Estimation of Optical and Electrical Properties of Zirconium Sulphide Thin Films Prepared by the Chemical Bath Deposition Technique and Using a Spectrophotometer

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ABSTRACT

Thin films of Zirconium sulphide (ZrS_2) on glass substrate were prepared by the chemical bath deposition method and the investigation of the optical and electrical properties of the film was carried out using PYE-UNICAM SP8-100 spectrophotometer while energy dispersive x-ray fluorescence was used to show the elemental content of the deposited film. The film deposited is a relatively poor optical, thermal, and electrical conductor; with a refractive property that is below that of the substrate. The film has a direct band gap of between 2.40 and 3.70 eV and an indirect band gap ranging between 2.30 and 5.00 eV. These films show high transmittance above 90% in the UV-VIS-NIR regions while exhibiting poor reflectance below 10% in the same region. Therefore, they could be used for thermal control and antireflection coatings.

(Key words: energy dispersive x-ray fluorescence, thermal coatings, antireflection coatings, photothermal applications, photovoltaic applications, energy efficient glazing, ZrS_2)

INTRODUCTION

Chemical bath deposited films are being developed for use in solar energy and other photonic application such as photothermal and photovoltaic conversion [1-10]. They are also being developed in the area of energy efficient glazing, which includes decorative and protective coatings, and in imaging techniques. According to Pederson, thin film formation by chemical bath deposition techniques was employed originally in the commercial production of silver mirrors [6]. Thin films play a vital role in nearly all-electronic and optical devices. They are used as antireflection coatings on windows, video screens, camera lenses and other optical devices. These films are generally less than 100 nm thick and are made from a transparent (dielectric) material with a refractive index less than that of the substrate [11]. For most semiconductors and insulators (where $k^2 \ll n^2$) there exists a relationship between R and n given [9,12-13] as:

$R = (n-1)^{2}/(n+1)^{2}$ ------------------------------------ 1

There is also a relationship between k and α given [9,12-13] as:

$K = \alpha\lambda/4\pi$ -- 2

where α is the absorption coefficient of the film and λ is the wavelength of electromagnetic wave. The relationship between ε and k is given [9,12-13] as:

$\varepsilon = \varepsilon_r + \varepsilon_I = (n + ik)^2$ ----------------------------------- 3

where ε_r and ε_i are real and imaginary parts of ε respectively. Optical conductivity σ_o is given [9,12-13] as:

$\sigma_o = \alpha nc/4\pi$ -- 4

where c is the velocity of light. Electrical conductivity (σ_e) is given [14,15] as:

$\sigma_e = K^2/\omega$ -- 5

while thermal conductivity by Weidmann-Franz-Lorentz law [16,17] is given as:

$\sigma_t/(\sigma_e T) = (\pi^2/3)(k_B/e)^2 = \text{constant}$ ---------------6

with,

$\sigma_t = (\pi^2/3)\,\sigma_e(k_B/e)^2 T$ ------------------------------- 7

where K is wave number, ω is wave frequency, k_B is the Boltzman constant, e is electronic charge and T is absolute temperature of the film.

Direct energy from the sun will contribute so much to the future needs if performance of the existing devices (solar technologies) can be improved and the cost lowered. A fertile area of upcoming research relates to the materials and the processes of manufacture. In this view all technologies employing solar energy must incorporate the various aspect of material science more effectively.

EXPERIMENTAL DETAILS

The use of the chemical bath deposition techniques for the preparation of zirconium sulphide thin films requires a soluble or slightly soluble zirconium compound. The chemical baths consist of solutions of 2 – 5 ml of 0.1 – 0.01 M zirconium nitrate (technical) $Zr(NO_3)_4$; 2 – 5 ml of 1 M thiourea $(NH_2)_2CS$; 2 – 5 ml of 0.01 M EDTA; 0.1 – 2 ml of 1 M sodium hydroxide (NaOH) made up to a required volume with distilled water. EDTA and sodium hydroxide act as complexing agents, while NaOH is used to produce an alkaline medium favorable for the deposition of the film. Some of the chemical baths were left without EDTA while some were left without NaOH. The preparation of the substrates and stepwise deposition preparation of thin films have been reported in the literature [3,6,18].

