

Dual solution synthesis of Al doped CuS thin films for optoelectronic and photovoltaic applications

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Abstract

Dual Solution Synthesis (DSS) was used to deposit CuS doped with Al. The Samples were subjected to annealing under varying temperatures of 319K and 373K. The thin films were firmly adherent to the substrates. The optical properties were measured using UV -1800 series double beam spectrophotometer. The transmittance is from 0.3% to 0.6% while the reflectance is between 0.176 to 0.204, as the wavelength ranges from 320nm to 1000nm; the average band gap obtained is $2.6 \pm 0.05 eV$. The thicknesses achieved are 100nm and 124 nm. Other Optical properties were determined for each sample which makes it suitable for applications in optoelectronic, solar energy conversions, solar cells, thin film absorbers, anti- reflective coating, aesthetic windows, UV filter and other uses.

Keywords: Transmittance; Absorbance; Reflectance; Absorption coefficient; Extinction coefficient; Refractive index; Optical conductivity

1. Introduction

Copper sulfide is a p-type semiconducting material which belongs to I-VI compound semiconductor metals. Chalcogenide thin films of copper sulfide have received particular attention since the discovery of the CdS/CuS heterojunction solar cell in 1954 (Osuwa and Mgbaja, 2013). Other applications of CuS thin films include laminated glazing, photo-thermal conversion, electro-conductive electrode, microwave shielding and solar control coatings (Grozdanov and Najdoski, 1995); Otth and Ekpunobi, 2010) It is also used in photo-detectors and photovoltaic applications. Electrical resistivity and conductivity of CuS thin films are dependent on various film and growth parameters including film composition, film thickness and impurity concentrations among others (Abdullah *et al.*, 2012; Panta and Subedi, 2012). Copper sulphide is a chemical compound of copper and sulphur. It has the chemical compound Cu_2S . It is found in nature as the mineral chalcocite. Copper sulphide is a compound composed of copper and sulphur. It has been the subject of numerous studies due to its potential applications in various fields, including electronics (Ekpekepo *et al.*, 2019), catalysis, and energy conversion. Another study published in the Journal of Power Sources explored the use of copper sulphide as an electrode material in lithium-ion batteries. Additionally, copper sulphide has also been studied for its potential in solar energy conversion. A study published in the journal Nanoscale examined the use of copper sulphide nanocrystals in solar cells. The study found that the copper sulphide nanocrystals exhibited high efficiency in converting sunlight into electricity. CuS has a wide range of well-established and prospective applications (Onwuemeka, *et al.*, 2019) such as photo-thermal conversion application, photovoltaic applications (Mitkari *et al.*, 2019); Thanikaikaran *et al.*, 2009); (Pradeepa *et al.*, 2021), electro-conductive electrode, microwave

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shielding coating and solar control coating. In addition, it is a promising material with potential application in Lithium-ion rechargeable batteries, gas sensor, catalyst and optoelectronic applications.

Copper sulphide doped with aluminum thin films are a promising material for applications in electronic devices and energy conversion. The aluminum doping modifies the electrical, optical and structural properties of copper sulphide thin films. These modifications lead to increased electrical conductivity, improved optical properties, and stability of the material. One of the primary applications is in photovoltaic devices (Onwuemeka and Ekpunobi, 2018), where copper sulphide/ aluminum thin films have been investigated as selective layers or buffer layers. By doping copper sulphide thin films with aluminum, researchers have improved the efficiency of copper sulphide-based photovoltaic devices. Additionally, copper sulphide doped with aluminum thin films have exciting potential in the field of spintronics. Spintronics is a field of electronics that exploits the intrinsic spin of electrons in addition to their charge. Research in this area has shown that copper sulphide doped with aluminum has magnetic properties that make it suitable for use in spintronic devices. Overall, the unique properties of copper sulphide doped with aluminum thin films make them an exciting area of research with promising applications in photovoltaic, spintronic, and electronic devices (Mitkari *et al.*, 2019); Thanikaikaran *et al.*, 2009). Copper sulphides (CuS) are important materials for applications in p-type semiconductors and optoelectronics. This find use in photo thermal conversion applications, photovoltaic applications, solar control coatings and other electronic devices fabrication of microelectronic devices, optical filters as well as in low temperature gas sensor applications (Onyema *et al.*, 2024).

