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Development of a High Performance SnO, SnO/TMC Nanostructures Thin Film Prepared by Spray Pyrolysis Technique

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Abstract
Thin films of the form: SnO, SnO/TMC were prepared using the spray pyrolysis technique at different substrate temperatures The films were characterized to investigate the effect of varying substrate temperatures on the optical and structural lproperties using UV-spectrophotometer and X-ray diffraction technique. The result showed that the optical transmittance decreased with increase in substrate temperature for SnO (core).The absorbance of the SnO thin films at various substrate temperatures vary from 0.10 – 0.7.For the biphasic films of SnO/ZnS, the absorbance decreases in the neighbourhood of 300nm-350nm, increases from350nm-600nm and decreases between 600-100nm for the different substrate temperature of 100º C, 150º C and 200º C.The reflectance spectra of SnO films were found fluctuating between maxima and minima while in the biphasic films the reflectance is low. The energy band gap increased with substrate temperature. Whereas for the biphasic films, the band gap was in the neighourhood of 1.30eV,1.20eV and 1.10eV for the different substrate temperatures respectively. The extinction coefficient (k) of SnO films increased with increase in substrate temperature while in biphasic films, the extinction coefficient showed significant reduction in magnitude irrespective of the substrate temperature. The refractive index of the film samples is generally low despite the substrate temperature. The XRD results indicated that the deposited thin films are polycrystalline in nature. The diffractograms obtained for biphasic films of SnO/Zns are characterized by relatively low intensity for all the samples irrespective of the substrate temperatures when compared to the uncoated SnO samples. The possible applications were discussed and these agree with the experimental data obtained.

Keywords: Tin Oxide (SnO), Transistion Metal Chalcogenides (TMC), (SnO/ZnS), transmittance, absorbance, reflectance, refractive index(n), band gap (E_g) , Spray pyrolysis technique and XRD.

Introduction
The study of tin Oxide thin film coated with transition metal chalcogenides in different substrates has continued to attract considerable attention of the many applications in semiconductor devices such as optoelectronic and solar energy devices. Tin oxide relies on the formation of a compact, adherent passive oxide film for its growth immunity in various substrates [1,2]. Thus, thin films of different metal oxides are frequently used for fabricating a wide range of electronic devices in modern industry. They are utilized in electronic devices as fundamental parts with different functionality such as optical devices for UV-visible spectral region applications, coloured layers, solar cells/collectors, automobile parts, barrier and insulating layers in electronic devices. These applications provide unique benefits in terms of lifetime and performance [3,4]. Oxide thin film materials have been receiving extensive attention, as one of the most attractive research topics in physics and among material scientists.

In recent years, many researchers had focused on the development of biphasic nanostructure materials on a nanometer scale, due to their device applications in several areas. The biphasic nanostructure composites are type of biphasic materials which have an inner structure of one material and outer structure of another material made of different components. These components exhibit unique properties arising from the combination of SnO and coating materials in their geometric designed form [5,6]. Moreso, they have been designed so that

the coating material can improve the reactivity of the surface, thermal stability, or oxidation stability of the SnO structured material. The coating materials are important because they can influence the charge, functionality, and as well as improve the dispersive nature of SnO structured materials [7-9]. The interest of the researchers was to deposit biphasic structured materials of the form SnO/ TMC. This would enable us to produce thin films which combine with unique properties of transition element and that of oxide of tin which makes it potential materials in window layers in heterojunction/CIGS solar cells, photonoic devices and other applications. However, report on the development/fabrication of a high performance SnO/ZnS nanostructure films prepared by spray pyrolysis technique is very rare in the literature, hence the best of our knowledge this research is novel and present a fundamental step towards identifying others possible pathways of utilizing SnO/TMC biphasic structured materials for application in different technological industries. Among these techniques is relatively new and less investigated process.

