SOLUTION GROWN, CHARACTERIZATION AND POSSIBLE APPLICATIONS OF COBALT SULPHIDE (CoS) THIN FILMS

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ABSTRACT

Good uniform thin films of cobalt sulphide (CoS) were successfully deposited on glass slides by improved solution growth technique (SGT) at 300K for 24 hours and at pH of 7 - 12. The effects of deposition bath pH and constitutions were studied. Optical properties of the deposited thin films were dependent on the pH values. Average values of optical properties include transmittance (T) from 0.822 to 0.899, refletance (R) from 0.055 to 0.093, coefficient of absorption (α) from 0.106 x 10^4 to 0.196 X 104 cm^{-1} and refractive index (n) from 1.61 to 1.88. The solid state properties include bandgap Eg from 2.12 to 2.66 eV, electrical conductivity (σ) from 0.90 x 10^{-3} to 1.53 X 10^{-3} $(ohm-cm)^{-1}$ and film thickness (t) from 383 to 487 Å. Films with refractive index (n) lower than 1.8 have high transmittance (T) and low reflectance (R) characteristics. Those with refractive index (n) greater than 1.8 have low transmittance (T) and high reflectance (R) properties. Possible applications of the deposited thin films were discussed.

INTRODUCTION

A number of studies on the deposition of thin films by solution growth techniques (SGT) have been published. The technology is one of the intensively studied thin film deposition methods for the preparation of various metal halide and chalcogenide films (Chopra and Das, 1983; Gang, 1984; Eze and Okeke, 1997; Okujagu and Okeke, 1997, Ilenikhena and Okeke, 2001 and 2002). This technique is simple, cheap, convenient, reproducible and easy for the coating of large surfaces.

Little report have been seen on cobalt sulphide (CoS) films. Black cobalt sulphide film was produced on nickel substrate by Smith and Ignatiev (1980) using electrodeposition technique. The film has a good selective absorbance and small reflectance spectra in the visible and near infrared regions. Basu and Pramanik (1986) used solution growth technique (SGT) with thioacetamide as complexing agent to produce cobalt sulphide (CoS) films. Ndukwe (1992) used solution growth technique (SGT) with triethanolamine (TEA) to produce cobalt sulphide (CoS) films on glass substrate. The author obtained a direct bondgap of 3.2 to 3.4 eV, refractive index of 2.62 and film thickness of 3400 to Eze and Okeke (1997) used solar assisted and an indoor solution growth technique with ammonia as complexing agent to produce cobalt sulphide (CoS) films at different deposition temperatures and times. They obtained film thickness which varies from 2100 to 5,100 A.

This paper report the deposition of good quality cobalt sulphide (CoS) thin films on glass substrate using improved solution growth technique with ammonia and triethanolamine as complexing agents at of 7 to 12 and at 300K for 24 hours.

EXPERIMENTAL DETAILS

Sample Preparation

Good quality thin films cobalt sulphide (CoS) were successfully produced on glass slides by solution growth technique (SGT) at 300K for 24 hours, using improved growth characteristics at pH of 7 - 12. The bath constitutions were 0.36M cobalt (II) chloride - 6 - water ($CoCl_2 \cdot 6H_2O$), 5.0M ammonia (NH_3) with 1.0M triethanol-amine (TEA) as complexing agents, 2.5M sodium hydroxide (NaOH) and 0.8M thiourea $[(NH_2)_2CS]$.

Distilled water was added to make the volume up to a required level in 50ml glass beakers while 0.25M ethelenediamine-tetrea acetate ($C_{10}H_{16}O_8N_2$) or EDTA solution was used to vary the pH values of the initial bath solutions. All the reagents were of the analytical reagent (A.R.) grade. Several bath constitutions were employed by varying the volumes of the bath constitutions. The bath mixtures were stirred using a glass rod. The pH values of 5-12 of the initial bath solutions were determined using Kent EIL 3055 digital pH/ Temperature meter.

