THE EFFECTS OF pH ON THE OPTICAL PROPERTIES OF MANGANESE ALLOYED ZINC SULPHIDE THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION TECHNIQUE.

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ABSTRACT
The effect of pH on the optical properties of manganese alloyed zinc sulphide thin films deposited by chemical bath method was studied. The bath precursors for the deposited ZnMnS thin films were zinc chloride ($ZnCl_2$) as source of Zn^{2+} ion, thiourea (H_2NCSNH_2) as source of S^{2+} ion, di-sodium ethylene-diamine-tetra-acetic acid, EDTA, ($Na_2C_{10}H_{14}N_2O_8.2H_2O$), tri-ethanol-amine (TEA) ($C_6H_{15}NO_3$) as the complexing agents, manganese tetra-oxo-sulphate (VI) monohydrate, ($MnSO_4.H_2O$) as source of Mn^{2+} ion, and ammonium hydroxide (NH_4OH) as pH adjuster. The deposition was carried out at room temperature of 303K in alkaline medium. Results of the study showed that the films have maximum absorbance of 0.5(50%) in UV region and minimum of 0.05(5%) in NIR regions, minimum transmittance of 37.50% in UV and maximum of 89.68% in NIR region, maximum reflectance of 0.20 in UV region and minimum of 0.05 in NIR region, minimum refractive index of 1.61 in NIR region and maximum of 2.64 in UV region, extinction coefficient of 0.04 in UV region and 0.004 in NIR region. Absorbance, reflectance, refractive index and extinction coefficient of the films increased as the pH of bath solution increased while transmittance decreased as it increased. The film has a band-gap of 3.88eV and is of interest for use as an absorber layer material in thin film photovoltaic solar cells.

Key words: Characterization, Thin films, Absorbance, Transmittance, and Band-gap.

1. INTRODUCTION

Thin film processing and the success of applications of these thin films based on new semiconductor materials depend on findings and compatible deposition technologies that are cost-effective and the techniques that will lead to large-area substrate coatings [1]. Due to their unique properties, which lead to new and exciting applications, thin films are increasingly gaining the attention of the scientific researchers and also the public [2]. Chalgonide metals of II-VI semiconductors account for the most investigated materials, due to their special properties [3][4][5]. An important question regarding thin films is concerned with the structural and dynamic changes that can occur upon replacement of either cations or anions in the binary or ternary based material. Modern day technology requires several types of thin films materials, which have been attracting an increasing interest for a variety of applications [6]. Thin films can be made of single or multi- compound (binary, ternary, or quaternary) depending on the elemental composition, alloy compound or multilayered coatings on substrates of different types, shapes or sizes [7].

Like other sulphide compounds, ZnMnS also attracted attention in the 1970 and 1980's for possible application as an optical storage medium [8][9]. However, recent investigations are directed towards studying its potential as a photovolatic or solar cell essentially due to its high absorption coefficient, low cost and low toxicity [10][11]. Being a layered chalcogenide, [12][13] of relatively low melting point[14], ZnMnS has been found to be a suitable candidate for thin film fabrication. The band-gap of the thin film semiconductor ZnMnS thin film is 3.80eV[15][16].While there is large number of reports on ZnMnS, more systematic studies have been undertaken considering its potential commercial application as a solar cell. Thin films of ZnMnS play an important role in various application fields such as energy sources, environment, health and medical treatments. It was reported for the first time that manganese alloyed zinc sulphide thin films were synthesized by chemical process, which have high efficiency of photoluminescence and ultrafast electron-hole recombination rate [17]. ZnMnS thin films were prepared by microemulsion method [18]. In this work, the effect of pH on the optical properties of manganese alloyed zinc sulphide thin films is investigated.