2.0 Experimental

The method used was Spray Pyrolysis technique which involves the use of Master Air brush Brand-Models G25, G255-SET and G26, G266-SET for deposition of desired films. Aqueous solution of 0.1M of Tin (II) Chloride ($SnCl_2$) was prepared by dissolving 19.0gram of salt in 100ml of distilled water.The equation of the reaction is shown in equation (1).

$$SnCl_2 + H_2O + NH_3 \rightleftharpoons SN(OH)_2 + NH_4Cl_2 \quad (1)$$

$$SN(OH)_2 \xrightarrow{\triangle} SnO_{(s)} + H_2O_{(g)} \quad (2)$$

Similarly, aqueous solution of O.1M zinc chloride ($ZnCL_2$) was prepared by dissolving 14.0gram of $ZnCL_2$ in 100ml of distilled water.Ammonia (NH_3) solution used as complexing agent and thiourea ($CSNH_2NH_2$)as a source of sulphur. The Microscopic glass slide or substrate of area 26mm x 76mm, thickness of 1.0mm and refractive index of 1.52) was used as the substrate and were thoroughly washed using detergent and distilled water. The washed slides were soaked in methanol for 1 hour and rinsed in distilled water, after which the slides were then oven dried at a temperature of 60^0C. The degreased, cleaned surface has the advantage of providing nucleation centres for the growth of the films. The reaction mechanism that results in the deposition of the films is through the reactions of the required precursors.

To obtain SnO thin film (core), 40ml of 0.1m tin (II) chloride ($SnCl_2$), two drops of ammonia (NH_3) solution were put into 50ml glass beaker. The mixture of was stirred under high-speed technique using magnetic stirrer for about 30 seconds in order to get uniform solution. Thereafter, 10ml of the resultant aqueous solution was measured out using pump syringe into spray pyrolysis sample bottle which was fastened on value rod of air brush and sprayed for 60 seconds (1 minute) on heated substrate at the temperature of 100^0C. These procedures were repeated for two different 10ml of solution at 150^0C and 200^0C respectively in each case using the compressor with the air brush at pressure of 22kg/cm^2.

To obtain SnO/ ZnS biphasic thin films, 40ml of 0.1M of zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH) and thiourea (NH_2CSNH_2) in the ratio of 5:5 plus 4 drops of ammonia (NH_3) solution were mixed into beaker to produce Zinc Sulphide (ZnS). The mixture was enhanced by using a magnetic stirrer for 30 minutes in order to obtain homogenous solution. After the stirring, 10ml of the solution was measured out using pump syringe into sample bottle that was fixed on nozzle value and sprayed on heated substrate/ slide of SnO films already deposited at 100^{o}C temperature. These were repeated for 2 different 10ml of the solution at 150^{o}C and 200^{o}C respectively. During deposition process the following parameters were measured; deposition distance (D.D) m, deposition height (D.H) m, deposition angle (α^o), nozzle air pressure (N.A.P), deposition time (D.T) s and substrate temperature.

Table 1: Paramaters of SnO and SnO/ZnS.

Samples	M(moles)	V(cm^3)	θ^o_1	θ^o_2	θ^o_3	D.D(cm)	α^o	D.H(m)	NAPD.(kg/cm^2)	T(S)
SnO	0.1	30	100	150	200	30	41	35.5	22	60
SnO/ZnS	0.1	30	100	150	200	35	28	36.5	22	60

3.0 Results and Discussion

Experimental results obtained in the course of these study include absorbance, transmittance, reflectance, refractive index, extinction coefficient and bandgap at various different substrate temperature are shown in Figures 1 to 6.

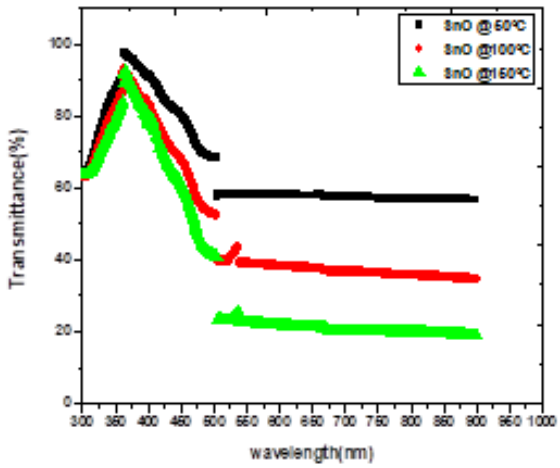

Fig. 1A: Plot of transmittance against wavelength for as-deposited SnO.

