

Opto-Electrical Analysis of Chemically Deposited Copper Indium Gallium diSelenide (CIGS) semiconductor Thin Films at different In:Ga ion concentration

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Abstract

This study reports the chemical bath deposition of Copper Indium Gallium diSelenide (CIGS) semiconductor thin films at varying In:Ga ion concentrations from a reaction mixture of Copper(II)chloride dehydrate, Triethanolamine, Sodiumselenophite, Indium(III)chloride tetrahydrate, Gallium trichloride, Ethylene Ditetraamine Acid and Ammonia for solar energy applications. The electrical properties of the films were obtained using Four Point-Probe System machine and the optical properties were measured using Avantes UV-VIS-NIR spectrophotometer in the wavelength range 200-900 nm. Reflectance spectra results revealed that the more gallium ion concentration in CIGS, the lower reflectance of the thin films in the visible and infrared range. It was observed that gallium doped CIGS (1:2) thin films had a higher transmittance than CIGS (1:3). The energy band gaps of the films decreased with increase in concentration of gallium to the minimum band gap of 2.3 eV and 2.6 eV for CIGS (1:3) as-deposited and annealed films respectively. The low reflectance, high transmittance and high band gap properties of the thin films make them good materials for

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antireflection coatings, solar cell absorbers, thermal control, photosynthetic coating and window layer in the fabrication of thin film hetero-junction solar cell and other optoelectronic devices.

Keywords: CIGS, Thin films, Optical, Solar energy, Chemical Bathi.

INTRODUCTION

Solar power could become more important form of renewable energy in future as a result of its usefulness. On the average, every square meter of earth's surface receives 164 watts of solar energy (Wood, 2016). In other words, one could stand a really powerful (150 watts) table lamp on every square meter of earth's surface and light up the whole planet with the sun's energy, or to put it another way, if one covers just one percent of the Sahara desert with solar panels, one could generate enough electricity to power the whole world. That's the good thing about solar power, there is an awful lot of it much more than one could ever use. But there is a downside too. One has to find some way of converting solar energy into other forms of energy that can use more easily, such as electricity.

BACKGROUND OF THE RESEARCH

A solar cell is an electronic device that catches sunlight and turns it directly into electricity. It is about the size of an adult's palm, octagonal in shape, and colored bluish black. Solar cells are often bundled together to make larger units called solar modules, themselves coupled into even bigger units known as solar panels (the black- or blue-tinted slabs one sees on people's homes, typically with several hundred individual solar cells per roof) or chopped into chips (to provide power for small gadgets like pocket calculators and digital watches). The use of PbS and PbSe as photo detectors form the first recorded application of chemically deposited semiconductor thin films (Bode, 1966). This was followed by CdSe photodetectors (Svechnikov and Kaganovich, 1980). Around 1980, the focus of CBD films slowly turned towards solar energy applications. One of the earlier developments towards this was in solar absorber coatings (Reddy, Pandya, Dutta and Chopra, 1987). Application in the field of solar control coating was suggested in 1989. It has been found that chemical bath deposited PbS and Cu_xS thin films offer comparable or superior solar control characteristic as against commercial solar control coatings deposited by much expensive vacuum coating techniques (Nair, Nair, Fernandez and Ocampo, 1989).

Fraunhofer (2014) explained that Copper Indium Gallium Selenide (CIGS) solar cell uses an absorber made of copper, indium, gallium, selenide (CIGS), while gallium-free variants of the semiconductor material are abbreviated CIS. It is one of three mainstream thin-film technologies, the other two being cadmium telluride and amorphous silicon, with a lab-efficiency above 20 percent and a share of 2 percent in the overall Photovoltaic (PV) market in 2013. There is a need to develop a robust and low temperature (~400 °C) deposition process for CIGS for the flexible substrate to facilitate roll to roll manufacturing and to extend the application for space market. In order to meet the current challenges of high demand for the generation of electricity from renewable energy sources, this study focused on the alternative techniques such as Chemical Bath Deposition technique to deposit CIGS semiconductor thin films which can be used for solar energy fabrication.

