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STRUCTURAL AND OPTICAL CHARACTERIZATION OF ALUMINUM ZINC CO-DOPED TIN OXIDE GROWN BY SOL-GEL SPIN COATING TECHNIQUES

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Abstract. *Aluminum Zinc co-doped Tin Oxide (AZSO) thin film was grown by sol-gel spin coating techniques onto a glass substrate using various doping concentrations (0, 2, 4, 6, and 8* wt%) *and the effect of doping on each sample were studied using structural analysis; X-ray Diffraction (XRD) pattern, gravimetric method; thin film thickness and UV photo-spectrometer; optical properties. The results of the XRD were revealed that all the peaks have a tetragonal phase of* SnO_2, *which were oriented at the 110, 101, and 211 planes. The film thickness was observed to vary with doping concentration. In the visible region, all the film samples were exhibited at average transmittance. The coefficient of absorption was gradually increased with an increase in photon energy at a certain level with a decrease in the absorption coefficient as the photon energy increases further. At 550-800 nm range of wavelength, a high extinction coefficient (k) was recorded and the refractive index curves show regular dispersion behavior. The optical conductivity of the films followed a similar pattern, which showed that conductivity increased to a peak at 3.60 eV. The energy bandgap of the film samples (AZSO1 - AZSO5) is 4.095 eV, 4.103 eV, 4.087 eV, 4.114 eV, and 4.106 eV, respectively. The studies show that the properties of Al-Zn co-doped* SnO_2 *films can be explored for optoelectronic applications.*

Key words: *sol-gel, spin coating, transmittance, doping, film thickness, wavelength.*

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1. INTRODUCTION

In recent times, the demand for thin-film coating on voluminous area substrates has been rapidly increased. The coating is sometimes required to make an object or a material harder, or more also to provide the surface with particular optoelectronics properties. Transparent conducting oxides (TCOs) are materials with high electrical conductivity properties that possess a low absorption rate in the visible region of the electromagnetic waves spectrum. TCOs are commonly grown using thin-film techniques and applied in the optoelectrical interfaces and circuitries (Stadler, 2012). Divalent (SnO) and tetravalent (SnO_2) are two types of oxidation states in which tin oxides (SnO_x) usually exist and they are respectively categorized into p and n-type semiconductors (Xu et al., 2013; Liu et al., 2010). Recently, tin (II) oxide enticed considerable consideration because of its ability in sustaining both structure and electronic characteristics (Guo et al., 2010). Tin oxides are one of the most favorable materials for future optoelectronic devices including translucent applications due to their high density of delocalized Sn 5s state in the valence band and Sn 5p state conduction band (Granato et al., 2013). There are various applications of Tin oxide (SnO_2) thin films in optoelectronic devices and gas sensors because of their electrical conductivity properties, chemical stability, and high transmittance at VIS-NIR wavelengths (Batzill and Diebold, 2005; Haridas et al., 2008; Ayllon and Lira-Cantu, 2009). There are various techniques to produce tin oxides; the most promising one among them is the sol-gel method because it is the simplicity in thin-film properties control during the process. The suitability of the films synthesized by sol-gel methods for device applications was also reported (Kim et al., 2011).

Bhat et al., (2007), employed sol-gel spin coating techniques to prepared Zn doped SnO_2 films and the analyses of the electrical and optical characteristics were carried out. The electrical properties of the doped films were analyzed as the dopant concentrations varied up to 10 wt%. They observed that there is an increase in sheet resistance of the doped SnO_2 films, as the dopant concentration increases. Sharipah et al., (2012), employed mechanochemical methods to synthesize and analyzed the optical characteristics of Zinc doped tin oxide; the X-Ray Diffraction (XRD) observed shown that Zinc has been better nobbled into SnO_2. They also detected a reduction in volume size when the concentration of the dopant increased and the Red Shift in the energy gap was due to the concentration of dopant (Zn). Sriram and Thayumanavan (2013), prepared Aluminum doped tin oxide (SnO_2:Al) thin films using spray pyrolysis Methods and 1.668 to 1.676 values of refractive indexes were obtained for the films concerning Aluminum concentrations. In the lower region wavelength, the extinction coefficient shows that the film's absorption was higher. The studies also affirmed the P-type characteristics of the synthesized films and the order of the carrier concentrations is 10^{16} - $10^{17}/cm^3$. In this study, Aluminum Zinc co-doped Tin Oxide (AZSO) was synthesized through Sol-Gel Spin Coating techniques using methanol as solvents. The structural, thin-film thickness, and optical characterization of the AZSO thin films were examined by X-ray diffraction (XRD), gravimetric method, and UV photo-spectrometer, respectively. The impact of the co-doped on the thickness, structural and optical characteristics of AZSO films were discussed and conclusions were drawn.