2. MATERIALS AND METHODS

Chemical bath deposition technique is used in the deposition of the thin films.
The precursors used in the deposition include zinc chloride ($ZnCl_2$) serving as source of Zn^{2+} ion, thiourea (H_2NCSNH_2) as source of S^{2+} ion, di-sodium ethylene-diamine-tetra-acetic acid (EDTA) ($Na_2C_{10}H_{14}N_2O_8.2H_2O$), tri-ethanol-amine (TEA) ($C_6H_{15}NO_3$) serving as the complexing agents, manganese tetra-oxo-sulphate (VI) monohydrate ($MnSO_4.H_2O$) as source of Mn^{2+} ion, and ammonium hydroxide (NH_4OH) serving as pH adjuster, glass slide substrates. All the chemicals used were of analytical grade. Two complexing agents were used to yield effective deposition, as only one complexing agent could not give impressing result within the stipulated time lapse. The slides before use were degreased in tri-oxo-nitrate (V) acid for 48hours, washed in cold water with detergent, rinsed with distilled water and dried in air. The degreased-cleaned surface provide nucleation centre for growth of the films, hence yielding highly adhesive and uniformly deposited films. The experiment was carried out at an average room temperature of 300K.

Five setups or reaction baths of different pH were prepared as shown in Table2.1. The concentrations and volumes of the precursors used are as shown in the table. The precursors for each setup is poured into a 100 ml beaker and stirred with glass rod to have a homogenous mixture before vertically inserting the glass substrate into the solution through synthetic foam. The stepwise reactions involved in the complex ion formation and film deposition processes for ZnMnS are stated below. Sulphide, S^{2-}, ions are released by the hydrolysis of thiourea, (H_2NCSNH_2)., and Zn^{2+} ions were released from the complex ion formed by the reaction of zinc chloride,($ZnCl_2$) with EDTA and TEA.

$$ZnCl_2 + EDTA \rightarrow Zn[EDTA]^{2+} + 2Cl^-$$

$$Zn[EDTA]^{2+} \rightarrow \boldsymbol{Zn^{2+}} + [EDTA]^{2-}$$

$$MnSO_4 + TEA \rightarrow MnTEA^{2+} + SO_4^{2-}$$

$$Mn[TEA]^{2+} \rightarrow \boldsymbol{Mn^{2+}} + TEA^{2-}$$

$$[NH_2]_2CS + OH^- \rightarrow [NH_2]_2CO^+ + HS^-$$

$$HS^- + OH^- \rightarrow H_2O + \boldsymbol{S^{2-}}$$

$$Zn^{2+} + Mn^{2+} + S^{2-} \rightarrow ZnMnS$$

Table 2.1: pH variation for deposition of manganese alloyed zinc sulphide (ZnMnS) thin films at room temperature

BATH NAME	$MnSO_4.H_2O$		$ZnCl_2$		EDTA		TEA		Thiourea		NH_4OH (10ml)	Time (Hrs)	pH	Temp (K)
	Conc. (Mol/dm^3	Vol (ml)	Conc. (Mol/dm^3)	Vol .(ml)	Conc. Mol/dm^3	Vol .(ml)	Conc. Mol/dm^3	Vol .(ml)	Conc. Mol/dm^3	Vol .(ml)				
MnZn Sp_1	0.5	10	0.05	5	0.5	5	0.5	5	0.25	10	10.0	24.0	**10.2**	300
MnZn Sp_2	0.5	10	0.05	5	0.5	5	0.5	5	0.25	10	10.0	24.0	**10.8**	300
MnZn Sp_3	0.5	10	0.05	5	0.5	5	0.5	5	0.25	10	10.0	24.0	**11.0**	300
MnZn Sp_4	0.5	10	0.05	5	0.5	5	0.5	5	0.25	10	10.0	24.0	**11.2**	300
MnZn Sp_5	0.5	10	0.05	5	0.5	5	0.5	5	0.25	10	10.0	24.0	**11.4**	300

3. THEORY

Calculation of optical properties

Optical properties of the films were calculated using the following formulae:-

Reflectance (R) $= 1 - (A + T)$ (1)

where A is absorbance, and T is transmittance [28].