2. Materials and Method

2.1. General Reaction Processes

3ml of 0.1M solution of ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$ (EDTA) solution, the complexing agent was made to react with 0.4M solution of hydrated copper sulphate in 50ml beaker forming blue precipitate, which dissolves in excess EDTA forming copper complex ion. De-ionized water was added to make up the beaker to 50ml and was stirred to have a uniform solution. 10ml of 0.2M of sodium thiosulphate solution ($Na_2S_2O_3$) as the anion precursor was prepared in a separate beaker of 50ml for completion of reaction process leading to the formation of CuS thin films. By further dipping it into a solution of Al complex ion for 20 seconds formed a doped sample of CuS and Al.

2.2. SILAR Process

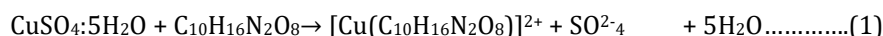
The glass substrates were first immersed into copper complex ion $[Cu(C_{10}H_{16}N_2O_8)]^{2+}$ which is the cation precursor band then rinsed in de-ionized water in order to remove some unadsorbed substances and to control the thickness of the deposits. The substrates were transferred into the 50ml beaker containing the solution of sodium thiosulphate ($Na_2S_2O_3$) and then rinsed in a de-ionized water, thus completing the SILAR cycles which involves – adsorption, rinsing, reaction and rinsing as depicts on the experimental set-up in Figure 1 Each dip-time lasted for 10 seconds and the entire process was repeated for 8 cycles in each beaker of the reactants and 3 seconds in each beaker of de-ionized water.

2.3. SGT deposition process

The freshly prepared CuS samples were quickly transferred into the beaker containing Al complex ion solution for 20 seconds as shown in Figure 2. The substrates were removed, rinsed in de-ionized water and dried in air.

2.4. Theory

0.4M solution of hydrated copper sulphate reacted with 0.1M solution of EDTA forming a complex solution of copper as given in equation (1)



The complex solution of Cu^{2+} reacting with 0.2M solution of sodium thiosulphate ($Na_2S_2O_3$) as given in equation (2) produces copper sulphide (CuS) thin films.



By transferring the sample containing the desired films into a freshly prepared solution of Al complex ion, a new substance is formed with the already deposited films of CuS. This is given in equation (3).



By subjecting extrinsic thin films of material of CuAlS, is obtained as given in equation(4)



Equation (4) completes the doping process after expelling all undesired substances and water of crystallization associated with the deposited samples through annealing at varying temperatures of 319K and 373K.

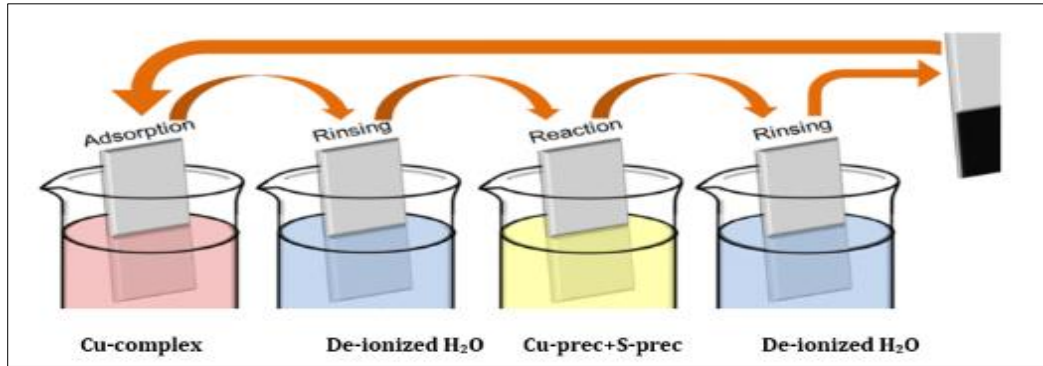


Figure 1 Experimental set up of Successive Ionic Layer Adsorption and Reaction (SILAR)Method (Onyema *et al.*, 2024)