Finally, a clean commercial-quality glass microscope slide (76 mm x 26mm x 1mm) was suspended vertically at the centre of each of the freshly prepared bath solution at room temperature (300K) for 24 hours. Each slide was positioned vertically from synthetic foam cover and clamped at the top with a plastic peg for chemical deposition. Prior to deposition, the glass slides were thoroughly cleaned by degreasing them in concentrated hydrochloric acid (HCl) for three days, washed in detergent solution, rinsed in distilled water, drip dried in air and were weighed by means of Mettler AE166 analytical balance. After deposition, the films were rinsed in distilled water, drip dried in air and reweighed. The deposited films on glass slides were obtained in alkaline medium at pH of 7-12. The details of the deposition bath constitutions of the various cobalt sulphide (CoS) thin film samples are shown in Table 1.

Film Characterization

The spectral absorbance (A) and transmittance (T) of the uncoated glass slide and the deposited thin firms on glass were obtained by a single beam CECIL CE1010 spectrophotometer in the ultraviolet (UV), visible (VIS) and near infrared (NIR) regions of the electromagnetic spectrum. Spectral reflectance (R) was obtained from the relationship between these qJlantities (Lampert, 1989) which allows for conservation of energy:

$$A + T + R = 1 \qquad (1)$$

The coefficient of absorption (α) was calculated (Cothiam, 1958) from the equation:

$$\alpha = \ln (T^{-1}) \times 10^{4}\,\mathrm{cm}^{-1} \qquad (2)$$

Refractive index (n) was computed (Pankova, 1971) from the expression:

$$n = (1 + R^{1/2}) / (1 - R^{1/2}) \qquad (3)$$

The values of the bandgap (E_g) were computed from relationship (Pankova, 1971; Harbeke, 1972 Chopra and Das, 1983) for possible transitions across the energy gap of a semiconductor. The optical absorption coefficient for direct transitions is given by

$$\alpha = A\,(h\nu - E_g)^{1/2} \quad \text{or}$$
$$\alpha^{2} = A^{2}\,(h\nu - E_g) \qquad (4)$$

where for allowed transition, $A = 3.38 \times 10^{5}\, n^{-1} (m_r/m_o)^{1/2} (Eg/h\nu)$, m_o is the free electron mass, n is reflective index and hν is photon energy.

For forbidden transitions,

$$\alpha = A\,(h\nu - E_g)^{3/2} \qquad (5)$$

where A is a slowly varying function of energy. The values of Eg were obtained from the straight line portion' of plots'of α^2 Vs hν for allowed transitions when extrapolated to the portion $\alpha^2 = 0$. The electrical conductivity (σ) of the films was obtained from the expression:

$$\sigma = 1/\rho = d/Sr \qquad (6)$$

where ρ is electrical resistivity, d is spacing of electrodes, S is area of the film and r is electrical resistance of the film. The value of electrical resistance of the film was determined by universal bridge B 150/3. Average film thickness (t) obtained by the optical method for films with absorbance (A) > 0.1 (Pankova, 1971 and Harbeke, 1972) at wavelength, A = 660nm is given by equation:

$$t = \ln [(1 - R)^{2}/T]/\alpha \qquad (7)$$

while the average thickness (t) of films with absorbance (A) < 0.1 (Theye, 1985) at wavelength, λ = 660nm is given by the equation:

$$t = \frac{\left\{ \mathrm{Tan}^{-1} \left[\dfrac{(n_o + n_s)2R - (n_o - n_s)^{2}}{(n_o n_s/n'')^{2} - (n_o n_s/n'')^{2} R} \right]^{1/2} \right.}{2\pi n}\,\lambda \qquad (8)$$

where n_o is the refractive index of the medium of incident light, n_s is the refractive index of the substrate, n is the refractive index of the film, R is the reflectance and λ is the wavelength of light.