Refractive index (η) $= \frac{1+\sqrt{R}}{1-\sqrt{R}}$ (2)

where R is reflectance. [29].

Absorption coefficient (α) $= \frac{A}{\lambda}$ (3)

where A is absorbance, and λ is wavelength [30][31].

Extinction coefficient (K) $= \frac{\alpha\lambda}{4\pi}$ (4)

where α is absorption coefficient, and λ is wavelength [30][31].

Photon energy (eV) $= E = h\nu$ (5)

Where **h** is Planck's constant = 6.63 x 10^{-34}Js**,** and **ν** is frequency of photon.

However, $\nu = \frac{c}{\lambda}$ (6)

Where **c** is velocity of light = 3.0 x 10^{8}m/s, and **λ** is wavelength.

Hence $E = \frac{hc}{\lambda}$, (7)

but $1eV = 1.602 \, x \, 10^{-19} J$,

Planck's constant $h = \frac{6.63 \, x \, 10^{-34} \, js}{1.602 \, x \, 10^{-19} j} \approx 4.14 \, x \, 10^{-15} \, eV$

Therefore, photon energy $E = \frac{4.14 \, x \, 10^{-15} \, eV \, x \, 3.0 \, x \, 10^{8} \, m/s}{\lambda(m)} = \cdots \ldots \ldots eV$

This is the band-gap energy, Eg [32].

4. RESULTS

4.3.2 pH Variation

(i) Absorbance (A)

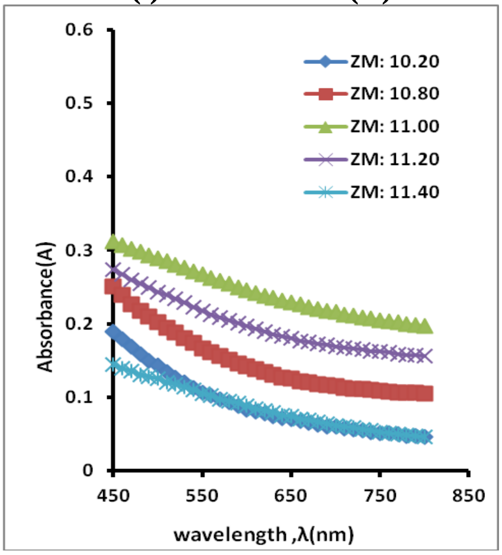


Fig 4.1: Graph of absorbance (A) versus wavelength λ(nm) for ZnMnS thin film.

(ii) Transmittance (T%)

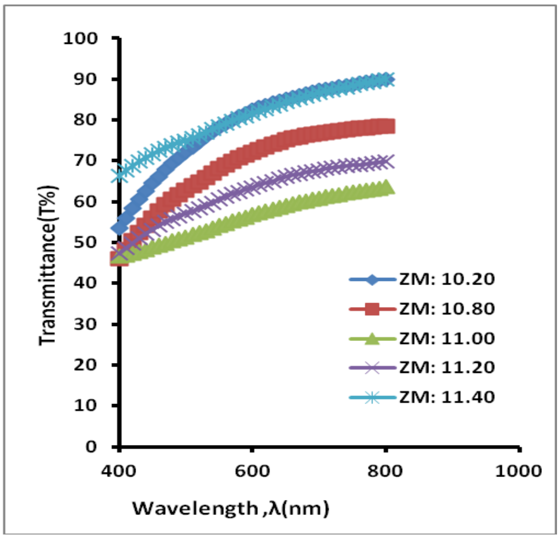
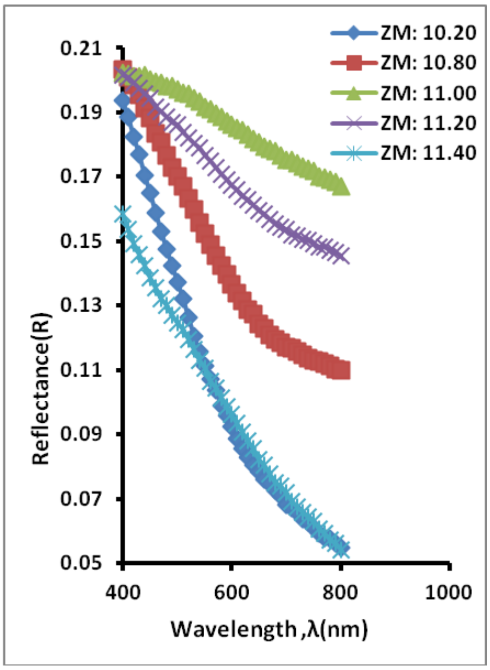