2. MATERIALS AND METHODS

The starting material $SnCl_4 \times 5H_2O$ of analytical grade was weighed upon electronic balance using 4.06 g of $SnCl_4 \times 5H_2O$ in 30 ml of methanol used as the solvent. The

solvent was poured in a closed container with 4.06 g of $SnCl_4 \times 5H_2O$ and the dopants ($AlCl_3$ and $ZnCl_2$) were later added in various doping concentration, the container was placed on the magnetic stirrer and was set to stir for 4 hours, and heat was not applied due to the boiling point of the methanol. After 4 hours the sol-gel solution was poured into a beaker and sealed so that it will be left to age at room temperature for 24 hours. However, the preparation and composition of the sol-gel solution for the un-doped tin oxide (SnO_2) and doped Aluminum Zinc co-Doped Tin Oxide (AZSO) samples are shown in Table1. The sol-gel solution of the un-doped and doped AZSO thin films was deposited on the microscopic slides (2.5 cm x 2.5 cm). To guarantee an impurity-free deposition, subsequent cleaning procedures were carried-out; the slides were washed with detergent for 10mins and later cleaned with acetone. For further sterilization, the slides were oven-dried at 50 ^oC for 30 mins and were kept in the glass rack to avoid any form of contamination. For the deposition of the AZSO solutions, the slide was placed at the center of the spin coater and it was set to spin at 1000 rpm. As the spin coater was set to spin, the sol-gel solutions for the AZSO films were dropped on the glass slide with the aid of a pipette which was dipped in the solution and was dropped on the glass slide 10 times within the time interval of 1 min. The glass slide was detached from the spin coater and was put in the oven to dry up for 5 mins. The process was repeated 10 times to obtain a uniform and transparent film.

Table 1 The preparation of the sol-gel solutions for an un-doped and doped AZSO

	Sample	Doping %	Mass of ($SnCl_4 \times 5H_2O$) (g)	Mass of ($AlCl_3$) (g)	Mass of ($ZnCl_2$) (g)	Composition	Volume of solvent used (methanol)
1	AZSO1	0	4.06	0.00	0.00	$SnCl_4 \times 5H_2O$	30 ml
2	AZSO2	2	4.06	0.09	0.05	$AlCl_3 \times ZnCl_2$. $SnCl_4 \times 5H_2O$	30 ml
3	AZSO3	4	4.06	0.17	0.1	$AlCl_3 \times ZnCl_2$ $SnCl_4 \times 5H_2O$	30 ml
4	AZSO4	6	4.06	0.26	0.15	$AlCl_3 \times ZnCl_2$. $SnCl_4 \times 5H_2O$	30 ml
5	AZSO5	8	4.06	0.35	0.20	$AlCl_3 \times ZnCl_2$ $SnCl_4 \times 5H_2O$	30 ml

3. Results and Discussion

Five samples of Al-Zn co-doped (0, 4, 6, 8, and 10 wt%) SnO_2 thin films deposited by sol-gel spin coating techniques were studied for their structural and optical properties.

3.1. Thickness of the thin films

Thin films thicknesses were determined by gravimetric techniques as shown in equation (1) below:

$$t = \frac{m}{\rho A} \qquad (1)$$

where m is the mass of the deposited film, ρ is the density and A is the area of the deposited films. The sample thickness for AZSO1, AZSO2, AZSO3, AZSO4, and AZSO5 have varying film thicknesses of 32.55, 35.75, 38.85, 37.64, and 36.52 nm respectively due to change in doping concentration.

