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Optical Properties of Chemical Bath Deposited Ag_2S Thin Films

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ABSTRACT

Thin films of Ag_2S were deposited at room temperature on glass substrates immersed in a bath mixture containing aqueous solutions of silver nitrate ($AgNO_3$), thiourea, Ethylenediaminetetra-acetate disodium Salt (EDTA) and ammonia solution. $AgNO_3$, for silver ion source, thiourea for sulphide ion source, EDTA as a complexing agent and ammonia for pH adjustment.. The films were studied for its optical properties using a Janway 6405 UV/VIS spectrophotometer and the results showed highest absorbance in the UV region (<400nm). Poor averaged reflectance, very low transmittance in the UV region which increases in the visible region/near infrared region, with an average of about 85% at >700nm. The optical band gap energy was found to be 1.8eV. Also the films exhibited averaged refractive index range of 1.9eV to 2.5eV.

Keywords: *optical properties, photovoltaic, Ag_2S thin films, chemical bath deposition technique, complexing agent*

I. INTRODUCTION

Silver sulphide is the sulphide of silver. This dense black solid constitutes the tarnish that forms over time on silver ware and other silver objects. Silver sulphide is insoluble in all solvents, but is degraded by strong acids. When formed on electrical contacts operating in an atmosphere rich in hydrogen sulphide, long filament known as silver whiskers can form. Silver sulphide has three forms, known as mono – clinic, acanthine; stable below 500^0C, body centred cubic so – called argentite, stable below 176^0C and a high temperature face – centered cubic form, stable above 586^0C [1]. The structure of Ag_2S is orthogonal It is found in nature as relatively low temperature mineral acanthine. Acanthine is an important ore of silver. silver sulphide is an important chalcogenides semi conductor compound and appears to be a promising solar absorbing material as its band gap (Eg 1.1 eV) is between 1 and 2eV, Ag_2S possessed a unique combination of various properties like high dark ionic or electronic conductivity, photoconductivity and photographic sensitivity in a broad range of wavelengths, as well as related photovoltaic and photo chronic effects, it's molar mass is 247.8gmol. It is a black cubic crystal, with density 7.23/cm^3, it melting point is 1098k(8250C), solubility in water is 8.5 x 10^{-12}m/1 and it is soluble in nitric acid and sulphuric acid [2]. Silver sulphide thin films is a functional material with applications in the contemporary advanced technologies extended over photoconductive and photovoltaic cells, solar selective coatings, ion selective electrodes and membranes to IR detectors, laser recording media etc. Silver sulphide thin films are very promising functional materials for many applications in different electronic components and devices like solar selective coatings, photoconductive and photovoltaic cells, infrared detectors, ion selective membranes and high resolution optical memories [3].In the last few years there is a growing interest in Ag_2S films because of their electrical and optical properties. Ag_2S exhibits a reversible semi conductor – to – metal phase (transition temperature T = 178^0C), accompanied by a change in the optical properties especially in the infrared (IR) wavelength region. This effect can be exploited for infrared millimeter wave devices. Further Ag_2S systems have been studied to develop superionic conductors, photosensitive materials for recording media as well as ion – selective electrode membranes [4]. Sulphide (Ag_2S) thin films have been prepared by many methods, such as chemical depositions, successive ionic layer absorption and reaction (SILAR), thermal evaporation, electro – deposition [2]. In this study, we synthesized Ag_2S thin film using a simple, cost effective and highly reproducible technique called the chemical bath method [5]. The technology is based on slow controlled precipitation of the desired compound from its ions in the reaction bath solution. A complexing agent acting as a catalyst is usually employed to control the reaction in a suitable medium as indicated by the pH to obtain crystal growth.

II. EXPERIMENTAL DETAILS

Thin films of Ag_2S were deposited at room temperature on glass substrates immersed in a bath containing silver nitrate ($AgNO_3$), thiourea, Ethylenediaminetetra-acetate disodium salt (EDTA) and ammonia solution. $AgNO_3$ as the source of silver ions , thiourea as the source of sulphide ions, EDTA as a complexing agent and ammonia for pH adjustment. The reaction mechanism is of the form:

$$AgNO_3 . + EDTA \rightleftharpoons Ag\,[EDTA]^{1+} + 3NO_3^-$$

$Ag[EDTA]^{+} \rightleftharpoons Ag^{+} + EDTA$

$(NH_2)_2CS + OH^{-} \rightleftharpoons CH_2N_2 + H_2O + HS^{-}$

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

$Ag^{+} + S^{2-} \longrightarrow Ag_2S$

The following parameters were optimized and the growth of Ag_2S was determined with respect to them: Time and complexing agent concentration. The variation in concentration of complexing agent was done by varying the volume for a given molarity.

