Effect of deposition time on the optical properties of Copper Sulphide thin films fabricated by chemical bath deposition method

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Abstract

The effect of deposition time on copper sulphide thin film deposited on a glass substrate was determined. The CuS thin film was deposited using chemical bath method. The bath for the deposited CuS was composed of copper (II) chloride dihydrate ($CuCl_2.2H_2O$), thiourea, triethanolamine (TEA) as the complexing agent. The deposition was maintained at room temperature in alkaline medium. The optical properties of absorbance and extinction coefficient were found to be directly proportional to both time of deposition and thickness of the films while transmittance, reflectance and refractive index were inversely proportional to the time of deposition and thickness.

Keywords: Optical properties, thin films, Complexing agent, band gap.

1: INTRODUCTION

The aim of this work is to grow copper sulphide thin films by solution growth method and determine the effect of variation of deposition time on the optical properties with a view to ascertaining the possible applications. Thin films of metal chalcogenide, like metal sulphides, metal selenides, and metal tellurides, possess useful electrical and optical properties and can be found in many technical applications. Copper sulphide (Cu_xS) thin films are one of the potentially useful metal chalcogenides with signification variation in properties depending on the stoichiometry, $1 \leq x \leq 2$. At room temperature, five stable phases of Cu_xS are known to exist in the bulk form: CuS (covellite), $Cu_{1.75}S$ (anilite), $Cu_{1.8}S$ (digenite), $Cu_{1.96}S$ (djurleite), Cu_2S (chalcocite)[1].The different phases of Cu_xS exhibit considerable variations of optical and electrical properties, therefore they can be used in different potential applications, such as solar control coatings, solar cells, photothermal conversion of solar energy, electroconductive coatings, microwave shielding coatings, etc[2]. Metal chalcogenide thin films find applications in superconducting films, diamond films, magnetic films, microelectronic devices, surface modification, hard coatings, photoconductors, IR detectors, solar control, solar selective coatings, optical imaging, solar cells, optical mass memories, sensors, fabrication of large area photodiode arrays catalyst etc[3,4]. Various methods are being used for deposition of thin films, like vacuum evaporation, electro deposition, electro conversion, dip growth, spray pyrolysis, successive ionic adsorption and reaction, chemical bath deposition, solution-gas interface technique, sol gel method, sputtering, thermal oxidation, molecular beam epitaxy etc. Methods like chemical vapour deposition, spray pyrolysis, vacuum evaporation requires attainment of high temperature for specific and useful deposition of chalcogenide thin film. On other hand, methods involved in chemical solution method need much low temperature for successful deposition of thin film. Chemical bath deposition in present period of time is being extensively used for preparing thin film because of the advantages of this technique like inexpensive method, occur at easily attainable temperature, simple and convenient for large scale deposition etc. Copper sulphides (Cu_xS) are important materials for applications in p-type semiconductors and optoelectronics [6].This finds use in photo thermal conversion applications[7,8]. Photovoltaic applications[9,10], solar control coatings[11], and other electronic devices[12], fabrication of microelectronic devices, optical filters as well as in low temperature gas sensor applications. Special attention is now given to the study of copper sulphide thin films probably due to the discovery of heterojunction solar cell[13]. Copper sulphide thin films could be prepared by a variety of methods, including solution-based techniques (for example, successive ionic layer adsorption and reaction (SILAR), photochemical deposition, electrodeposition, chemical bath deposition (CBD), etc.) and gas phase techniques (for example, chemical vapor deposition (CVD), thermal co-evaporation, sputtering, etc.)[14]. Copper sulphide has complex crystal chemistry owing to its stability to form stoichiometric compounds. Copper sulphide thin films are very attractive materials for a wide variety of technological applications such as ferroelectric thin films, high-density optical data storage or semiconductors [15]. Optoelectronic devices [16], energy storage and conversion[17], solar cells, gas sensors[18] etc, due to their structural, optical and electrical properties[19]. The copper sulphide exhibits high transmission in the visible region and absorption throughout the near IR region (800 - 1500nm)[20]. It also exhibits fast ion conduction at higher temperatures. Therefore copper sulphide is suitable for the fabrication of solar cells.