Table 1: Details of deposition bath constitutions of various cobalt sulphide (CoS) thin films

Deposition			Volumes of bath solution (ml)						
Bath Solution PH	Temp. (K)	Temp. (hrs)	$CoCl_2.6H2O$ mol. = 0.36M	NH_3 Mol. = 5M	TEA Mol. = 1M	NaOH Mol. = 2.5M	$(NH_2)_2CS$ Mol = 0.8M	H_2O	EDTA Mol. = 0.25M
5	300	24	9	2	1	1	5	22	32
6	300	24	8	2	1	1	6	22	30
7	300	24	8	3	2	2	6	19	26
8	300	24	7	3	2	2	7	19	26
9	300	24	7	4	3	3	7	16	21
10	300	24	6	4	3	3	8	16	20
11	300	24	6	5	4	4	8	13	18
12	300	24	5	5	4	4	9	13	15

The surfaces of the deposited thin films were observed using an electron microscope (Leitz Periplan Diaplan SE 2344) at a magnification of 400X. The x- ray diffraction patterns of uncoated glass and deposited films on glass were obtained by Diano Corporation X – ray diffractometry model XRD 2100* E which uses a copper target (Cuk_α =1.540502, current 30m A and accelerating voltage 45kV).

RESUL TS AND DISCUSSION

Effects of pH and complexing agent

It was observed that cobalt sulphide (CoS) films were deposited on glass only in alkaline medium. The chemical reaction for the deposition is given by the equation:

$$CoCl_2.6H_2O + NH_3 + (NH_2)CS + 20H^- \rightarrow CoS\downarrow + CH_2N_2 + 8H_2O + NH_3 + Cl_2$$

We observed during deposition of the films that the concentration of the bath constitutions has significant effects on the film formation.

For example, low concentration of the complexing agents, results in incomplete formation of the complex ions of Co^{2+}, spontaneous precipitation of the salt materials in solution and no deposition of the films. In some cases, powdery or amorphous films were obtained. Very high concentration of the complexing agents reduced the concentration of the metal ions due to the formation of the metal complex ions instead of the metal chalcogenide films.

Optimum concentration of the starting materials, complexing agents and deposition time were favourable for the formation of good quality cobalt sulphide (CoS) thin films.

Optical and Solid State Properties

The spectral transmittance (T) and spectral reflectance (R) of the uncoated glass slide and cobalt sulphide (CoS) thin films deposited on glass at pH of 7 -12 and 300K for 24 hours are shown in Figure 1. The deposited of CoS films on glass slides modify the spectral transmittance (T) and reflectance (R) Rroperties of the glass at differentwavelength regions, depending on the film thickness, and thus making it spectrallyselective. Apart from the film produced at pH of 9, the spectral transmittance (T) values of the deposited films on glass are high while the spectral reflectance (R) are low. The transmittance (T) rises sharply with increasing wavelength (λ) .from ultraviolet (UV) tosome values at about λ = 420 nm and later increases slowly in the visible (VIS) region to some values at about λ = 860nm and later increases_slowly in the near infrared (NIR) region, depending on the film absorbance (A). The values of transmittance (T) range from 0.815 - 0.824 in the ultraviolet (UV) and from 0.877 - 0.936 in the visible (VIS) and near infra red (NIR) regions of electromagnetic spectrum. The spectral reflectance (R) decreases sharply with increasing wavelength (λ) from the ultraviolet (UV) to some values at about λ = 420 nm in the visible (VIS) region and decreases slowly into the near infrared (NIR) region to some values at about λ = 940nm in the near infrared (NIR) region, depending on film absorbance (A). The low values of spectral reflectance (R) decrease from 0.109 to 0.065 in the ultraviolet (UV) region and to about 0.058 in the visible (VIS) and near infrared (NIR) regions. The film produced at pH of 9 has relatively low spectral transmittance (T) and high reflectance (R). It was observed that films with high transmittance (T) have low reflectance (R) and vice versa. Average values of coefficient of absorption (α) of the films produced at pH of 7 - 12, with the exception of the film produced at pH of 9, range from 0.106 - 0.159 x 10^4 cm^{-1}. The average value of coefficient of absorption of film produced at pH of 9 is 0.196 x 10^4 cm^{-1}. This large α value of 10^4 cm^{-1} is within the a range of 10^4 - 10^5 cm^{-1} for semiconductor thin film desirable for the production of polycrystalline thin film solar cells (Meakin,1989). The variation of refractive index (n) with -photon energy (hv) of the deposited cobolts sulphide (CoS) thin films on glass at pH of 7 - 12 is shown in figure 2. Values of refractive index (n) range from 1.51 to 2.13. It is observed, from figures 1 and 2, that the deposited CoS thin films with refractive index (n) lower than 1.8 have high spectral transmittance (T) and low spectral reflectance (R). Films with n greater than 1.8 have low spectral transmittance (T) and high spectral reflectance (R). The average optical properties of the deposited CoS thin films at wavelength, λ = 660nm is shown in table 2.