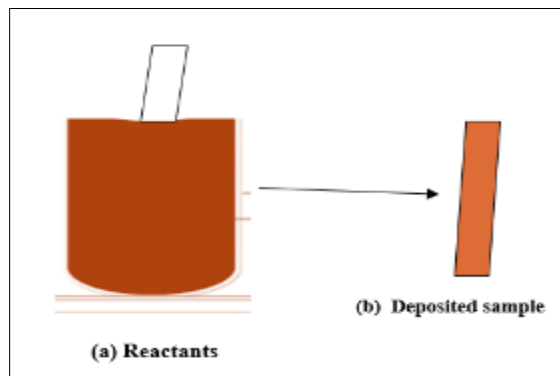


Figure 2 Set-up of Solution Growth Technique (Onwuemeka *et al.*, 2018) (a) Reactants (b) Deposited sample

3. Results and Discussion

3.1. Elemental Composition and Thickness measurements

The thickness measurements and elemental compositions were carried out using Rutherford Back Scattering Spectroscopy (RBS). Figure 3, is sample A deposited at 273K, has thickness value 124nm at annealing temperature of 319K. And compositions of Cu: 9.32% and S: 5.45%. Al, which is the dopant, has 1.23%. Figure 4, shows sample B deposited at 273K, has thickness value 110nm at annealing temperature of 373K. It has elemental compositions of Cu: 5.91%, S: 9.37%. and Al here, has 1.10%. Tables 1 and Table 2 depicts the elements in the substrates before and after depositions. Layer 2, shows the elements before deposition and Layer 1 represents the elements after deposition. Other elements present are part of the substrates used.

Table 1 Elements on sample A

Element	Layer1 (%)	Layer 2 (%)
Ca	-	0.60
Si	-	16.53
O	-	69.40
Fe	-	0.46
Na	-	7.77
Al	1.23	2.28
Mg	-	0.47
Ti	-	0.14
S	5.45	0.67
Cu	9.32	-

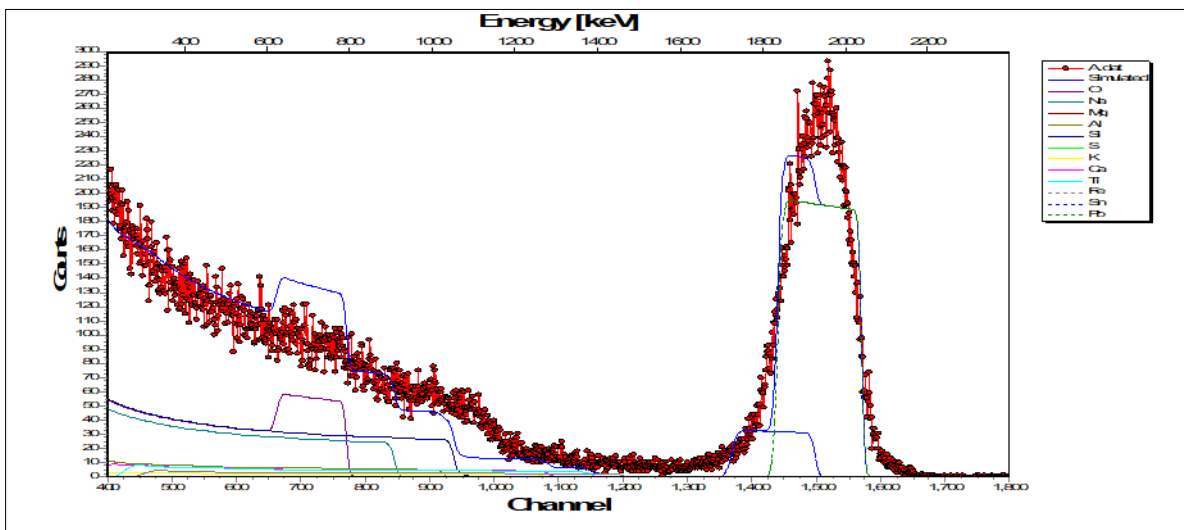


Figure 3 The Rutherford backscattering spectrometry (RBS) for sample A, 124nm

Table 2 Elements on sample B

ELEMENT	Layer 1 (%)	Layer 2 (%)
Ca	-	0.60
Si	-	16.53
O	-	69.40
Fe	-	0.46
Na	-	7.77
Al	1.10	2.28
K	-	0.47
Mg	-	0.14
Ti	-	0.67