2: MATERIALS AND METHODS

In this study, Copper sulphide thin films were grown on glass substrates by chemical bath deposition (CBD) technique at room temperature. Prior to deposition, the glass substrates were degreased in trioxonitrate (v) acid, washed with detergent, rinsed with distilled water and dried in air. The deposition of CuS thin film was based on the reaction between aqueous solution of copper (II) chloride dihydrate ($CuCl_2.2H_2O$) and thiourea (SC $(NH_2)_2$), in an alkaline medium using triethanolamine (TEA) (N $(CH_2CH_2OH)_3$) as a complexing agent. For deposition, five reaction baths (50mls beaker) were used. 10.0mls of $CuCl_2.2H_2O$ were measured into each of the 50ml beaker using burette, 2.0mls of TEA , 3.0mls of thiourea , 5.0mls of ammonia solution were added to each setup, the mixture was then topped to 60mls level by addition of distilled water and stirred gently to ensure uniformity of the mixture. Copper chloride and thiourea were the sources of Cu^{2+} and S^{2-} ions respectively. The deposition process was carried out at different deposition times of 3, 6, 9, 12 and 15 hours in order to determine the optimum condition for the deposition of CuS thin film. The experiment was conducted at room temperature (303K). A cleaned glass substrate was vertically immersed into each of the setup with the help of the synthetic foam. At the end of each deposition time, the films were washed with distilled water, hanged to dry and kept for analysis. Absorbance of the films was characterized using Janway 6405 UV/VIS spectrophotometer. Other optical properties of the films, like transmittance, reflectance, absorption Coefficient (α^2), extinction coefficient (K), refractive index (η), etc were calculated using the appropriate formular.

3: THEORY

Calculation of optical properties

Optical properties of the films were calculated using the following formulae

3.1: Transmittance

$T = 10^{-A}$

A = absorbance of the film

3.2: Refractive index (n)

$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$ Rubby and Suman (2011) [21]

R = reflectance

3.3: Reflectance

The Reflectance

$R = 1 - (A + T)$ Rubby and Suman (2011) [21]

A = absorbance, T = transmittance,

3.4: Absorption coefficient (α)

$\alpha = \frac{A}{\lambda}$

A = Absorbance and λ = wavelength

3.5: Extinction coefficient (k)

$k = \frac{\alpha\lambda}{4\pi}$ Nabeel (2011) [22],

α = absorption coefficient and λ = wavelength

3.6: Photon energy (hυ)

E = hυ Nadeem *et al* (2000) [23],

h = Planck's constant = 6.63×10^{-34}Js, υ = frequency of photon,

However, $v = \frac{c}{\lambda}$

c = velocity of light = 3×10^8m/s and λ = wavelength,

Hence, $E = \frac{hc}{\lambda}$

But, $1eV = 1.602 \times 10^{-19} J$, Planck's constant $h = \frac{6.63 \times 10^{-34} Js}{1.602 \times 10^{-19} J} \approx 4.14 \times 10^{-15} eV$

∴ Photon energy $E = \frac{4.14 \times 10^{-15} eV \times 3 \times 10^8 m/s}{\lambda(m)}$ = …..eV