(a) Optimization of time

In this experiment, five reaction baths (50mls beakers) were used. 5mls of silver nitrate was measured into a 50ml beaker using burette; 5mls of thiourea was then added and stirred gently to achieve uniform mixture. On addition of thiourea the solution remains colourless. 5mls of ammonia solution was then added, the solution turned pale yellow. 2.5mls of EDTA was now added and the solution remain pale yellow, the mixture was then topped to 50mls level by adding 32.5mls of distilled water and stirred to achieve uniform mixture. A glass substrate was dipped vertically into all of the five reaction baths. The baths were left to stand for different time intervals as indicated in Table. 1, after which the substrates were removed and dried in air.

Table: .1: Optimization of time

Slide No.	Volume of complexing agent (mls)	Volume of $AgNO_3$ (mls)	Volume of thiourea (mls)	Volume of ammonia solution (mls)	Time (hours)
AgS_a	2.50	5.00	5.00	5.00	4.00
AgS_b	2.50	5.00	5.00	5.00	8.00
AgS_c	2.50	5.00	5.00	5.00	12.00
AgS_d	2.50	5.00	5.00	5.00	16.00
AgS_e	2.50	5.00	5.00	5.00	20.00

(b) Optimization Complexing Agent

In this experiment, five reaction baths (50mls beakers) were used. 5mls of silver nitrate was measured into a 50ml beaker using burette; 5mls of thiourea was then added and stirred gently to achieve uniform mixture. On addition of thiourea the solution remain colourless. 5mls of ammonia solution was then added, the solution turned pale yellow. Various volumes of EDTA were then added as indicated in Table. 2 and the solution remain pale yellow, the mixture was then topped to 50mls level by adding distilled water and stirred to achieve uniform mixture, after about 10 minutes, the mixture turned dark brown. A glass substrate was dipped vertically into all of the five reaction baths. The baths were left to stand for 12 hours after which the substrates were removed and dried in air.

Table .2: Optimization Complexing Agent

Slide No.	Volume of complexing agent(EDTA) (mls)	Volume of $AgNO_3$ (mls)	Volume of thiourea (mls)	Volume of ammonia solution (mls)	Time (hours)
AgS_1	2.50	5.00	5.00	5.00	12.00
AgS_2	5.00	5.00	5.00	5.00	12.00
AgS_3	7.50	5.00	5.00	5.00	12.00
AgS_4	10.00	5.00	5.00	5.00	12.00
AgS_5	12.50	5.00	5.00	5.00	12.00

Optical characterization of the synthesized silver sulphide thin film were carried out using a Janway 6405 UV-visible spectrophotometer, were the absorbance in arbitrary units were obtained. Parameters which include: Absorbance (A), Transmittance (T), Reflectance (R), Absorption Coefficient (α), Refractive Index (n) and Photon energy (E), were then calculated using theory. Surface morphology of the films were also viewed with an Olumpus optical microscope.

III. RESULTS AND DISCUSSION

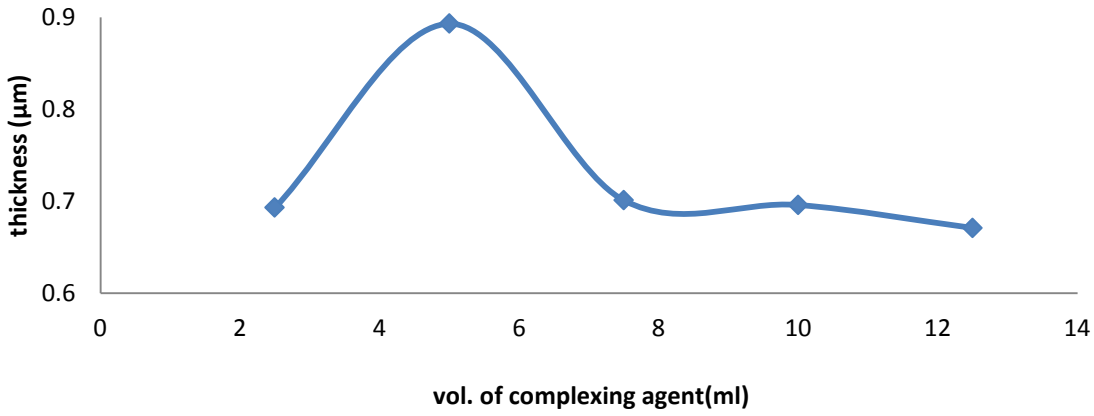

Fig. 1: Plot of thickness versus vol. of complexing agent for silver sulphide thin film