Fig 4.2: Graph of transmittance (T%) versus wavelength λ(nm) for ZnMnS thin film.

(iii) Reflectance (R)



(iv) Refractive index (η)

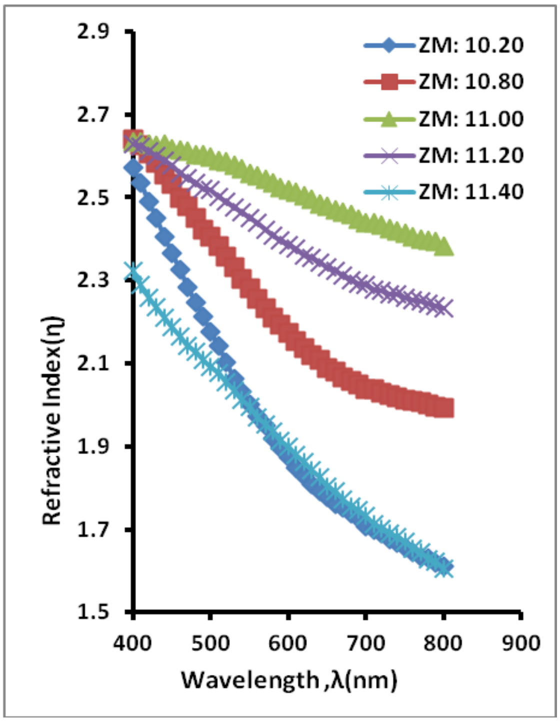


Fig 4.3: Graph of reflectance (R) versus wavelength λ(nm) for ZnMnS thin film.

Fig 4.4: Graph of refractive index (η) versus wavelength λ(nm) for ZnMnS thin film.

(v) Extinction coefficient (K)

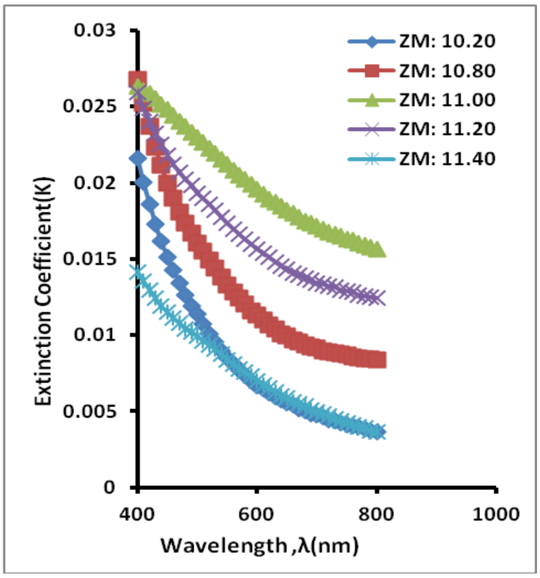


Fig 4.5: Graph of extinction coefficient (K) versus wavelength λ(nm) for ZnMnS thin film.