The chart for the thin-film thickness of all the five samples was shown in Fig. 1(a). The chart shows the varying thickness of each sample when measured after deposition, as shown in the chart, AZSO3 has a thickness of 38.85 nm which is the highest thickness of the film.

3.2. Structural characteristics

The intensity of X-ray diffraction pattern (in arbitrary unit) against 2θ (in degree) of un-doped and Al-Zn co-doped SnO_2 films prepared on glass substrates were shown in Fig. 1(b). The broad hump in the range $2\theta = 20^o$-80^o was due to the amorphous nature of the glass substrate and noise. Results of XRD were revealed that all the peaks have a tetragonal phase of SnO_2, which were oriented at the 110, 101, and 211 planes (Doyan et al., 2018). The observed diffraction peaks in the diffractogram can be indexed and well corresponding with the typical (JCPDS File No. 10625) values (Bolzan et al., 1997). The crystallite sizes of the thin films were evaluated using Debye-Scherrer's formula.

$$Dkhl = \frac{k\lambda}{\beta\cos\theta} \tag{2}$$

It has been detected that the mean crystalline size of un-doped and Al-Zn doped SnO_2 film is about 38 nm and 27 nm respectively.

3.3. Optical characteristics

The distinction of the transmittance and the performance of each film with the wavelength were shown in Fig. 1(c), it also indicates the optical transmission ranges for un-doped and Al-Zn doped SnO_2 thin films for the five samples. All the films exhibited an average transmittance between the wavelength regions of 400 to 800 nm. There was an increase in the transmittance as the Al-Zn doping concentration increases. The average percentage of transmission of all the thin film samples lies between 51% and 73% in the visible region; AZSO3 has the highest transmission value of about 73%. The transmittance (T) was estimated using equation (3):

$$A = \log(\frac{1}{T}) \tag{3}$$

Fig. 1(d) is the absorption bands for un-doped and Al-Zn co-doped SnO_2 thin films. The absorption bands show that the deposited films have average absorbance in the visible regions, while AZSO3 has the lowest absorbance of all the five samples. In general, the film has the highest transmittance in Fig. 1(c) has the lowest absorbance in the visible region, which shows that as the wavelength increases there is a decrease in the absorbance of the thin films. Also as the film thicknesses increased, there is an increase in the absorbance of the thin films as a result of scattering losses.