METHODOLOGY

The reagents used were of LR (Laboratory Reagent) and purchased from Sigma Aldrich Company. The precursors used in this study were copper (II) chloride dihydrate ($CuCl_2 \cdot H_2O$) as the source of Cu^{2+} and Triethanolamine (TEA) as a complexing agent,

sodiumselenophite (Na_2SeSO_3) as a source of selenium ion (Se^{2-}) and Indium(III)chloride tetrahydrate ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$) as a source of indium ion (In^{3+}) and Gallium trichloride (GaCl_3) was used as the source for Gallium ion (Ga^{3+}) whereas Ethylene Ditetraamine acid (EDTA) was used as a complexing agent for In^{2+} in the reaction mixture of both. Ammonia (NH_3) was used to adjust the pH of the solution. The sodium selenosulphite was prepared by refluxing 9.0 g of selenium power with approximately 15.0 g of anhydrous sodium sulphite (Na_2SO_3) in 200 ml of distilled water for 6 hours at 80 °C thereby making 0.2 M of Na_2SeSO_3 . CIGS thin films were deposited on glass substrates by CBD technique at 85 °C. Before commencement of the deposition, the glass substrates were degreased in HCl for about 24 hours, washed with detergent, rinsed with distilled water and dried in air. The mixture for the CIGS baths were prepared by mixing 10 mls of 0.3 mol of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ and 5 mls of TEA in a 50mls beaker, 10 mls of 0.2 mol of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, 10 mls of 0.4 M of GaCl_3 complexed with 5 mls of 0.5M EDTA in a 100 mls beaker, this step was repeated for 0.6 M and 0.8 M of GaCl_3 for 1:2, 1:3 and 1:4 $\text{In}^{3+} : \text{Ga}^{3+}$ concentration ratio respectively. The pH of the solution of each bath was adjusted by addition of $\text{NH}_3(\text{aq})$. After which 10 mls of Na_2SeSO_3 and some distilled water was added to obtain a final volume of 100 mls. The reaction mixture was initially stirred and maintained a temperature of 85 °C for deposition. Four cleaned glass substrates were vertically immersed into the chemical baths with the help of synthetic foam. The deposition process was carried out at room temperature and 9 hours in order to determine the optimum condition for the deposition of CIGS. Thin films allowed to dry under ambient condition then annealed at 450 °C. The as-deposited and the annealed samples were labeled S_{21} and S_{22} respectively. The various deposition temperatures and the pH (11.5-11.3) were monitored with Mettler Toledo AG 8603 pH meter. The substrates were removed from the reaction bath, dried in open air at room temperature and kept. Table 1 shows the chemical bath compositions while Figure 1 shows the schematic experimental set-up for the deposition of the thin films.

Table 1: Chemical Bath Compositions for the deposition of CIGS Thin films

Baths (In:Ga)	Cu	In	Ga	Se	pH
	Concentration (M)				
$\text{S}_{1:2}$	0.3	0.2	0.4	0.2	10.13
$\text{S}_{1:3}$	0.3	0.2	0.6	0.2	10.84
$\text{S}_{1:4}$	0.3	0.2	0.8	0.2	10.73

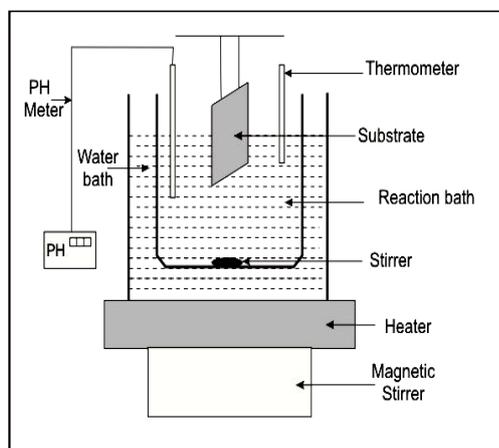


Figure 1: Schematic experimental set-up for Chemical Bath Deposition of CIGS

RESULTS AND DISCUSSION

The electrical properties were obtained using Four Point-Probe System machine and the Sheet resistance, resistivity and conductivity of the deposited thin films were calculated. Furthermore, the optical properties (reflection, transmission and absorption data) of the thin films were measured using Avantes UV-VIS-NIR spectrophotometer in the wavelength range 200-900 nm.