(vi) Complex dielectric constant ($\mathcal{E}_c$)

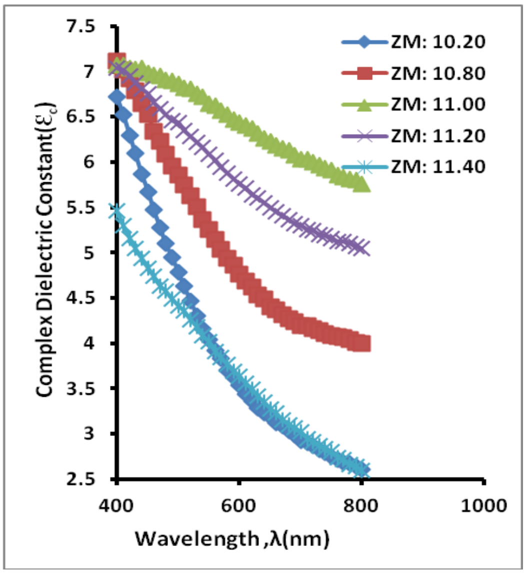


Fig 4.6: Graph of complex dielectric constant ($\mathcal{E}_c$) versus wavelength λ(nm) for ZnMnS thin film.

(vii) Optical thickness (µm)

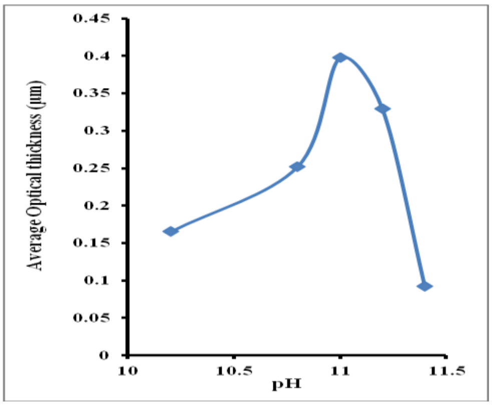


Fig.4.7: Graph of Average optical thickness(µm) versus pH for ZnMnS thin film.

(viii) Absorption coefficient squared (α^2)

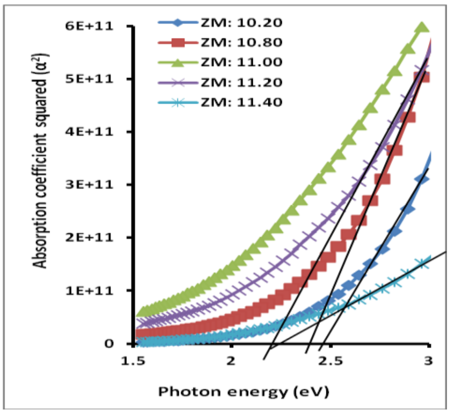


Fig 4.8: Graph of absorption coefficient squared (α^2) versus photon energy (eV) for ZnMnS thin film.

Average optical conductivity (S^{-1})