The deposited CoS thin films with high transmittance (T), low reflectance (R) (or low thermal emitance) and low refractive index (n) could find useful applications in: (i) thermal control window coatings for cold climates and heat mirror coatings for temperature regions with very cold winter (Lampert, 1979) where windows cause loss of energy mainly by thermal radiation to environment. (ii) films with low refractive index (Lampert, 1979, 1989; Ndukwe, 1992) could find applications in production of antireflection coatings on transparent covers or windows of solar thermal devices. The films produced at pH of 9 with low transmittance, high reflectance and high refractive index could find useful applications in: (i) the construction of poultry houses (Ileje, 2000) to allow enough infrared (IR) radiation to warm the day old chicks during the day and reduce the high cost of energy consumption in providing heat to warm the chicks especially in remote and rural areas where electricity is not accessible. They will also reduce the hazards associated with the use of lamps, stoves and electric bulbs while at the same time protecting the chicks from ultraviolet radiation. (ii) eyeglass coatings to protect the skin around the eye from sunburn (Ndukwe, 1992) which is common among persistent eyeglass users. (iii) the production of antidazzling coatings (Ndukwe, 1992) for car windscreens and driving mirrors to reduce the dazzling effect of light at night. (iv) the production of cold mirror coatings (Lampert, 1979) for tropical regions with very hot summer to cool the interior by increasing thermal losses from the heated interior to exterior and screening the interior from excessive thermal energy from incoming solar radiation during summer and (v) the manufacture of thin film solar cells (Markvart, 2000).

The values of bandgap (E_g) of the deposited thin films range from 2.12 - 2.66eV. The average film thickness (t) obtained by optical method at wavelength, λ = 660nm ranges from 383 - 487 Å. The bandgap values of 2.12 - 2.66eV and film thickness of 3.83 - 487 Å are relatively low when compared with bandgap values of 3.2 - 3.4 eV and film thickness 3400 to 5700Å reported by Ndukwe (1992). The values of the bandgap and film thickness compared favourably with cadmium sulphide (CdS) thin film which has a bandgap of 2.4eV. The bandgap values are within the visible region (~1.5 – 3.0eV) of the electromagnetic spectrum and could be employed in the production of solar electricity for rural electrification and communication. The low values of film thickness compares favourable with thin film layer of few hundreds angstrom required for active semiconductor materials with large α values used in thin film solar cells (Davis *et al*., 1979). Electrical conductivity (σ) of the film varies from 0.90 - 1.33 x 10^{-5} (ohm -cm)$^{-1}$ within the range of 10^{-12} - 19^{2} (ohm - cm)$^{-1}$ for semi conductors (Webber *et al*., 1974; Pohl, 1962; Inokuchi and Akamatu, 1963; Paushkin *et al*. 1994). The values of the solid state properties, shown in table 3, could be employed in solar energy and other photonic applications. The surfaces of the deposited CoS thin films, observed under electron microscope, shown in figure 4, reveal the presence of some granular particles. X-ray diffraction patterns of the uncoated glass and the deposited CoS thin films, in figure. 5, on glass substrates show some peaks in the coated samples and hence the crystalline nature of the deposited films.

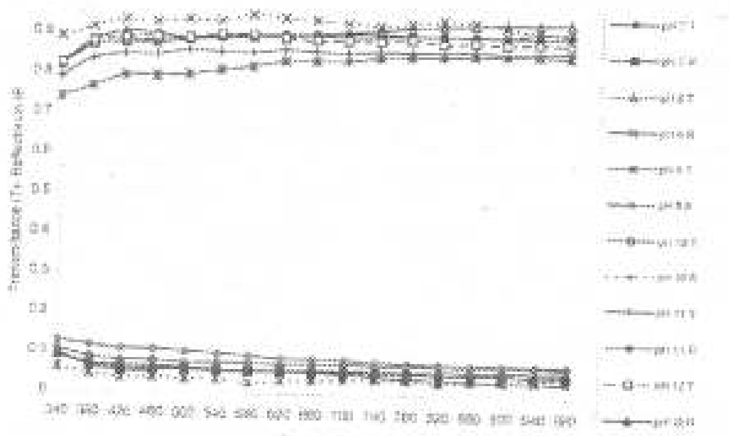

Fig. 1: Transmittance (T), reflectance (R) spectra of uncoated glass slide and CoS thin films deposited on glass by solution growth technique at pH of 7 - 12 and 300K for 24 hours