Table 2: Electrical results summary of the deposited CIGS films

Samples	Resistivity (Ωm)	Conductivity (Ωm^{-1})	Sheet resistance, R_s (Ω/m^2)
CIGS (1:2) as-deposited	1.73×10^{-4}	5.780×10^3	8.660×10^{-3}
CIGS (1:2) Annealed	2.42×10^{-3}	4.132×10^2	1.208×10^{-1}
CIGS (1:3) as-deposited	3.77×10^{-4}	2.652×10^3	1.880×10^{-2}
CIGS (1:3) annealed	1.33×10^{-3}	7.520×10^2	6.670×10^{-2}

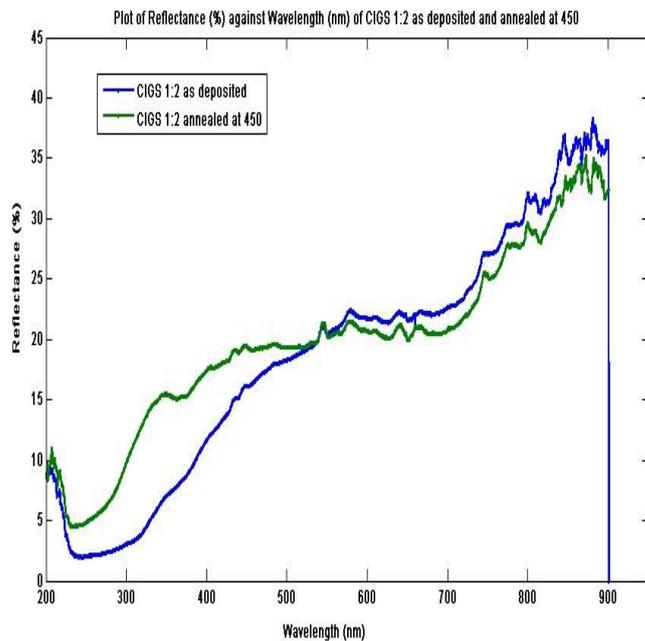


Figure 2: Graph of reflectance against wavelength for CIGS (1:2)

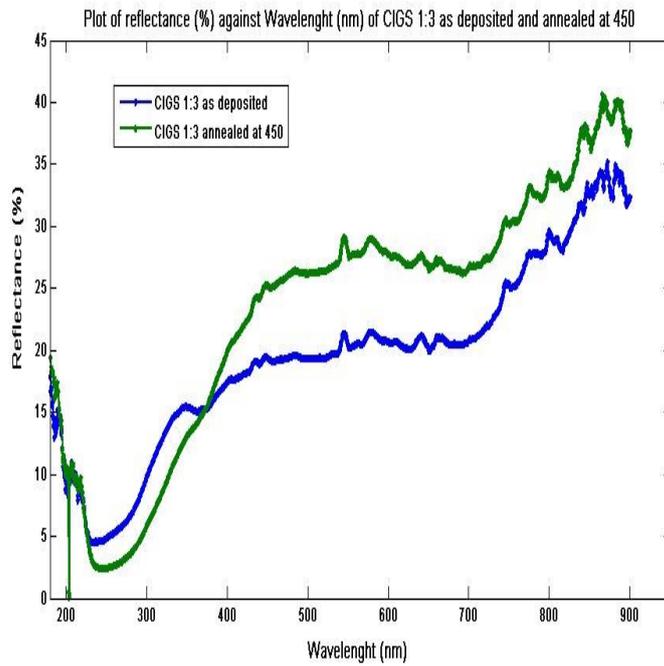


Figure 3: Graph of reflectance against wavelength for CIGS (1:3)

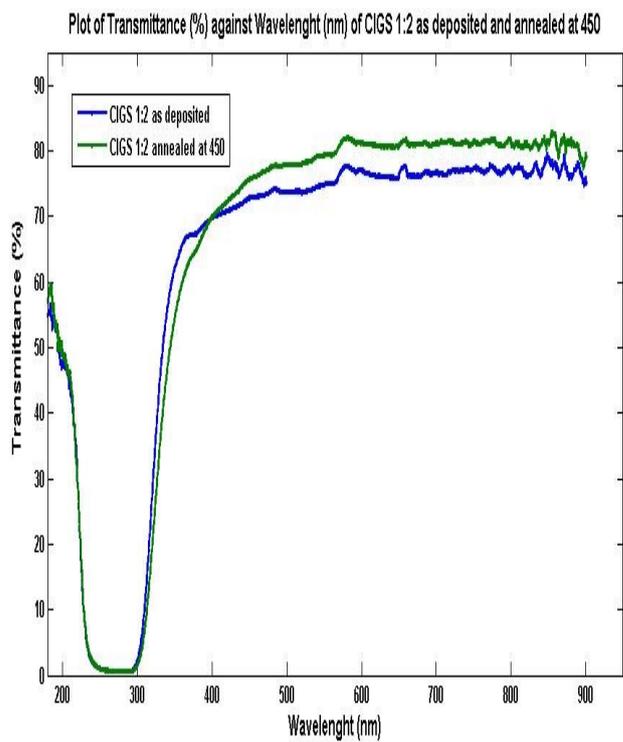


Figure 4: Graph of transmittance against wavelength for CIGS (1:2)