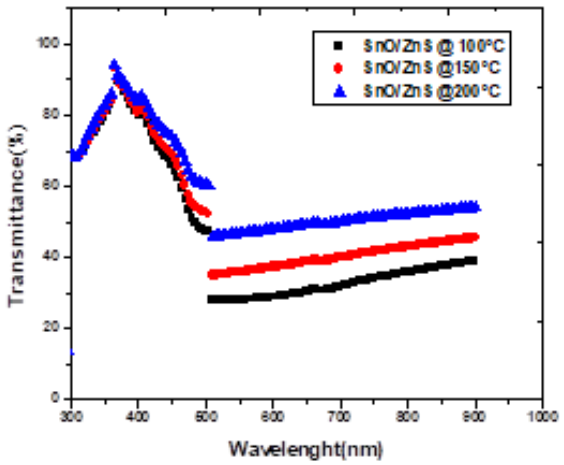

Fig.1 B: Plot of transmittance against wavelength for SnO/ZnS annealed at 100ºC, 150 ºC and 200ºC.

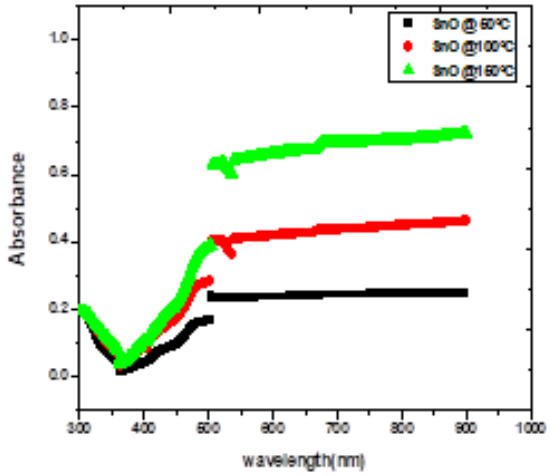

Fig. 2A: Plot of absorbance against wavelength for as-deposited SnO.

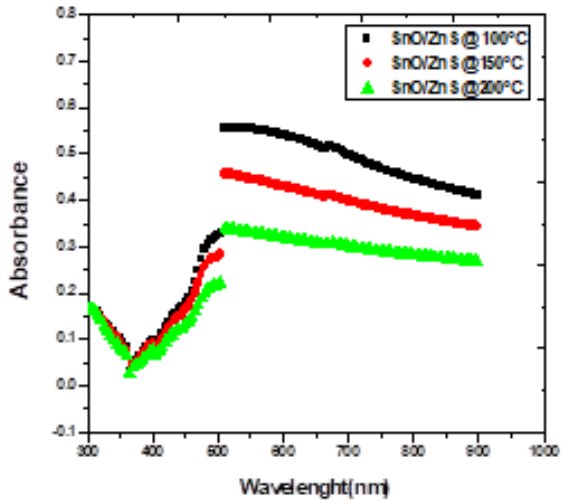

Fig. 2B: Plot of absorbance against wavelength for SnO/ZnS annealed at 100ºC, 150 ºC and 200ºC.

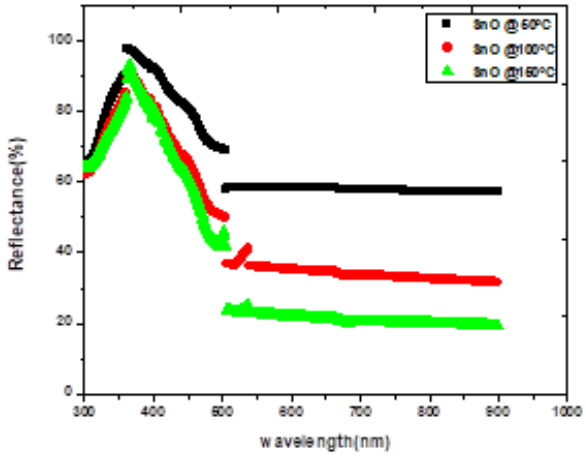

Fig. 3A: Plot of reflectance against wavelength for as-deposited SnO.

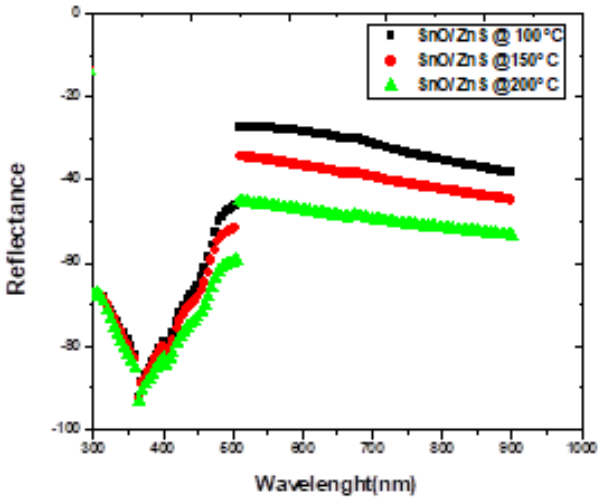

Fig. 3B: Plot of reflectance against wavelength for SnO/ZnS annealed at 100ºC, 150 ºC and 200ºC.