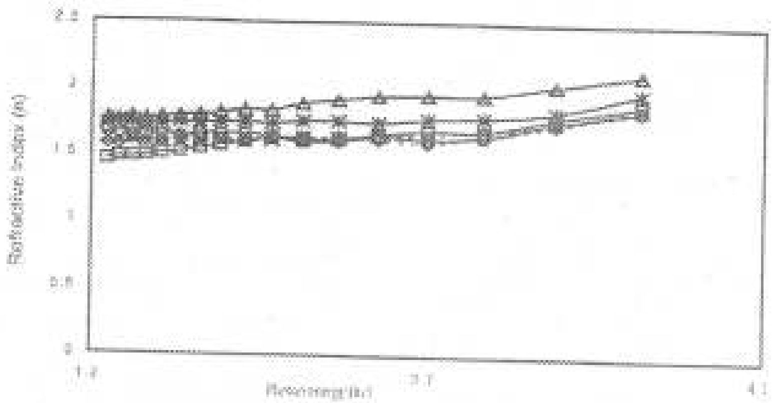

Fig. 2: Variation of n with hν for CoS thin films deposited on glass by solution growth technique at pH of 7 - 12 and room temperature 300K for 24 hours

Table 2: Average optical properties of uncoated glass slide and cobalt sulphide (CoS) thin films deposited on glass slides

Average Optical properties	Uncoated Glass Slide	Deposition time (hrs)	Deposition temp (K)	Initial bath solution pH 7	8	9	10	11	12
A	0.033	24	300	0.049	0.046	0.085	0.051	0.069	0.054
T	0.927	24	300	0.893	0.899	0.822	0.899	0.853	0.883
R	0.040	24	300	0.058	0.055	0.093	0.060	0.078	0.063
$\alpha \times 10^{4}$ cm^{-1}	0.076	24	300	0.133	0.106	0.196	0.117	0.159	0.124
n	1.50	24	300	1.63	1.61	1.88	1.65	1.77	1.67

Table 3: Solid state properties of colbalt sulphide (CoS) thin films deposited on glass slides

Solid State properties	Deposition time (hrs)	Deposition temp (K)	Initial bath solution pH 7	8	9	10	11	12
E_g (eV)	24	300	2.66	2.50	2.12	2.36	2.36	2.56
$\sigma \times 10^{-5}$ $(\Omega\ cm)^{-1}$	24	300	0.90	0.95	1.05	1.19	1.22	1.33
t(Å)	24	300	475	487	385	468	417	458

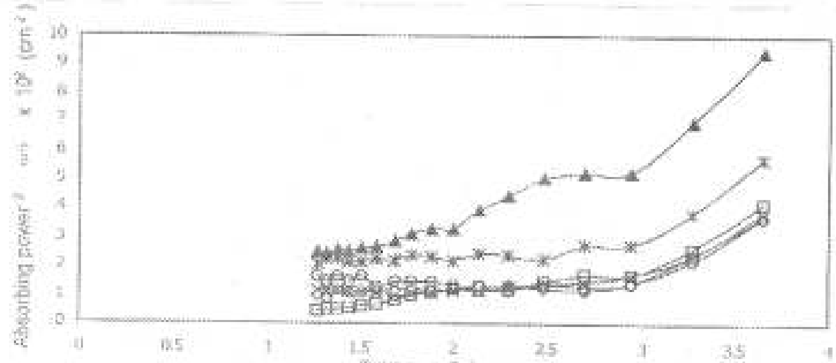

Fig. 3: Plots of α^2 with photon energy (hν) for cobalt sulphide (CoS) thin films deposited on glass by solution growth technique at pH of 7 - 12 and 300K for 24 hours