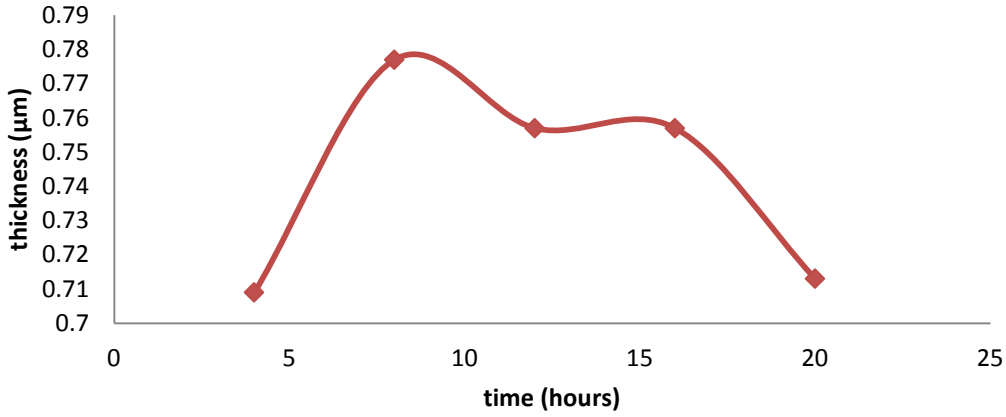

Fig. 2: Plot of thickness versus time for silver sulphide thin film

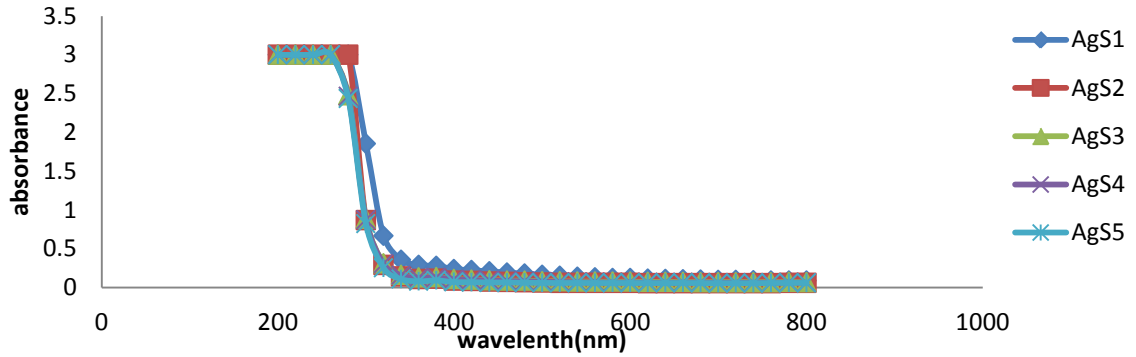

Fig. 3: Plot of absorbance versus wavelength for silver sulphide thin film (slide AgS_1, AgS_2, AgS_3, AgS_4 and AgS_5)

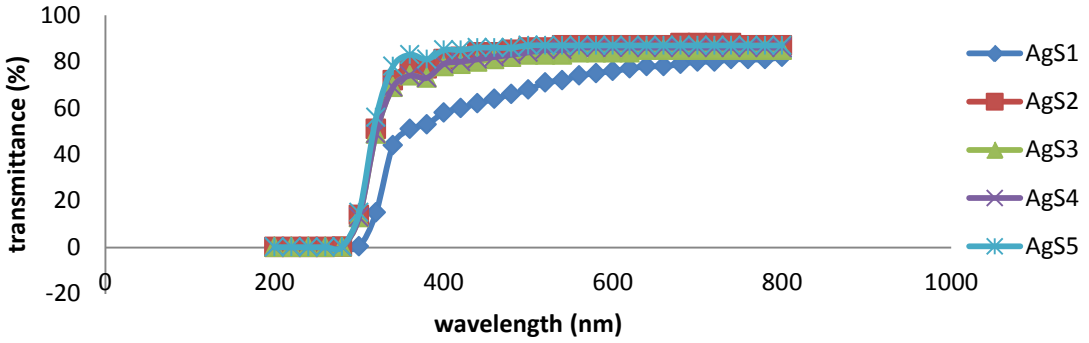

Fig. 4.: Plot of transmittance versus wavelength for silver sulphide thin film (slide AgS_1, AgS_2, AgS_3, AgS_4 and AgS_5)