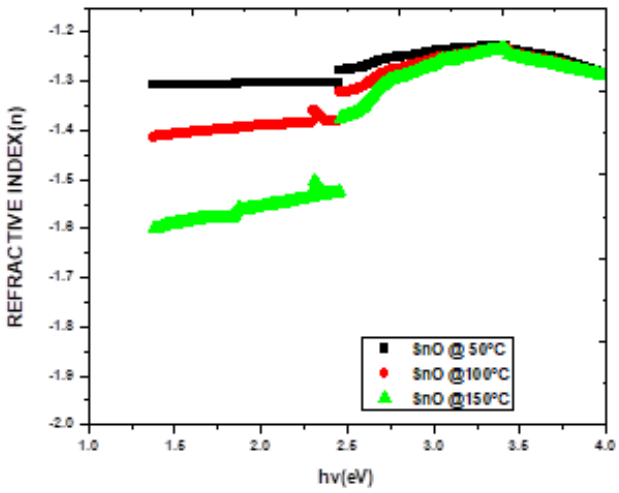

Fig. 4A: Plot of refractive index against photon energy for as-deposited SnO.

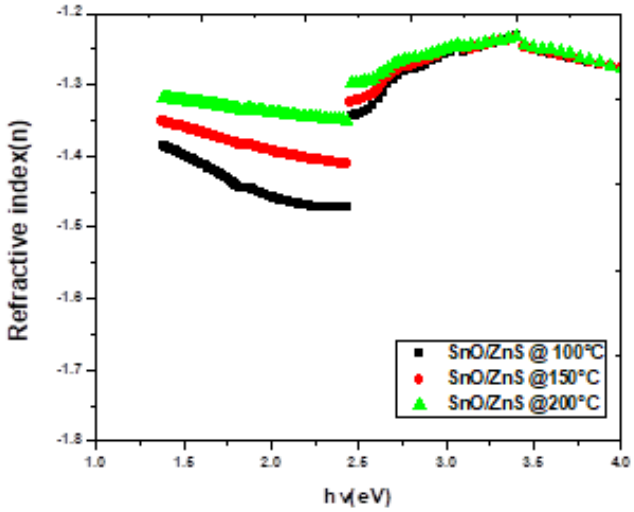

Fig. 4B: Plot of refractive index against Photon energy for SnO/ZnS annealed at 100ºC, 150 ºC and 200ºC.

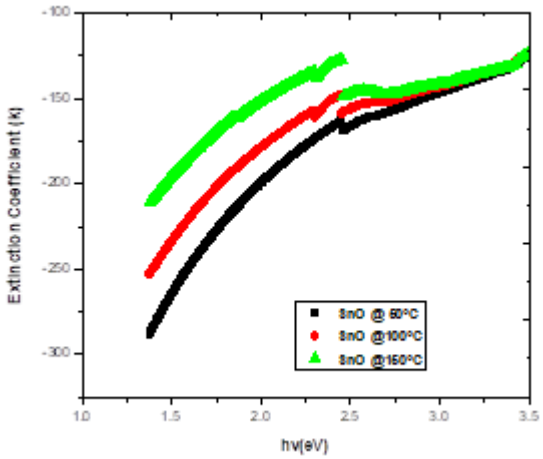

Fig. 5A: Plot of extinction coefficient (k) against photon energy for as-deposited SnO.

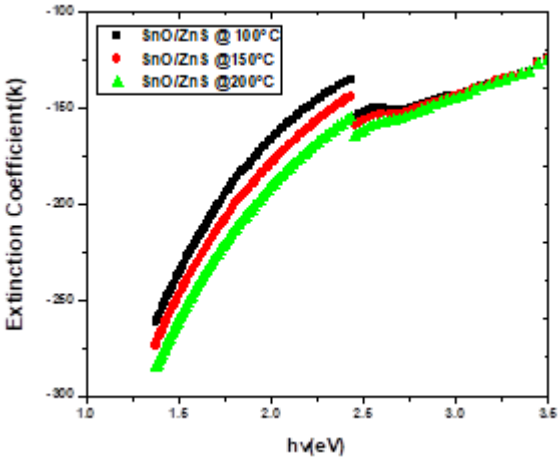

Fig. 5B: Plot of extinction coefficient (k) against Photon for SnO/ZnS annealed at 100ºC, 150 ºC and 200ºC.