—◇— pH 7 —□— pH 8 —▲— pH 9 —×— pH 10 —✳— pH 11 —○— pH 12

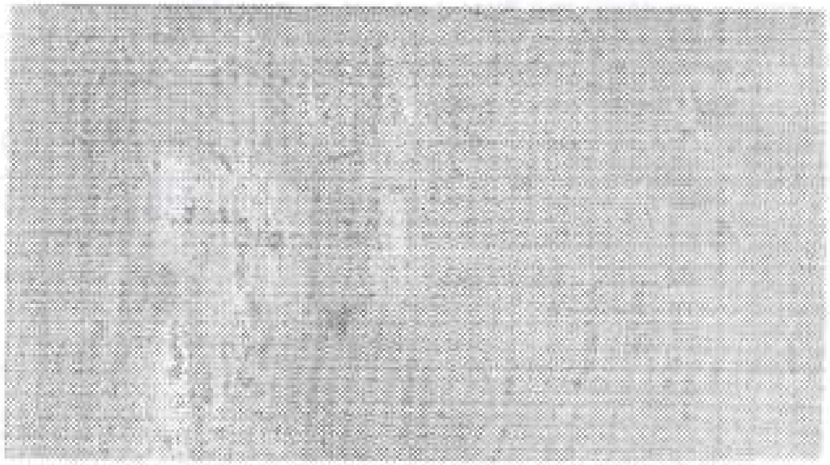

Fig. 4: Electronmicropgraph of Cobalt sulphide (CoS) thin film grown on glass bysolution growth technique (SGT) at pH of 9 and 300K for 24 hours at 400X

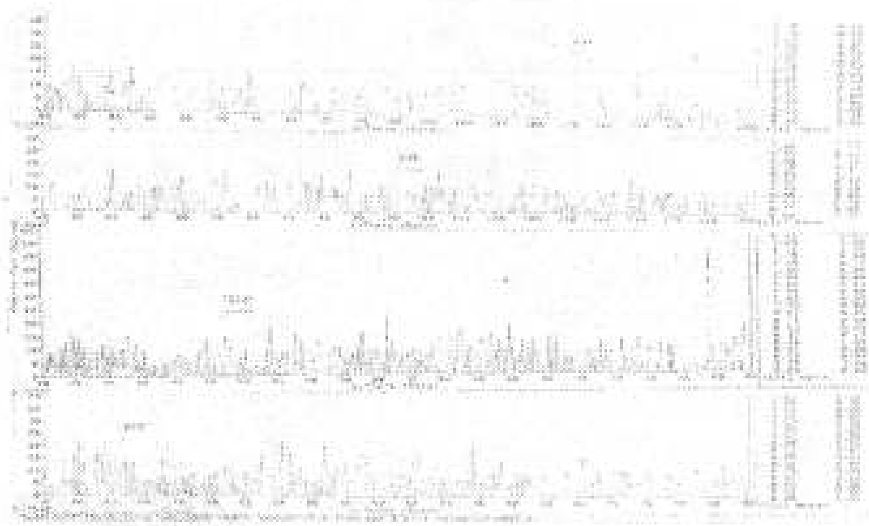

Fig. 5: X-ray diffractograms of uncoated glass and Cobalt sulphide (CoS) thin film grown on glass by solution growth technique (SGT) at pH of 9 and 300K for 24 hours

CONCLUSION

Good quality uniform thin films of cobalt sulphide (CoS) were successfully deposited on glass slides at 300K for 24 hours and at pH of 7 - 12 using improved solution growth technique (SGT). Advantages of this technique include simple deposition method, convenient, low cost, easily reproducible and can be used for high and low temperature deposition techniques. The deposited thin films with refractive index (n) lower than 1.8 have high spectral transmittance (T) and low reflectance (R). Films with high transmittance (T) and low reflectance (R) could be employed in thermal control window coatings and heat mirror coatings in architectural industries and also in antireflection coatings for solar thermal devices. The films with low transmittance (T) and high reflectance (R) could be useful in the construction of poultry houses. The deposited films would find application in production of thin film solar cells.

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