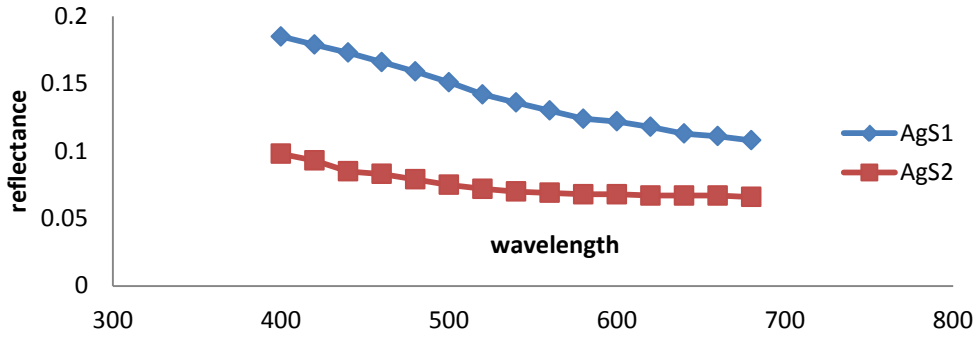

Fig. 5: Plot of reflectance versus wavelength for silver sulphide thin film (slide AgS_1, AgS_2,)

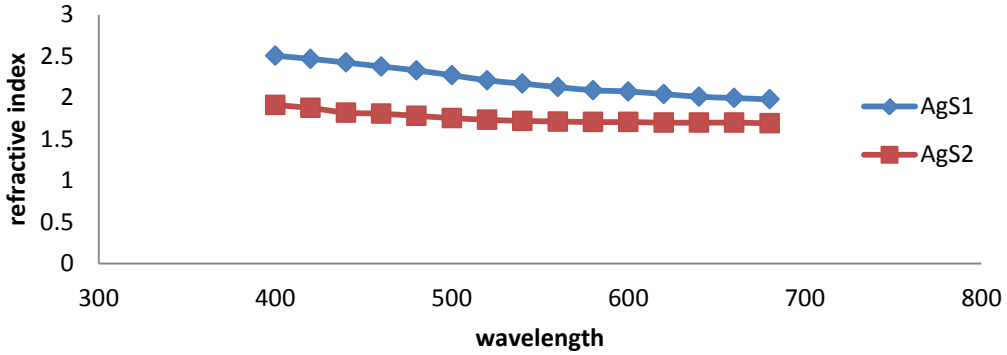

Fig. 6: Plot of refractive index versus wavelength for silver sulphide thin film (slide AgS_1, AgS_2,)

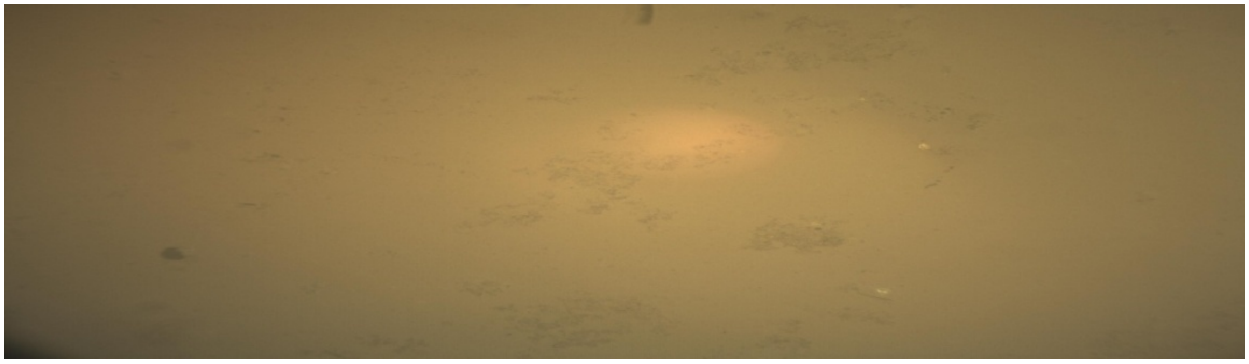

Fig. 7: optical micrograph of silver sulphide thin film (slide AgS_a,)