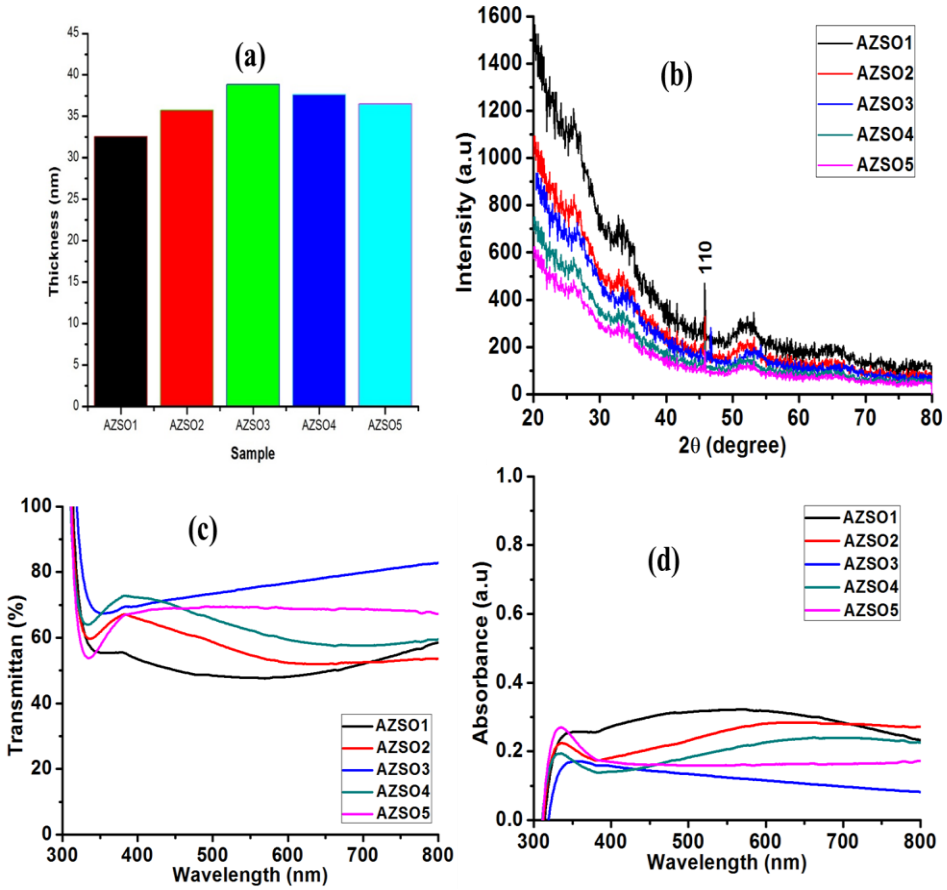

Fig. 1 (a) The chart of the thickness of each sample, (b) XRD pattern of an un-doped and Al-Zn doped SnO_2 films, (c) Transmission bands of an un-doped and Al-Zn co-doped SnO_2 films (d) The plot of absorption spectra for an un-doped and Al-Zn co-doped SnO_2 films

The variations of coefficient of absorption (α) with photon energy for un-doped and Al-Zn co-doped SnO_2 thin films for all the five samples were presented in Fig. 2(a). The variation of coefficient of absorption (α) was determined using equation (4):

$$\alpha = 2.303\left(\frac{A}{d}\right) \tag{4}$$

The result has shown that as the photon energy increases, there is a steady increase in the coefficient of absorption, at some certain level with a decrease in the absorption coefficient as the photon energy increases further for all the samples. According to Kocman and Nuffield (1973), the principle of interband absorption reveals that at the optical absorption edge, the coefficient of absorption (α) changes with the photon energy (eV).

Fig. 2(b) reveals the variation of extinction coefficient against wavelength of un-doped and Al-Zn co-doped SnO_2 thin film for the five samples.