S	9.37	-
Cu	5.91	-

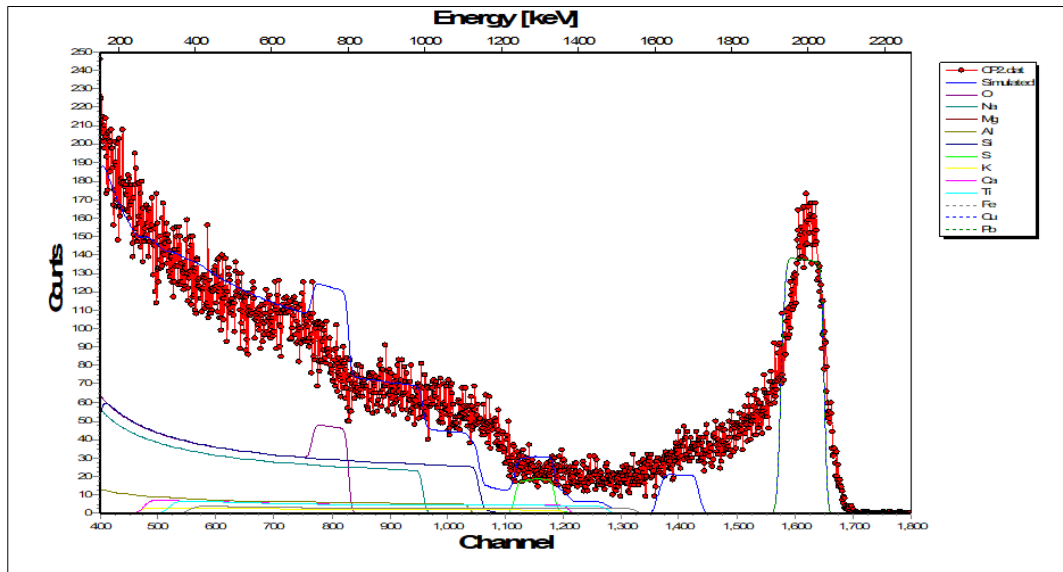


Figure 4 The Rutherford backscattering spectrometry (RBS) for sample B, 110nm

3.2. Surface Structure

The morphological studies of samples A and B were determined using Phenom Proxy by Phenom World Eindhoven, Netherland. Sample A as revealed by scanning electron microscope (SEM) in Figure 5 shows that it has smooth dark surface with tiny white spots which indicate the inter-atomic interactions between the constituent ions of Cu, Al and S that made up the emergent thin film compound, which also shows the bonding strength of the entire material. Figure 6 is the image of sample B as studied by scanning electron microscope; it shows that the deposited sample has a smooth surface having tiny white spots. The material exhibits interactions of combining substances during chemical reactions.