Deposition times ranged from 6 hours to 24 hours at room temperature. After deposition the slides were removed, rinsed in distilled water, and air drip-dried.

The reaction equations are given as:

$$Zr\,(NO_3)_4 + EDTA \leftrightarrow (Zr\,(EDTA))^{4+} + NO_3^-$$

$$(Zr\,(EDTA))^{4+} \leftrightarrow Zr^{4+} + EDTA$$

$$(NH_2)_2\,C\,S + OH \leftrightarrow CH_2N_2 + H_2O + HS$$

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

$$Zr^{4+} + S^{2-} \leftrightarrow ZrS_2 \downarrow$$

Different reaction baths were prepared with different dip times and various quantities of the different components of reaction mixture were used in an attempt to optimize the results. In order to carryout the energy dispersive x-ray fluorescence (EDXRF) analysis, a cross section of the film was analyzed by using a focused electron beam. The elements present in the film were identified by the mean pulse heights (photon energies) at which peaks occurred and the concentration of the constituent elements were estimated from the peak heights (intensities). These were carried out using radioisotope 25 mCi Fe-55, 25 mCi Cd-109, and 30 mCi Am-241 that were used for excitation of the characteristic K-lines of light and medium elements. Light elements up to Chromium Z = 24, can be detected by the use of Fe-55 while medium elements from Germanium Z = 32 to Molybilium Z = 42, were effectively excited by Cd-109 sources. The Absorbance (A) of the film in the wavelength range 200-800 nm was studied using a spectrophotometer. These were used for the estimation of the optical and electrical properties such as refractive index (n), extinction coefficient (k), and dielectric constant (ε). Others include optical (σ_o), electrical (σ_e) and thermal (σ_t) conductivities. The optical method was used to estimate the thickness of the film, which has been discussed in literature [19].

RESULTS AND DISCUSSION

The energy dispersive x-ray fluorescence technique was employed to characterize the thin films. The blank background of the plain glass side (Table 1) was run to determine the elements present at different energy and fractional concentration.

Table 1: Energy Dispersive X- Ray Fluorescence Analysis Results of Reference Slide

Elements	E (KeV)	*INT (c/s)*	S	T	Conc. (fract)
K	3.312	0.040	1.97E+03	0.0025	7.84E–03
Ca	3.690	0.286	2.99 E+03	0.0033	2.89E–02
V	4.949	0.049	8.08 E+03	0.0066	9.05E–04
Fe	6.400	0.055	1.68 E+04	0.0131	2.45E–04
Pb	10.540	0.036	3.00 E+04	0.0462	2.59E–05
Rb	13.375	0.062	7.95 E+04	0.0783	9.86E–06
Sr	14.142	0.135	8.70 E+04	0.0876	1.75E–05
Zr	15.746	0.461	1.03 E+05	0.1072	4.10E–05
Mo	17.443	0.062	1.20 E+05	0.1275	4.01E–06

The coated glass slide (Table 2) with ZrS_2 was then introduced in the x-ray path. The zirconium peak was recorded at 15.746KeV with a fractional concentration 4.09E-05 and sulphide peak at 2.307 KeV with fractional concentration at limit of detection (LOD) of about 2.15E-03. On comparing the reference slide with the coated slide it is observed that other peaks appeared which were due to the composition of glass slides.

Table 2: Energy Dispersive X- Ray Fluorescence For ZrS2 Thin Film On Glass Slide.