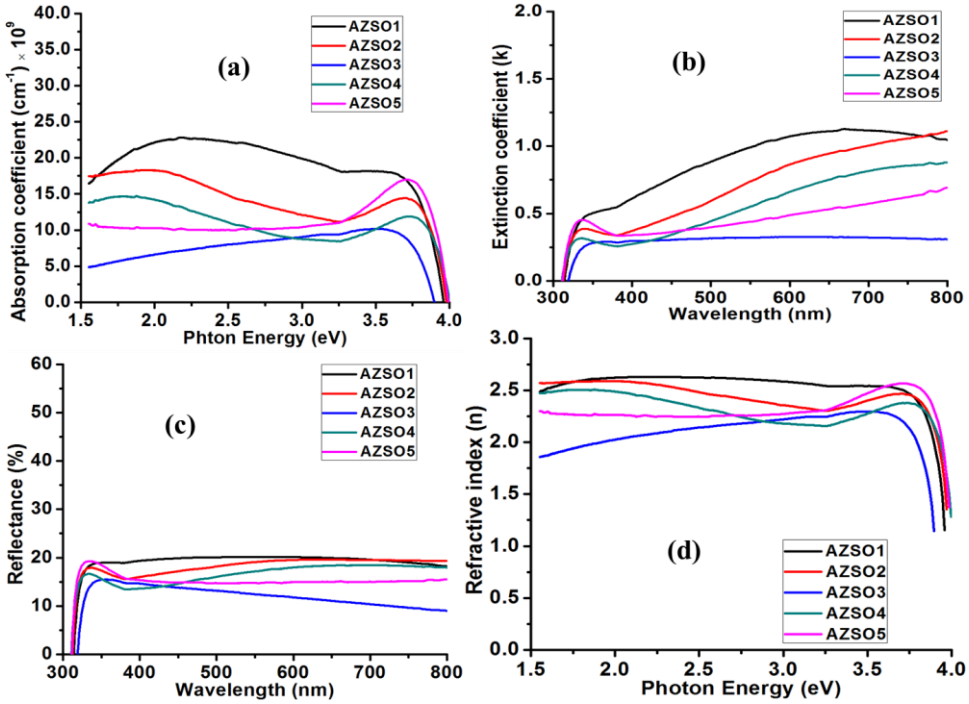

Fig. 2 (a) Plot of Absorption Variation Coefficient against photon energy for un-doped and Al-Zn co-doped SnO_2 films, (b) Variation of Extinction Coefficient against Wavelengths for un-doped and Al-Zn co-doped SnO_2 films, (c) Plot of Reflectance Spectra for an un-doped and Al-Zn co-doped SnO_2 films, (d) Plot of refractive index Variation against photon energy for an un-doped and Al-Zn co-doped SnO_2 thin films

The coefficient of extinction (K) was calculated by the following:

$$K = \frac{\alpha\lambda}{4\pi} \tag{5}$$

The extinction coefficient (k) is high in the wavelength range of 550– 800 nm and low in the wavelength range of 300 – 450 nm. In the case of polycrystalline films, light absorption ensues at the grain boundaries which leads to non-zero of k for wavelengths greater than the fundamental absorption edge (Sahay et al., 2007).

Variation of reflectance against wavelength of un-doped and Al-Zn co-doped SnO_2 thin film for the five samples were shown in Fig. 2(c). AZSO thin films have low reflectance for almost all the wavelengths. The reflectance with average wavelength was observed at the range of 300 – 400 nm and a steady reduction in the range of 450 – 800 nm wavelengths.

Fig. 2(d) presents the disparity of refractive index against wavelength of un-doped and Al-Zn co-doped SnO_2 thin films. It was observed that as the photon energy increases from 1.5 eV to 2.7 eV, the refractive index also increases. However, as the photon energy increased beyond the 3.5 eV, the refractive index decreased, while the curves of the refractive index show the standard dispersion behavior. The thin films' optical bandgap variations are usually proportional to the shifting of the peak position (Yakuphanoglua et al., 2009).

Fig. 3(a) shows the optical band gap of un-doped and Al-Zn co-doped SnO_2 thin films. The relation for the bandgap (Eg) was given by:

$$\alpha = \frac{A(h\nu - Eg)^{1/2}}{h\nu} \tag{6}$$

The energy bandgap was estimated by plotting the square of the product of absorption coefficient $(\alpha h\nu)^2$ against photon energy ($h\nu$) whose intercept on the energy axis gives the optical band gap energy for all the samples as shown in Fig. 3(a). The calculated band gap for 0%, 2%, 4%, 6% and 8% of Al-Zn co-doped SnO_2 are 4.095 eV, 4.103 eV, 4.087 eV, 4.114 eV and 4.106 eV, respectively. Higher values of the energy gap observed for film samples are associated with the quantum confinement effects (Ruby and Suman, 2011).

The optical conductivity variations with the incident photon energy were illustrated in Fig. 3(b). The relation to determining the conductivity (σ) was given as:

$$\sigma = \frac{\alpha nc}{4\pi} \tag{7}$$

The optical conductivity behavior of all the samples followed a similar pattern as observed from the graph. It shows that conductivity increased to a peak at 3.60 eV, and AZSO1 having the highest peak. This similar pattern of optical conductivity can be inferred from the absorption coefficient and refractive index of the samples which are greatest at the UV region and diminished as the wavelength increases (Al-dujayli et al., 2013).