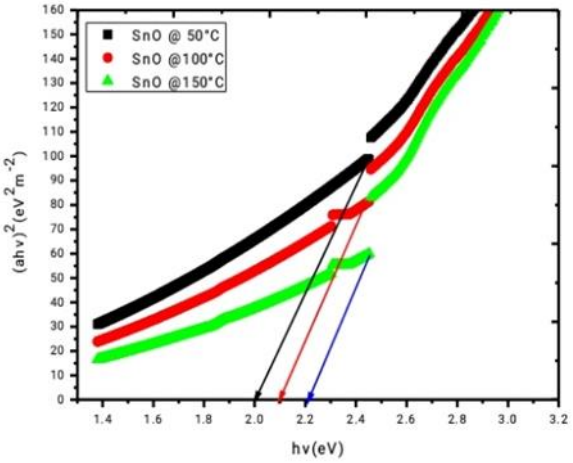

Fig.6A: plot of $(\alpha hv)^2$ againsthv for as-deposited SnO.

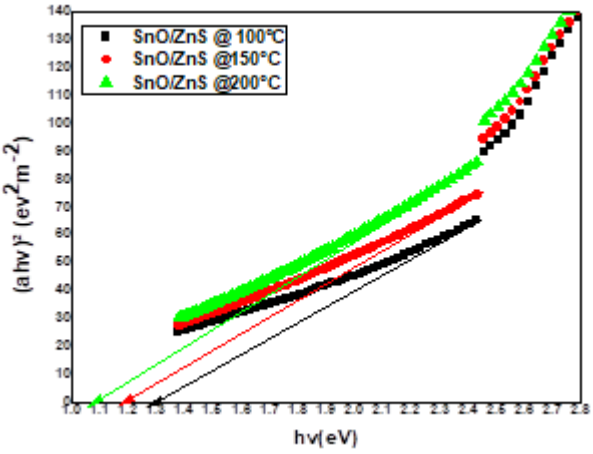

Fig 6B: plot of $(\alpha hv)^2$ againsthv for SnO/ZnS annealed at 100ºC, 150ºC and 200ºC.

The UV-visible transmittance spectral for the SnO thin film and SnO/ZnS biphasic thin films prepared at different substrate temperatures are presented in Figure 1A and B. From the figure, it can be seen that all SnO thin films and biphasic thin films have high transmittance in visible region of solar spectrum (> 95%). Relatively high transmission of all prepared SnO thin films and all biphasic films has sharp fall of transmission at band edge. This is an indication of low surface roughness and good homogeneity of thin films. Similar results have been reported in studies using CuS core shell in the recent years [10,11].

UV-V is spectroscopy has been done on all the five samples in the scanning range 300- 900 nm and at different substrate temperatures of 100 ^{0}C, 150 ^{0}C and 200 ^{0}C as shown in Fig. 2 (A-B). The plots show that the absorption spectral of the core SnO is showing a slight blue shift than the biphasic thin films which is usual nature of biphasic nanostructure. This is also in support of the findings of [3]. This blue shift could be attributed to quantum grain size in the films, due to their small crystalline crystals.

As shown in Fig. 2 (A-B), SnO and SnO/ZnS at different substrate temperatures, the absorbance decreases in the neighborhood of 300-350 nm, increases from 350-500 nm and then decreases from 500-900 nm. It is possible that this was caused by uniform adsorption of the formed oxide layer on the substrates, thus resulting in the decrease of the wavelength of thin film. However, the average absorption

of SnO/ ZnS composite was lower than that of the core SnO. This indicates that the formation of the SnO/ ZnS composites modified the absorbance spectra of the SnO (core) thin film. Moreso, SnO/TMCs (SnO/ ZnS) composites displayed better absorbance better in the visible region compared with other regions. These properties make the films potential coating materials such as anti- reflecting, eye glass and solar control coatings among others.