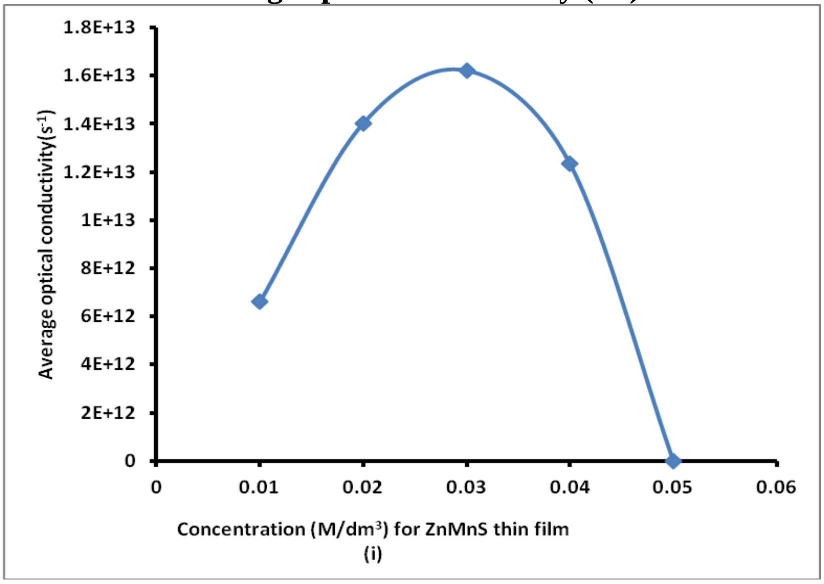


Fig.4.9: Graphs of average optical conductivity (µm)

4.3.7 Structural properties of manganese alloyed zinc sulphide, (ZnMnS), thin films

(a) Scan electron microscopy (SEM) of ZnMnS thin films

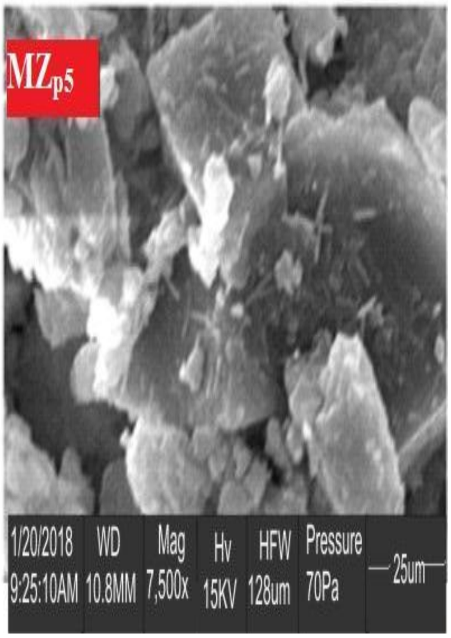


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Fig.4.10: SEM of ZnMnS thin film (11.40 pH value).

(b) Energy dispersive x-ray spectroscopy (EDXS) for ZnMnS thin films

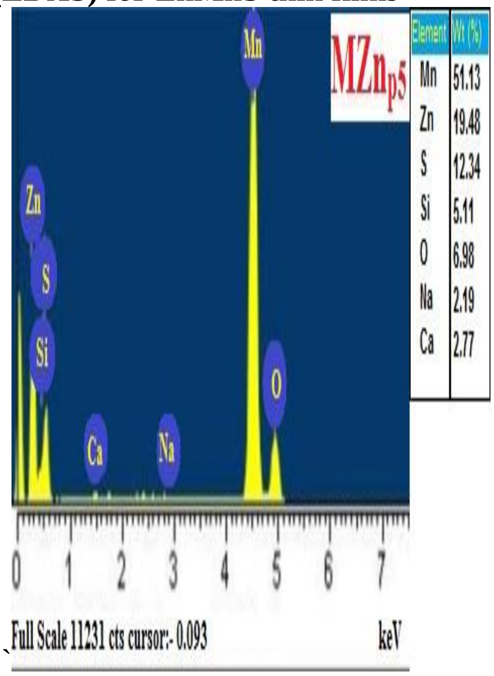


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**Fig.4.11: EDXS of ZnMnS thin film (11.40 pH value).**
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(c) X-ray diffraction (XRD) for ZnMnS thin films