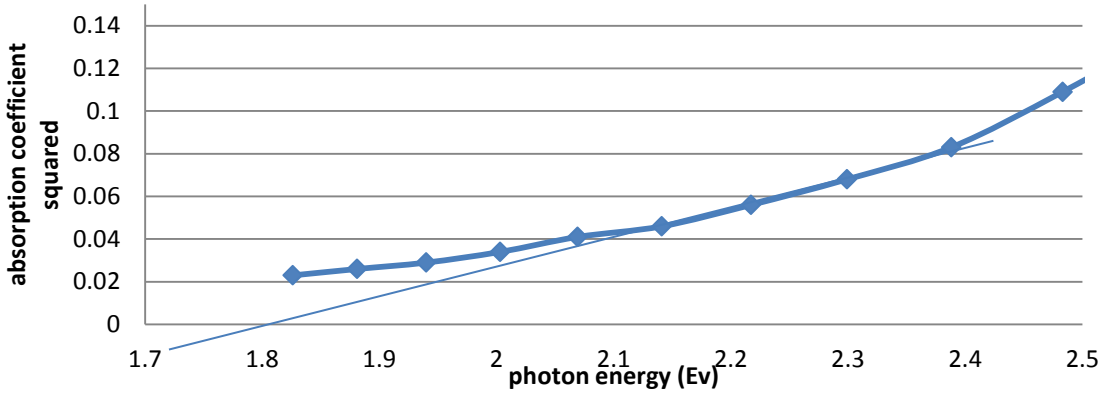

Fig. 8: Plot of absorption coefficient squared versus photon energy for silver sulphide thin film

Figs.1 and 2 are plots of thickness against complexing agent and thickness against time respectively. Fig.1 indicates that thickness increased from about 0.7μm to about 0.9μm with 2mls to 4mls volume of complexing agent. At 6mls and above

volume of complexing agent, the thickness of the film remain almost uniform. This indicates that as complexing agent increases, the thickness decreases. Fig .2 indicates that the longer the time, the thicker the film upto a point after which the thickness became almost constant, with the lowest thickness at 20hours deposition time.

Fig .3 shows a graph of absorbance (A) against wavelength (nm) for silver sulphide thin film (slide AgS_1, AgS_2, AgS_3, AgS_4 and AgS_5). All the films show almost the same absorbance spectral, with the highest absorbance in the UV region (<400nm). This result is consistent with the findings of [6].This high absorbance in the UV region makes this material important in photovoltaic technology.

Fig .4 is graph of transmittance against wavelength for silver sulphide thin film (slide AgS_1, AgS_2, AgS_3 AgS_4 and AgS_5). The films show very low transmittance in the UV region which increases in the visible / near infrared region, with an average of about 85% at >700nm. This high transmittance in the visible region makes silver sulphide films useful aesthetic window glaze materials. Also, the high transmittance of the film makes it suitable for solar energy collection, because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid.

Fig .5 is a graph of reflectance against wavelength for silver sulphide thin film (slide AgS_1, AgS_2). Generally all the films show a very low reflectance throughout the UV/VIS/NIR region. This low reflectance value makes silver sulphide thin film an important material for anti-reflection coating.

Figs .6 shows the plot of refractive index (n) against wavelength. Refractive index range of 1.9eV to 2.5eV was obtained. This moderately high refractive index makes this material useful in photovoltaic technology.

Figs .7 shows the optical micrographs of silver sulphide thin film (slide AgS_a). The micrograph shows that the surfaces of the silver sulphide films are dense. It shows uniformity in the distribution of the grains. The grains are very small.

Figs. 8 is a plots of absorption coefficient squared against photon energy (eV) for silver sulphide thin film. The energy gap for this film was obtained by extrapolating the linear part of the curve to the energy axis. It is observed from the figure that Ag_2S thin film exhibits direct band transition, from this graph, band gaps of 1.8eV was obtained. This is in close agreement with the finding of [6], who reported a band gap of 1.71eV, [7] who reported a band gap energy of 1.56eV and [8].

IV. CONCLUSION

Silver sulphide thin films have been successfully fabricated using chemical bath deposition technique. Solutions of silver nitrate ($AgNO_3$), thiourea, Ethylenediaminetetra-acetate disodium Salt (EDTA) and ammonia solution formed the reaction bath. Good quality thin films of silver sulphide were deposited. It showed a uniform distribution of particles as shown in photomicrograph. The grains are small. The films were found to have high absorbance in the ultra violet region and depreciate as the wavelength increased. They have generally high transmittance in the visible / near infra-red region. It has high refractive index. The energy gap for the fabricated Ag_2S thin film was found to be 3.00 eV.

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