Figures. 3(A-B) depicts the plot of reflectance against wavelength for SnO and SnO/ZnS biphasic thin films deposited in this study. From the plots, all SnO thin film, the reflectance was high in the visible region between 300 and 350 nm and there is a sharp decrease in the reflectance in the wavelength range 0f 350-500 nm and then gradually decreased in the wavelength range 0f 500-900 nm. From the figures, it can be seen that the reflectance of the biphasic thin film showed a sharp drop in reflectance followed by a sharp increase in wavelength. The rate of increase of reflectance was very high at 500 nm of wavelength and then slowed down subsequently. This indicated that the formation of biphasic composites SnO/ ZnS completely altered the reflectance of spectra of SnO component which could be attributed to the rearrangement of the crystal lattice.

The highest reflectance value recorded was > 96 % for the core SnO thin film while lowest reflectance value was < 20% for the biphasic thin films. Reflectance value < 20% is an ideal for solar control glazing to avoid glare problems. They could be applied as thermal control and antireflection coatings since they exhibit high transmittance throughout the visible regions. This corresponds to the transmittance plot shown in Figure 3. The observed low- reflectance for the biphasic SnO/TMC thin films could be attributed due to high transmittance and high refractive index. [12, 13]

The refractive index against photon energy for the deposited SnO thin films and the biphasic thin films of SnO/ZnS are presented in Fig.4. Maximum refractive index of about 1.22 is displayed by the SnO thin film which is in close agreement to that obtained by [14]. The plots depicts that coating of the SnO thin film with ZnS has effect on the refractive index by increasing refractive index value of the biphasic thin films by 1.44. It is observed observed from the plot that the refractive index value of biphasic thin films tend to decrease as photon energy increases at a point the refractive index increases as a photon energy increases. This behavior was attributed due to the formation of the thin film oxide layer formed on the substrates during the deposition and hence, the optimum performance of the substrate was noticed.

The extinction coefficient (K) is a measure of light loss due to scattering and absorption per volume. The plot of extinction coefficient against photon energy for the deposited SnO thin and biphasic thin films at different substrate temperatures are shown in Fig.5. We observed a gradual increase in the K value towards the higher photon energy value. The plot depicts that the extinction coefficient decreases with increasing substrate temperatures. The results revealed that biphasic thin films were evenly distributed on the SnO thin film which makes the film homogeneous in the process. This is in line with findings of [19,20].

The relation between absorption coefficient and photon energy ($h\nu$) for the SnO thin film and SnO/ZnS biphasic thin films are shown in Fig.6 (A-B). From this relation, the optical band gap can be determined through the extrapolation of its linear portion of plot to zero absorption coefficient.The plot shows that the band gaps are 2.00 eV, 2.10 eV and 2.20 eV for the SnO thin film at 100 ^{0}C, 150 ^{0}C and 200 ^{0}C substrate temperatures respectively. The energy bandgap of SnO thin films with increase in substrate temperature indicated blue shift. This could be attributed to increase in crystalline size with substrate temperatures of 100^{o}C, 150^{o}C and 200^{o}C respectively. Increase in optical bandgap with increase in substrate temperature has been reported by [3,14]. A comparison of the plots for the determination of the bandgap indicates that the energy bandgap of the biphasic composites of SnO/ZnS are slightly lower than those of the SnO. This is an indication that the combination of SnO and ZnS components to form SnO/ZnS biphasic composite configuration (heterojunction) modified the SnO with fascinating synergetic properties offered by the composites shifted the fundamental absorption edge towards longer wavelength and consequently bandgap decreases. This provides tuning effect of the bandgap for specific application. As seen from the graph, the optical bandgap showed a red shift upon biphasic formation with the energy bandgap decreasing from 13.0ev, 1.20ev and 1.10ev for the investigated SnO/ ZnS thin films. The bandgap energy showed by these films make them ideal for use as window layer in heterojunction solar cells, CIGS solar cells, photonic devices, photovoltaic solar cells [17,18,21] and other applications. The observable breaks in the plotted graphs are shown in figures 1-6 (A and B) can be caused by quantum size effects associated with the phase transition resulting to deposition at different substrate temperatures of 100^{o}C, 150^{o}C and 200^{o}C [3,21].

X-ray diffraction (XRD) analysis

The XRD patterns of the deposited films are shown in figures 7A to 7B.