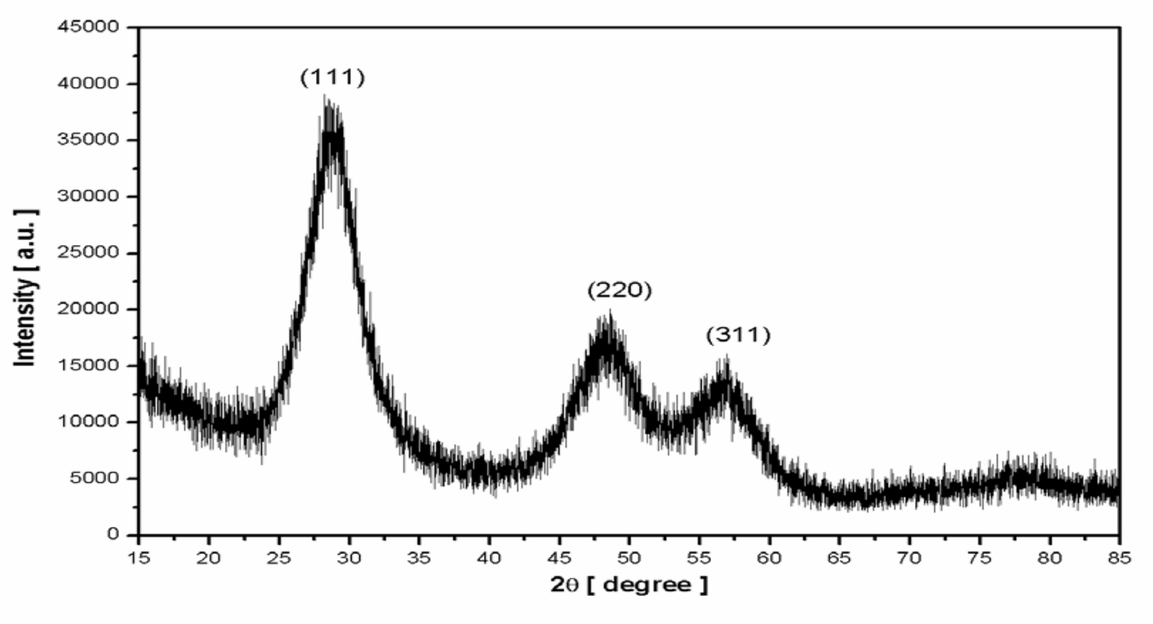

Fig.4.12: XRD pattern of alloyed ZnMnS thin film.

Table 4.1 XRD Analysis of Chemically Deposited ZnMnS thin film

Content	Structure	$2\theta^0$	FWHM (eV)	hkl	Lattice constants (Å)	d-spacing (Å)	Crystallite size (D) $x10^{-9}$ m	Dislocation density (ρ) $x10^{-13}$ (line m^{-2})	Microstrain (Ɛ) $x10^{-3}$
ZnMnS	Tetrahedral Crystalline Solid	28.50	3.36	111	a=3.2495 b=3.2495 c=5.2069	2.931	74.51	5.552	4.652

5. Discussion

From Fig.4.1, the films have low absorbance which decreases as the wavelength increases, maximum of 0.32 (32.00%) in VIS region and decreases to minimum of 0.05 (5.00%) in NIR region. The absorbance increases as pH of the bath solution increases. However, in higher pH values of 11.20 and 11.40, the films peeled off the substrate due to heavy thickening caused by impurity and started building up afresh. Fig.4.2 reveals that the films have high transmittance which increases as the wavelength increases, minimum of 45.59% in VIS region and increases to maximum of 95.68% in NIR region. The transmittance of the films increases as pH of the bath solution decreases. In higher pH values of 11.20 and 11.40, the films peeled off the substrate due to heavy thickening caused by impurity and the films started building up afresh. From Fig.4.3 the films have low reflectance which decreases as the wavelength increases, maximum of 0.205 (20.50%) in VIS region and decreases to minimum of 0.055 (5.50%) in NIR region. The reflectance increases as pH of the bath solution increases. In the higher pH values of 11.20 and 11.40, the films peeled off the substrate due to heavy thickening caused by impurity and the films started building up afresh. The low absorbance, reflectance and high transmittance in visible region makes the film a good material for solar cell. High transmittance in NIR region makes it a good material for photo-thermal heating. Fig.4.4 shows that the films have high refractive index which decreases as the wavelength increases, maximum of 2.68 in the VIS region and minimum of 1.64 in NIR region. This makes it a good material for film stack for antireflection coating. The refractive index increases as pH of the bath solution increases although pH values of 11.20 and 11.40 deviated as their films peeled off the substrate due to heavy thickening caused by impurity. From Fig.4.5, extinction coefficient of the films decreases as wavelength increases. It also increases as the pH of the bath solution increases. However, the pH values of 11.20 and 11.40 deviated as their films peeled off the substrate due to heavy thickening caused by impurity. Fig.4.6 shows that the complex dielectric constant maximum value of 7.25 and minimum value of 2.55. It increases as the pH value increases also. The optical thickness as shown in Fig.4.7 increases from 0.075μm to 0.40μm and as the pH value increases from 10.20 to 11.00, but is not favoured by the pH values of 11.20 and 11.40. Hence the pH values of 11.20 and 11.40 deviated as their films peeled off the substrate due to heavy thickening caused by impurity. From Fig.4.8, the films have a band-gap range of 1.88eV to 2.45eV, and decreases as the pH values increases.