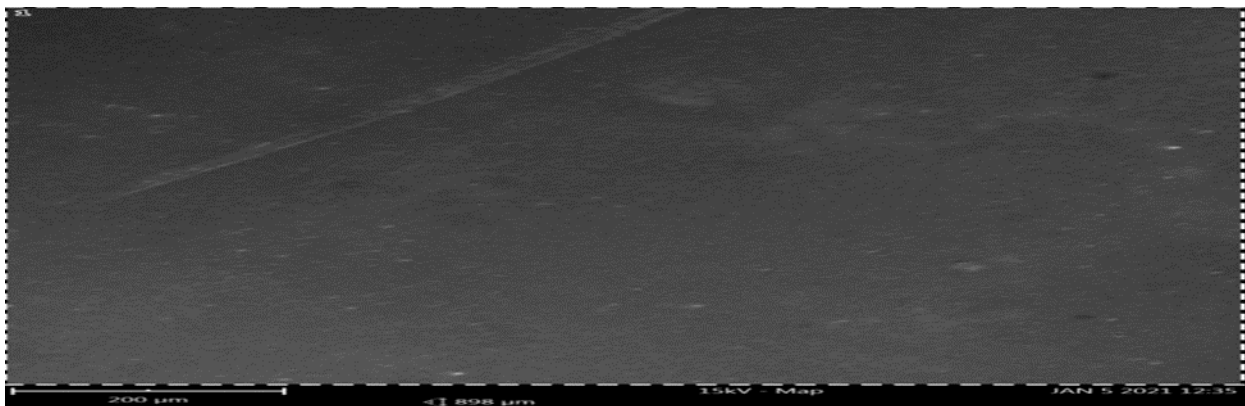


Figure 5 SEM image of sample A thin film at annealing temperature 319K

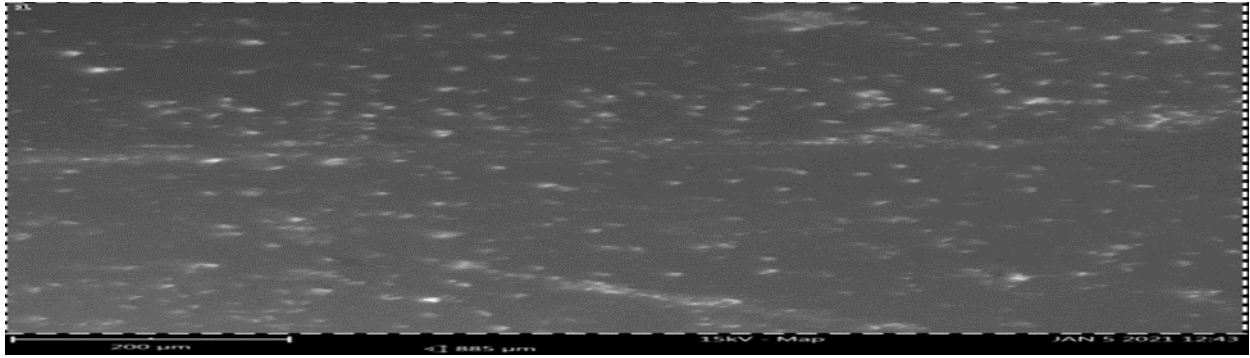


Figure 6 SEM image of sample B thin film at annealing temperature of 373K

3.3. Optical Properties

In the optical characterization of samples, the transmittance which is the ratio of the incident intensity to the transmitted intensity of the radiation was taken as the default. The samples were scanned for transmittance from the UV (ultraviolet), through visible down to near infrared regions of electromagnetic spectrum. This ranges from 350nm to 1200nm wavelength. Absorbance, reflectance, absorption, coefficient, refractive index, extinction coefficient, real dielectric constant, imaginary dielectric constant, optical conductivity and energy band gap were determined using relevant equations. The transmittance was measured by UV double beam 1800 series spectrophotometer.

3.3.1. Transmittance

The transmittance spectra in Figure 7 shows that the films of sample A has low transmittance in the UV (30% - 35%) at the wavelength range (320nm - 400nm). Sample B shows also low transmittance (41% - 46%) at the wavelength range (350nm - 400nm) in the UV. There is an increase in transmittance from 30% to 60% for sample A as the wavelength increases from the UV through the visible to near infrared (NIR) regions (320nm - 1100nm) and (41% - 60%) for sample B as the wavelength increases from 320nm to 1100nm from the UV through the visible to near infrared (NIR) region of electromagnetic spectrum. The average transmittance of these samples implies they can be applied in the areas of optical coating, solar panels, anti-reflection coating, Liquid crystal Display (LED).