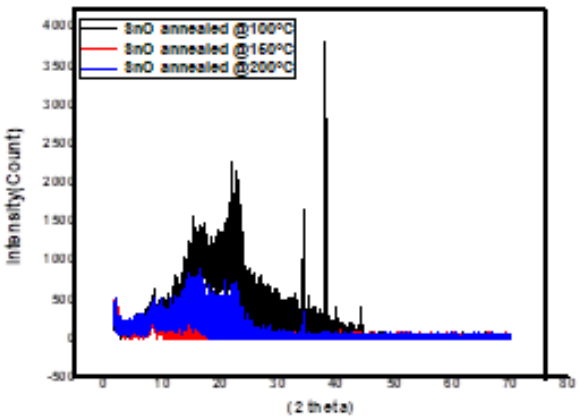

Fig 7A: XRD pattern of as-deposited SnO.

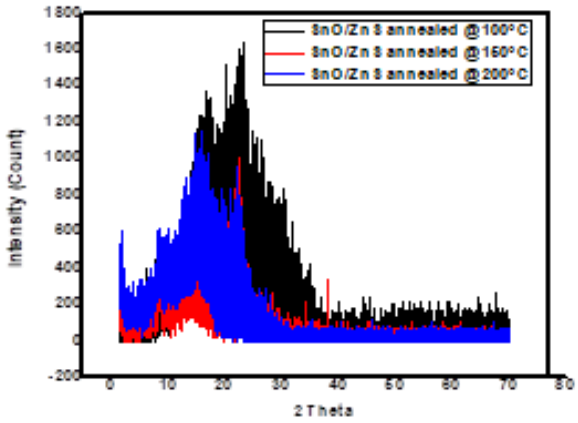

Fig.7B: XRD pattern of SnO/ZnS annealed at 100 ºC, 150 ºC and 200 ºC.

4.0 X-ray Diffraction analysis

The structure of the SnO thin films were studied using X-ray diffraction (XRD) technique. The diffraction spectra were measured at angle 2θ scanning from 0 to 90º deepens diffraction angle with CUKα radiation λ 2 1.54060nm). Figure 7A as deposited SnO thin films with slightly different thickness on glass deposited at different substrate temperatures. Peak broadening recorded diffraction pattern of the crystalline thin films in line with the results of the optical properties as observed in the graph for determination of the band gap energy. The peak broadening could be attributed to quantum size effect due to phase transition resulting to deposition at different substrate temperatures of 100ºC, 150ºC and 200ºC. The peak broadening could also cause by the thin films was not fully oxidized at these deposition temperatures since the melting point of tin is high (232º)C. XRD patterns with distinct diffraction peaks, corresponding to (111), (200) and (101) lattice planes or the cubic SnO obtained corresponds to the values of the inter-planar distance, d. These patterns indicate that the peaks increase in substrate temperature [14].

The XRD pattern of SnO/ ZnS deposited at different substrate temperature has peak broadening in the crystalline films. Study revealed that the films of SnO/ ZnS are polycrystalline in nature. The observed diffraction peaks found at 2θ values of 37.6º, 20º and 35º respectively corresponding to (101), (112) and (211) planes with low reflection peaks at (110), (114) and (105) planes. The observed variation difference of the peaks could be attributed to the interface between the SnO and ZnS atoms in the lattice of SnO/ ZnS and the non-uniformity in the evaporation process during the time of deposition.

5.0 Conclusion

On the basis of this study, the following conclusions are drawn:Spray pyrolysis deposition techniques have been successfully used to deposit tin oxide (SnO) thin films and the bisphasic nanostructured composites in the form of SnO/ZnS on glass substrate at different substrate temperatures of 100ºC, 150ºC and 200ºC.The results obtained in this study yield high quality layers of naonostructured composite thin films. The results confirmed that SnO thin films and biphasic composites (SnO/TMCs) have transmittance in UV-region at shorter wavelengths of solar spectrum > 90%. These properties make the composites materials useful in UV-photodetectors or sensors (UV light sensors/detectors), photonics, photocatalysts among other applications. The results obtained by absorbance spectra of the bisphasic composite thin films showed that they absorbed better in the visible region as compared regions. These properties make the films potential candidate for coating materials, anti-reflection coating and solar control, eye glass coating and solar cell fabrications. Other optical and solid-state properties such as absorption coefficient, extinction coefficient, and refractive index were evaluated. The evaluated bandgaps of biphasic composites are 1.30eV-1.10eV. These wide values of bandgaps make the films potential window layers for CIGS solar cells or photovoltaic cells, photonic devices and other applications. In addition, the XRD analysis reviewed that the films of SnO/ ZnS are polycrystalline in nature.

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