Elements	E (KeV)	INT (c/s)	S	T	Conc. (fract.)
Ca	3.690	0.306	3.23E+03	0.0033	2.90E-02
Fe	6.400	0.071	1.81E+04	0.0130	2.99E-04
Rb	13.375	0.100	8.59E+04	0.0775	1.48E-05
Sr	14.142	0.146	9.40E+04	0.0867	1.76E-05
Zr	15.746	0.491	1.11E+05	0.1061	4.09E-05
Si	1.739	0.101	2.02E+03	0.0004	1.23E-01
S	2.307	0.014	9.34E+04	0.0007	2.13E-03
K	3.312	0.143	4.27E+04	0.0016	2.01E-03
Tl	4.508	0.033	1.18E+05	0.0029	9.60E-05

Different excitation sources were used which resulted in some discrepancies observed in elements for both the uncoated and the coated slides, for example in Table 1, the peaks of elements of V and Mo are observed are due to excitation sources 25 mCi Fe-55, and 25 mCi Cd-109 while in Table 2 the peaks elements of Si and Tl observed resulted due 30 mCi Am-241 excitation source. The fact that Zr appeared on the both the uncoated and coated slides shows that glass slides are rich in Zr. The difference in the intensity and concentration of both the uncoated and coated were the only evidence that elemental Zr from the starting solution was deposited on the slide. The sulphide intensity and concentration being low is evidenced by the fact that sulphur is not in the composition of glass, however, changing the concentrations of the starting solutions could increase such intensity and concentration.

The optical characterization of the Zirconium sulphide (ZrS_2) thin film was done using PYE UNICAM SP8-100 ultraviolet spectrophotometer in UV/visible range, which was used to estimate optical and electrical properties of the film.

The transmittance-reflectance spectra for the films produced with different reaction mixtures and dip times are shown in Figure 1. This shows a very high transmission above 90% on the average, for the UV/VIS/NIR regions. This could be useful in the coating of windows especially where much of the infrared radiation i is required to warm up the inside of and at the same time admit visible light.

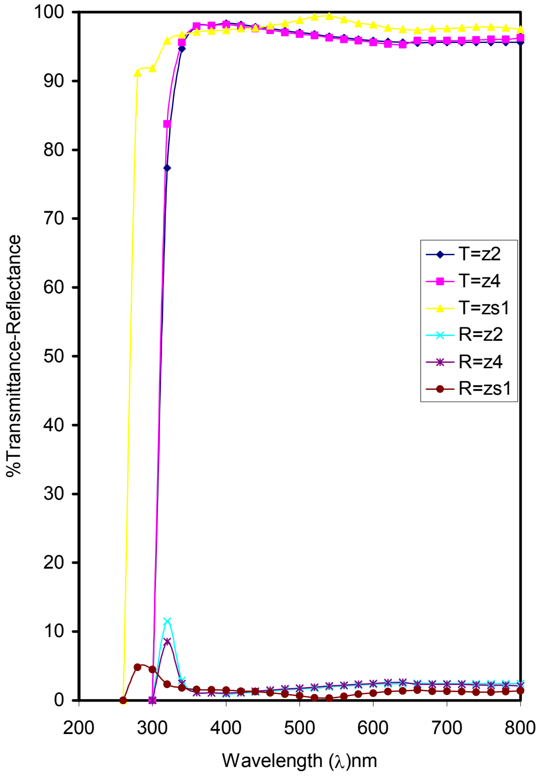

Fig. 1: Spectral Transmittance-Reflectance for ZrS_2 Film.

These transmittance spectra of Zirconium sulphide films make them suitable materials for thermal control and antireflection coatings. The optical and electrical properties of the film as estimated from spectrophotometer are shown in Table 3

The very small values of k and ε_i [20] shows that a material is an insulator, which is exhibited by ZrS_2 thin film. This indicates that ZrS_2 thin film is a poor optical and electrical conductor; hence the film deposited under this condition could serve as insulator.

The plots of log α against $h\nu$ are in Figure 2, which show that the film satisfies the exponential behavior of the absorption edge. The slopes remain unchanged which agrees with the finding

Table 3: Variations Of Optical And Solid State Properties With Photon Energy And Wavelength.