4: RESULTS

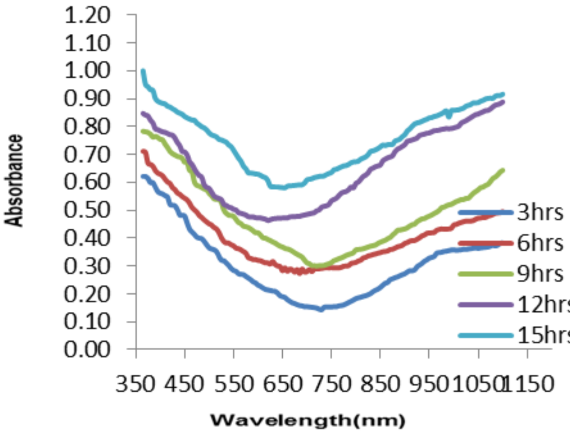


Fig.1: Absorbance versus wavelength for CuS thin film

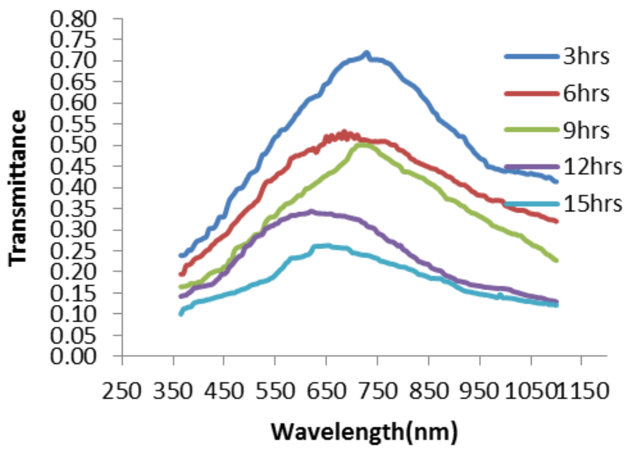


Fig.2: Transmittance versus wavelength for CuS thin film

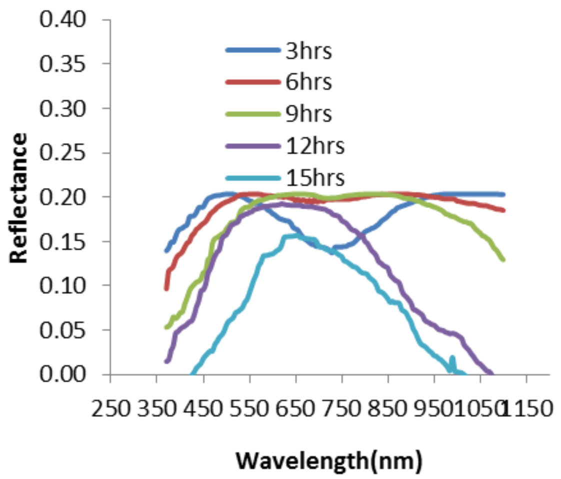
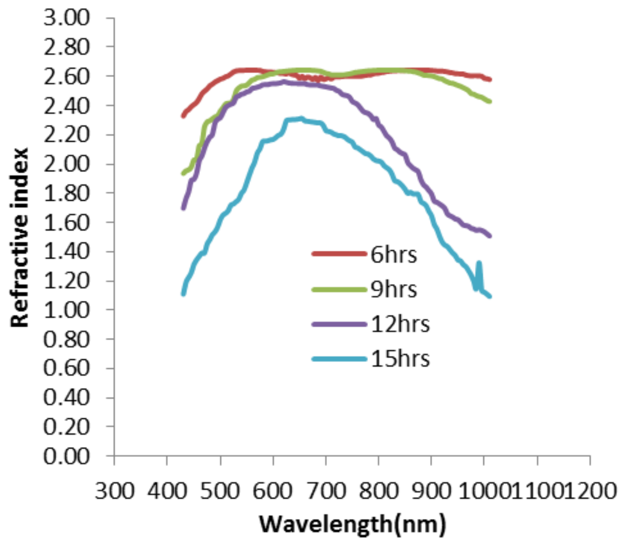


Fig.3: Reflectance versus wavelength for CuS thinfilm

Fig.4: Refractive index versus wavelength for CuS thin film.