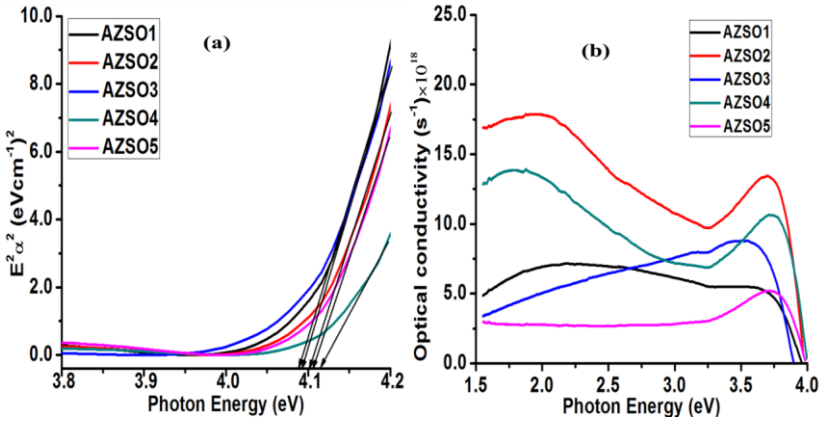

Fig. 3 (a) Plot of an Optical band gap of un-doped and Al-Zn co-doped SnO_2 thin films, (b) Variation of optical conductivity with photon energy for an un-doped and Al-Zn co-doped SnO_2 thin films

4. CONCLUSION

Al-Zn co-doped (0, 4, 6, 8, and 10 wt%) SnO_2 thin films have been successfully grown using sol-gel spin coating methods. The effect of Al-Zn doping concentrations on the characteristics of SnO_2 has been analytically studied as a result of increasing Al-Zn concentration. The XRD examination was used to confirm the tetragonal crystal structure of SnO_2. The change in grain size for the increase in doping has been confirmed from XRD analysis. UV absorption spectra showed that the Al-Zn (4 wt%) co-doped SnO_2 thin film has the highest average transparency in the visible region. The refractive index values of the films also vary from each other as a result of differences in the film thickness. The optical analyses have shown that the bandgap variation does not be influenced by the doping concentration, when the highest bandgap energy was observed at Al-Zn (6 wt %) co-doped SnO_2 thin film to be 4.114 eV. This study indicates that the Al-Zn co-doped SnO_2 films can be finely tuned for the desired application with specific values.

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STRUKTURNA I OPTIČKA KARAKTERIZACIJA KALAJ-OKSIDA DOPIRANOG ALUMINIJUMOM I CINKOM TEHNIKOM SOL-GEL *SPIN COATING*

Tanak film sačinjen od kalaj-oksida dopiranog aluminijumom i cinkom (AZSO), dobijen tehnikom sol-gel spin coating*-a na stakleni supstrat, uz različite koncentracije dopiranja (0, 2, 4, 6 i 8 masenih procenata) i efekti dopiranja ispitivani su strukturnom analizom; difrakcijom X-zraka (XRD), gravimetrijskom metodom; foto-spektrometrijom; analizom optičkih osobina. Rezultati XRD analize su pokazali da svi pikovi imaju tetragonalnu fazu SnO_2 usmerenu ka ravnima 110, 101 i 211. Uočeno je da debljina filma zavisi od koncentracije dopiranja. U vidljivom delu spektra svi uzorci filma pokazivali su prosečnu transmitancu. Koeficijent apsorpcije povećavao se sa energijom fotona do određenog nivoa, nakon čega počinje da opada. U opsegu talasnih dužina 550-800 nm, zabeležene su visoke vrednosti ekstinkcionog koeficijenta (k), a krive refrakcionog indeksa pokazuju očekivani efekat disperzije. Slična zavisnost uočena je i za optičku provodljivost filmova, koja raste do maksimalne vrednosti na 3,60 eV. Vrednosti zabranjenih zona iznosile su 4,095 eV (uzorak AZSO1), 4,103 eV (AZSO2), 4,087 eV (AZSO3), 4,114 eV (AZSO4) i 4,106 eV (AZSO5). Ova studija je pokazala da bi filmovi sačinjeni od SnO_2 i dopirani aluminijumom i cinkom mogli da imaju optoelektronsku primenu.*

Ključne reči: *sol-gel*, spin coating, *transmitanca, dopiranje, debljina filma, talasna dužina*