Λ (nm)	$h\nu$ (eV)	n	k $\times 10^{-3}$	ε_r	$\varepsilon_I \times 10^{-3}$	$\sigma_o \times 10^{14}\ s^{-1}$	$\sigma_e \times 10^{2}$ $\Omega^{-1}m^{-1}$	$\sigma_t \times 10^{-2} W^{-1}$ $m^{-1}K^{-1}$	$\alpha\tau \times 10^{14}$	$\alpha t \times 10^{-3} m^{-1}$
200	6.205	1.058	0.403	1.119	0.852	0.006	0.057	0.416	0.247	2.890
220	5.641	1.055	0.423	1.113	0.893	0.006	0.054	0.396	0.236	2.778
240	5.171	1.052	0.440	1.108	0.925	0.006	0.051	0.376	0.225	2.664
260	4.773	1.058	0.524	1.119	1.108	0.006	0.057	0.416	0.247	2.890
280	4.432	1.066	0.641	1.135	1.366	0.007	0.065	0.476	0.280	3.216
300	4.137	1.263	2.720	1.594	6.868	0.034	0.304	2.235	1.017	5.994
320	3.878	1.409	4.513	1.985	12.715	0.060	0.527	3.879	1.485	1.393
340	3.650	1.103	1.214	1.216	2.678	0.012	0.105	0.769	0.429	4.520
360	3.447	1.047	0.593	1.096	1.243	0.005	0.046	0.337	0.203	2.430
380	3.266	1.044	0.592	1.091	1.236	0.005	0.043	0.317	0.192	2.311
400	3.103	1.042	0.586	1.085	1.221	0.005	0.041	0.298	0.181	2.189
420	2.955	1.047	0.692	1.096	1.450	0.005	0.046	0.337	0.203	2.430
440	2.820	1.055	0.846	1.113	1.785	0.006	0.054	0.396	0.236	2.778
460	2.698	1.060	0.969	1.124	2.055	0.007	0.059	0.436	0.258	3.001
480	2.585	1.068	1.143	1.141	2.442	0.008	0.068	0.497	0.291	3.321
500	2.482	1.073	1.282	1.152	2.753	0.008	0.073	0.537	0.312	3.526
520	2.387	1.079	1.429	1.164	3.082	0.009	0.079	0.579	0.334	3.723
540	2.298	1.087	1.632	1.181	3.547	0.010	0.087	0.641	0.366	4.005
560	2.216	1.092	1.795	1.192	3.920	0.010	0.093	0.683	0.387	4.184
580	2.140	1.097	1.965	1.204	4.313	0.011	0.099	0.726	0.408	4.356
600	2.068	1.103	2.143	1.216	4.725	0.012	0.105	0.769	0.429	4.520
620	2.002	1.108	2.328	1.227	5.158	0.012	0.110	0.812	0.450	4.677
640	1.939	1.111	2.462	1.233	5.467	0.013	0.113	0.834	0.461	4.752
660	1.880	1.097	2.236	1.204	4.908	0.011	0.099	0.726	0.408	4.356
680	1.825	1.097	2.304	1.204	5.056	0.011	0.099	0.726	0.408	4.356
700	1.773	1.097	2.372	1.204	5.205	0.011	0.099	0.726	0.408	4.356
720	1.724	1.097	2.440	1.204	5.354	0.011	0.099	0.726	0.408	4.356
740	1.677	1.095	2.440	1.198	5.341	0.011	0.096	0.704	0.398	4.271
760	1.633	1.092	2.436	1.192	5.320	0.010	0.093	0.683	0.387	4.184
780	1.591	1.092	2.500	1.192	5.460	0.010	0.093	0.683	0.387	4.184
800	1.551	1.087	2.418	1.181	5.254	0.010	0.087	0.641	0.366	4.005