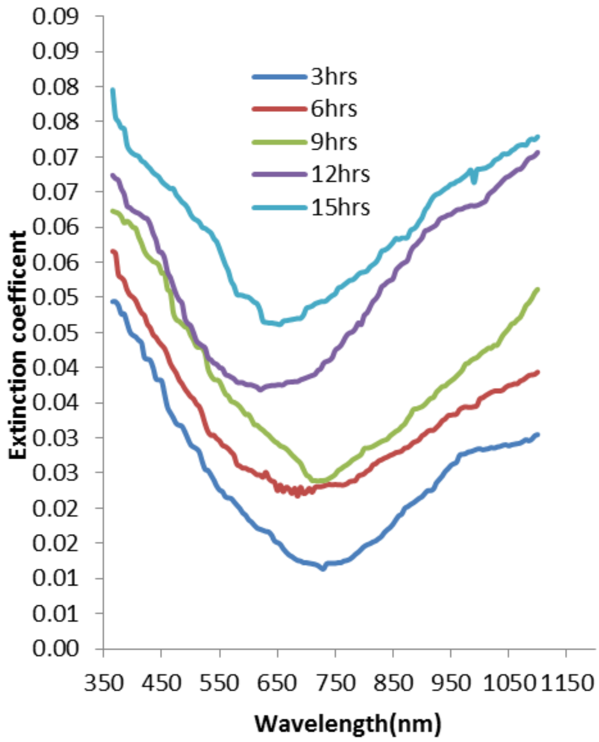


Fig .5: Extinction coefficient versus wavelength for CuS thinfilm

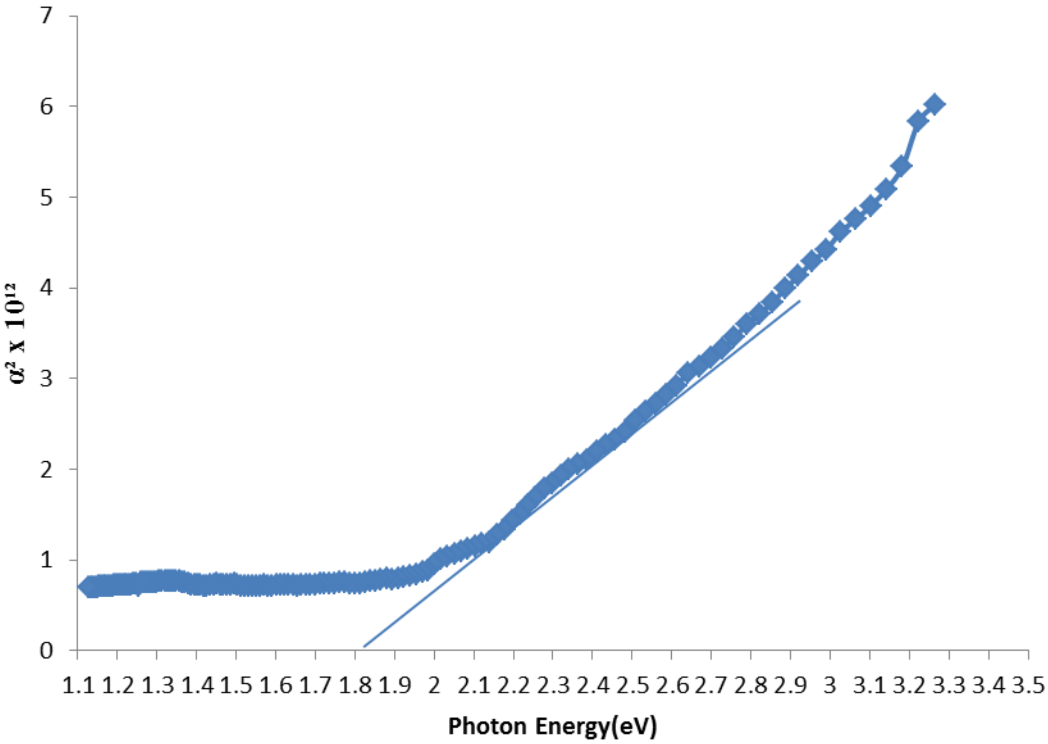


Fig.6: (Absorption Coefficient)^2 versus Photon energy for 15-hours deposition time thin film.

5: DISCUSSIONS

From fig.1, absorbance of CuS films is generally high in the UV region, maximum of 1=100% and minimum of 0.6=60%. The absorbance of the films is high in the NIR for films of higher deposition time, maximum of 0.9=90%. However the absorbance is generally low in the visible spectrum. This makes the films suitable for coating of eye glasses to prevent UV radiation from getting to the eyes. It is also useful for coating of windows to prevent UV radiation and aid visibility since absorption in the visible region is low. Low absorption in the visible region makes it a veritable material for buffer layer in solar cell. The absorbance of the films is directly proportional to time of deposition.

Fig.2 reveals the films as having low transmittance in the UV and NIR regions and maximum in the VIS region, 0.7=70% for film of 15hrs deposition time and low values for lower deposition time. High transmittance in the visible region makes CuS films efficient for window glaze materials for visibility and buffer layer in solar cell. However the transmittance of the films is inversely proportional to deposition time.

Fig. 3, Shows that the reflectance of the films is generally low in all the regions, maximum in the UV 0.2=2% and minimum in the UV and NIR. The reflectance of the films is inversely proportional to the deposition time. This low reflectance value makes CuS thin films an important material for anti-reflection coating such as coating of windscreens and driving mirrors to prevent the effect of dazzling light from vehicles following behind at night.

As shown in fig.4, the refractive index (η) of the CuS thin films is high with maximum value 2.6 in the visible region and is inversely proportional to the deposition time. Refractive index of a material is a number which indicates the number of times slower that a light wave (electromagnetic wave) would travel in the material than in vacuum. Thus, this high refractive index value makes the films good material for film stack which can be applied in color selective coating. The high refractive index also makes the films useful in multilayer antireflection coatings. As shown in fig. 5, the extinction coefficient of the films is maximum in the visible region and minimum in in the UV and NIR. This property is directly proportional deposition time. Result in fig.6, shows the relation between square of absorption coefficient and photon energy. The band gap was determined by extrapolating the straight portion of the graph to the energy axis at $\alpha^2 = 0$.The band gap energy is 1.825eV. As a wide bandgap material it permits devices to operate at high voltages, frequency, and temperature. It has the potential of emitting light in visible color range.

6: CONCLUSION

CuS thin film could be deposited on a glass substrate using a less sophisticated chemical bath deposition (CBD) method in alkaline medium. The optical properties viz: absorbance and extinction coefficient of the films are directly proportional to the deposition time while transmittance, reflectance and refractive index are inversely proportional. The bandgap of the film is fairly high.

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