From the Fig.4.9, the optical conductivity increases as the concentration of the bath solution increases from 0.01M to 0.02M except at the concentrations of 0.03M, 0.04M and 0.05M in which the optical conductivity decreases. That is to say those higher concentrations did not favour the optical conductivity.

Fig.4.10 reveals that the WD is 10.80mm, magnification of 7500x, Hv of 15KV, HFW of 128μm, pressure of 70pa, and scale measure of 25μm.

The EDXS analysis in Fig.4.11 shows that the films consist of major elements Mn 51.13; Zn 19.48; S 12.34, with other trace elements which could be from the substrate. This result confirms components of the thin film ZnMnS.

The XRD pattern in Fig.4.12 illustrates the three specific diffraction peaks originating from (111), (220) and (311) planes of the zinc blende structure. The peaks confirm the crystallinity of the films.

In Table 4.1, the XRD analysis shows that deposited thin film is crystalline which has a tetrahedral structure. The lattice constants are a = 3.2495 Å, b = 3.2495 Å and c = 5.2069 Å. The crystallite size of the film is 74.51nm, dislocation density of 5.552 x 10^{-13} (line m^{-2}) and the microstrain of 4.652 x 10^{-3} at hkl of 111, FWHM of 3.36eV.

6. CONCLUSIONS

Zinc manganese sulphide (ZnMnS) semiconductor thin film could be grown by chemical bath technique. The absorbance, reflectance, refractive index and extinction coefficient of the films increase as the pH of the bath solution increases while the transmittance decreases as it increases.

All the optical properties mentioned above decrease as the wavelength increases, except their transmittance which increases as the wavelength increases. Their thin film semiconductor materials of all the optical properties mentioned above are more sensitive and favourable for opto-electronic devices than the doped single or binary compounds. Hence they can be used for light emission devices (LED), and multi-junction solar cells, solar cars in solar arrays, and in fiber optic temperature sensors, near-infrared laser diodes, forward-looking-infrared (FLIR) grade, cathode ray tube screens, and x-ray tube screens that glow (luminescent) in the dark, and electroluminescent panels. They are used in thin film resistors, photo-resistors (light dependent resistors), cathodoluminescence (when excited with electron beam), conductivity increases when irradiated with light (used as a photo-resistor).

These findings are in agreement with other scientific researchers and technologists of thin films. According to them, the Visible Transmitting Film (VTF) has energy band gap ranging from 1.50eV to 3.90eV and since the as-grown thin films have energy band of range 1.88eV to 2.45eV, it then means that they are also Visible Transmitting Films (VTF), which behave more like transparent and ionic insulators.

However, chemo-dynamic reactions and thermo-dynamic reactions in the bath solutions caused by impurities resulted to certain deviations in the films which led to peeling off of the thin films from the substrate due to heavy thickening and the thin films started building up afresh.

7. REFERENCES

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