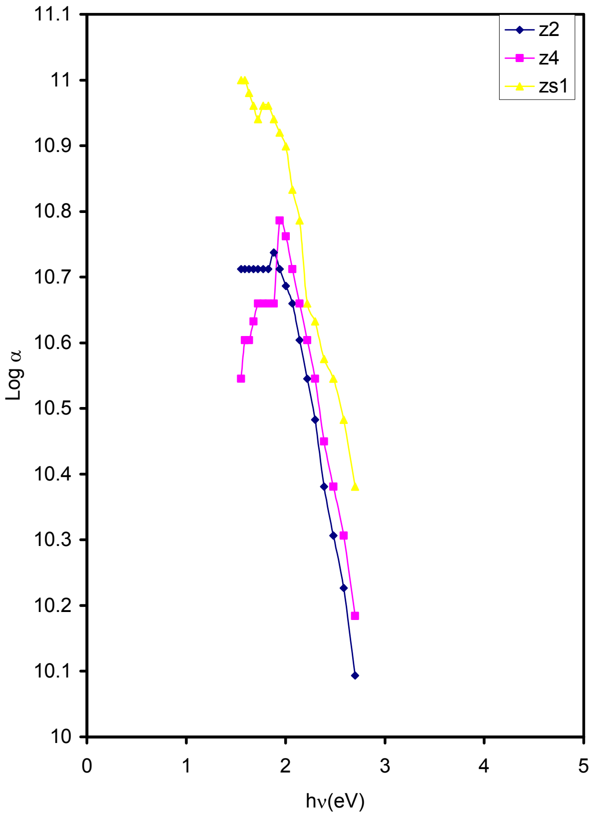

Fig. 2: Plots of Log α against hν for ZrS_2 Samples.

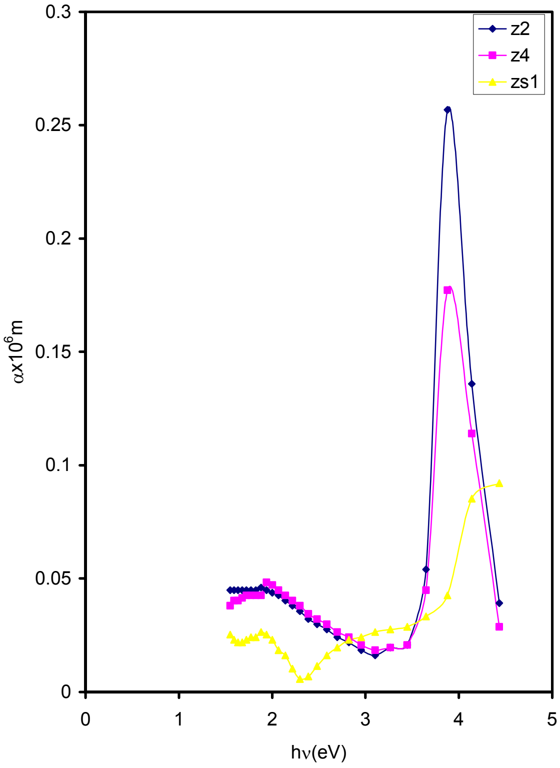

Fig. 3: Plots of Absorption Coefficient α against Photon Energy for Samples of ZrS_2 Film.

of Fayek et al [21] on crystalline and amorphous materials. Figure 3 gives the variation of α with photon energy (hν) studied for ZrS_2 samples. There are absorption edges, which are characteristics of crystalline state of the film.

In both crystalline and amorphous semi-conductors, near the fundamental absorption edge, there is the dependence of absorption coefficient on the photon energy. In high absorption region, the form of absorption coefficient with photon energy is given in a more general term [13, 22] as:

$$\alpha h\nu = A\,(\alpha h\nu - Eg)^{n} \quad \text{----------------------------------} \ 8$$

for direct transitions, and:

$$\alpha h\nu = B\,(\alpha h\nu - Eg)^{n} \quad \text{---------------------------------} \ 9$$

for indirect transitions, where ν is the angular frequency of the incident photon, h is Plank's constant, A and B are constants, Eg is the optical energy gap and n is the number which characterizes the optical processes. The variable n has the value .5 for the direct allowed transition, 1.5 for forbidden direct allowed transition and 2 for the indirect allowed transition.

The usual method for determining the values of Eg involves plotting of $(\alpha h\nu)^{n}$ against hν. If appropriate value of n is used to get the linear graph, then the value of Eg will be given by the intercept on the hν axis. These results were found to obey equation 8 for n=1/2 direct photon transitions, and n =2 for indirect photon transitions as shown in figures 4, and 5 respectively. The film has direct band gap between that range between 2.40 and 3.70 eV and indirect band gap that range between 2.30 and 5.00 eV.

