanese Journal of Applied Physics, 49(3S), 03CD02.

[24] Godo, H., Kawae, D., Yoshitomi, S., Sasaki, T., Ito, S., Ohara, H., & Yamazaki, S. (2010). Temperature dependence of transistor characteristics and electronic structure for amorphous In–Ga–Zn-Oxide thin film transistor, Japanese Journal of Applied Physics, 49(3S), 03CB04.

[25] Takechi, K., Nakata, M., Eguchi, T., Yamaguchi, H., & Kaneko, S. (2009). Temperature-dependent transfer characteristics of amorphous InGaZnO4 thin-film transistors, Japanese Journal of Applied Physics, 48(1R), 011301.

[26] Takechi, K., Nakata, M., Eguchi, T., Yamaguchi, H., & Kaneko, S. (2009). Comparison of ultraviolet photo-field effects between hydrogenated amorphous silicon and amorphous InGaZnO4 thin-film transistors, Japanese Journal of Applied Physics, 48(1R), 010203.

[27] M. o. E. chunichi Industry and Technology Award (27th), Trade and Industry Award.

[28] Durdu, S., Aktug, S. L., Aktas, S., Yalcin, E., Cavusoglu, K., Altinkok, A., & Usta, M. (2017). Characterization and in vitro properties of anti-bacterial Ag-based bioceramic coatings formed on zirconium by micro arc oxidation and thermal evaporation, Surface and Coatings Technology, 331, pp. 107-115.

[29] Tsarkova, L., Knoll, A., Krausch, G., & Magerle, R. (2006). Substrate-induced phase transitions in thin films of cylinder-forming diblock copolymer melts, Macromolecules, 39(10), pp. 3608-3615.

[30] Zalakain, I., Ramos, J. A., Fernandez, R., Etxeberria, H., & Mondragon, I. (2012). Silicon and carbon substrates induced arrangement changes in poly (styrene‐b‐isoprene‐b‐styrene) block copolymer thin films, Journal of applied polymer science, 125(2), pp. 1552-1558.

[31] De Meux, A. D. J., Pourtois, G., Genoe, J., & Heremans, P. (2015). Comparison of the electronic structure of amorphous versus crystalline indium gallium zinc oxide semiconductor: structure, tail states and strain effects, Journal of Physics D: Applied Physics, 48(43), 435104.

[32] Ling, L., Tao, X., Zhongxiao, S., Chunliang, L., & Fei, M. (2016). Effect of sputteringpressure on surface roughness, oxygen vacancy and electrical properties of a-IGZO thin films, Rare Metal Materials and Engineering, 45(8), pp. 1992-1996.

[33] de Jamblinne de Meux, A., Bhoolokam, A., Pourtois, G., Genoe, J., & Heremans, P. (2017). Oxygen vacancies effects in a ‐ IGZO: Formation mechanisms, hysteresis, and negative bias stress effects, physica status solidi (a), 214(6), 1600889.

[34] Li, X., Wang, Y., Liu, W., Jiang, G., & Zhu, C. (2012). Study of oxygen vacancies′ influence on the lattice parameter in ZnO thin film, Materials Letters, 85, pp. 25-28.

[35] Liu, H., Zeng, F., Lin, Y., Wang, G., & Pan, F. (2013). Correlation of oxygen vacancy variations to band gap changes in epitaxial ZnO thin films, Applied Physics Letters, 102(18), 181908.

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

[37] Valencia, S., Marín, J. M., & Restrepo, G. (2009). Study of the bandgap of synthesized titanium dioxide nanoparticules using the sol-gel method and a hydrothermal treatment, The Open Materials Science Journal, 4(1).

[38] J.N. Hodgson, Optical Absorption and Dispersion in Solids, Chapman & Hall, London, 1970.