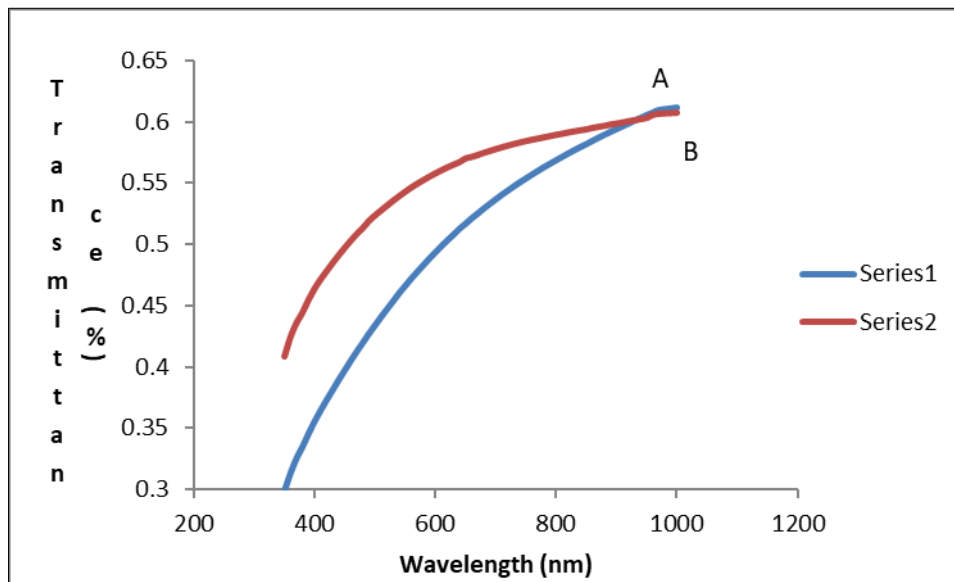


Figure 7 Graph of transmittance against wavelength for CuS:Al thin film sample A and B

3.3.2. Energy Band Gap (E_g)

In Figure 8, the optical energy band gap is obtained in k space from the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where A is a constant, $h\nu$ is the photon energy, E_g is the energy band gap and α is the absorption coefficient. The energy band gaps of sample A and B are evaluated by extrapolating the linear portions of the plot $(\alpha h\nu)^2$ against $h\nu$ at $\alpha h\nu = 0$. A direct band gap value

of $2.5 \pm 0.05 \text{ eV}$ is obtained for sample A. Sample B has direct band gap of $2.7 \pm 0.05 \text{ eV}$. The two samples have in average, energy band gap of $2.6 \pm 0.05 \text{ eV}$. The narrow band gap obtained in this work makes the CuS:Ala good material for the production of laser diodes and light emitting diodes (LED).

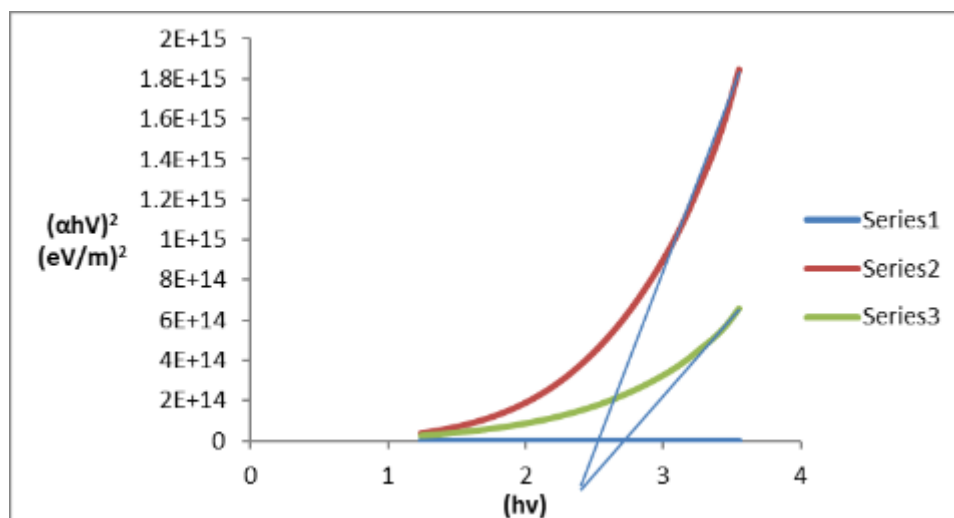


Figure 8 Graph of $(\alpha h\nu)^2$ against photon energy $h\nu$ for CuS:Al thin film sample A and B

4. Conclusion

CuS:Al, doped thin films were deposited on glass substrate using dual solution synthesis; successive ionic layer adsorption and reaction and solution growth technique at constant temperature of 40°C of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solution while other reactants were kept at room temperature of 20°C . EDTA solution was used as the complexing agent. The deposited samples were annealed between 319K and 373K respectively using Master Chef Annealing Machine. The optical properties were measured using UV -1800 series double beam spectrophotometer. The alloyed thin films exhibited appreciable good transmittance from the UV region, through the visible to near infrared regions of the electromagnetic spectrum. Direct average energy band gap of $2.6 \pm 0.05 \text{ eV}$ was obtained for CuS:Al thin films. Other Optical properties investigated are absorbance, reflectance, and optical conductivity, absorption coefficient using appropriate equations. These material thin films prepared under this condition with wide energy band gap and good transparency in the visible region can be found useful in many areas of applications such as flat panel displays for optoelectronics, photovoltaic for energy conversions, photocells, transparent electrodes etc.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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