CONCLUSIONS

We have successfully grown thin films of Zirconium sulphide using EDTA and sodium hydroxide as complexing agents in chemical baths. The films were characterized using PYE UNICAM SP8-100 ultra violet spectrophotometer and EDXRF. The EDXRF shows the elemental contents of the thin films. The characterizations reveal film thickness between 0.034 – 0.058 μm with average n ranging between 1.38 – 1.55 and

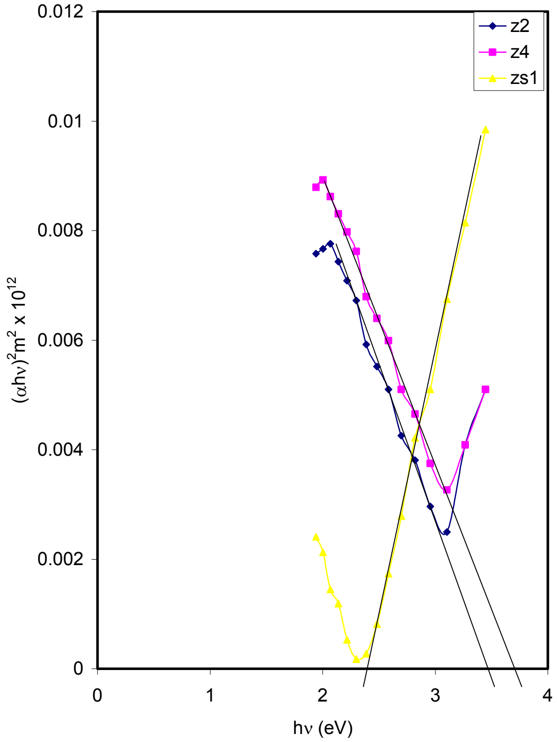

Fig.4: Plots of $(\alpha h\nu)^2$ against hν for ZrS_2 Samples.

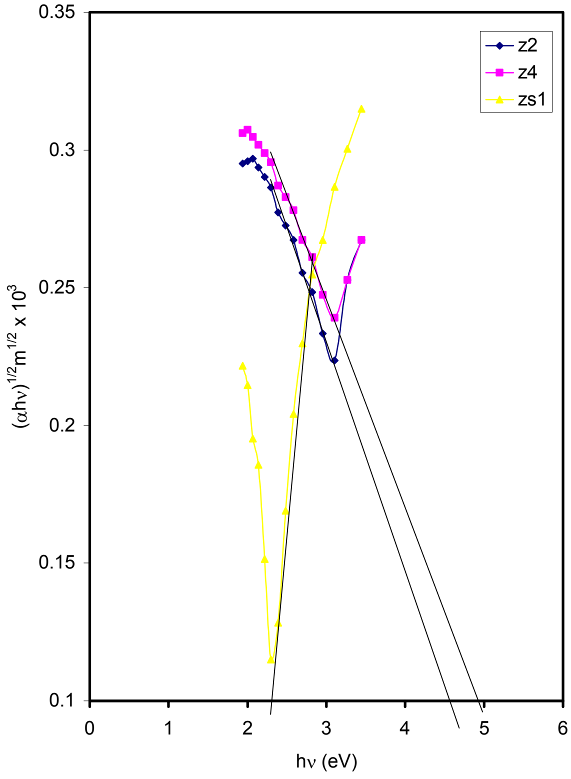

Fig.5: Plots of $(\alpha h\nu)^{1/2}$ against hν for ZrS_2 Samples.

with high transmittance between 77 and 98%. The film has direct band gap that range between 2.40 and 3.70 eV and indirect band gap that range between 2.30 and 5.00 eV. This could be useful in the coating of windows especially where much of the infrared radiation is required to warm up the inside of the container/vehicle and at the same time allow the admittance visible light. These transmittance spectra of Zirconium sulphide films make them suitable materials for thermal control and antireflection coatings.

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