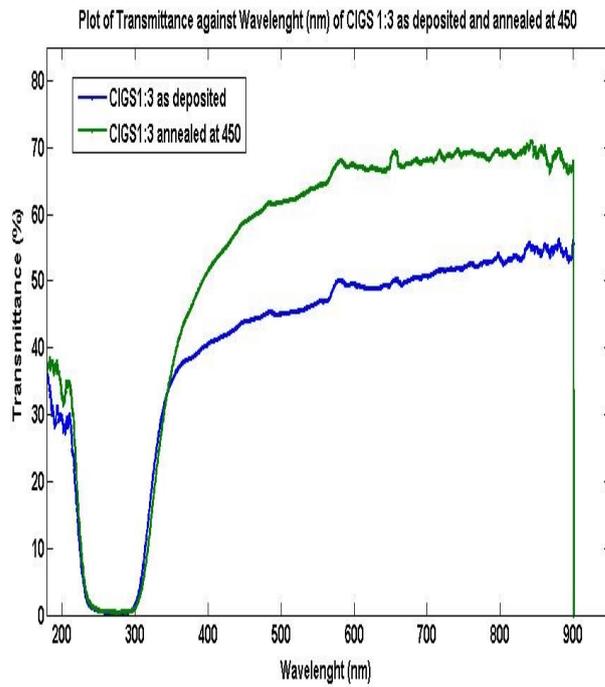


Figure 5: Graph of transmittance against wavelength for CIGS (1:3)

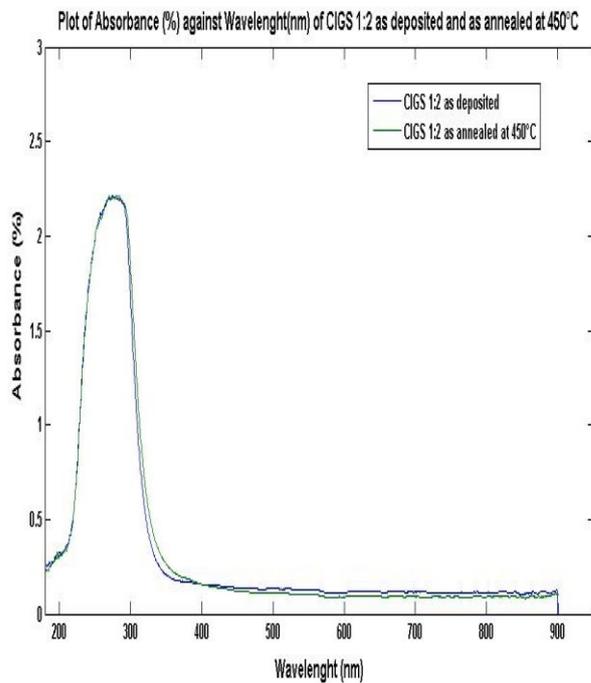


Figure 6: Graph of absorbance against wavelength for CIGS (1:2)

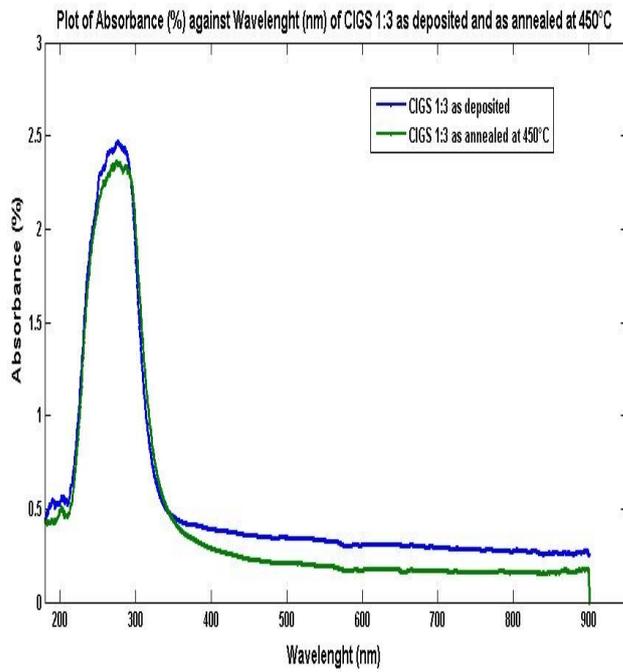


Figure 7: Graph of absorbance against wavelength for CIGS (1:3)

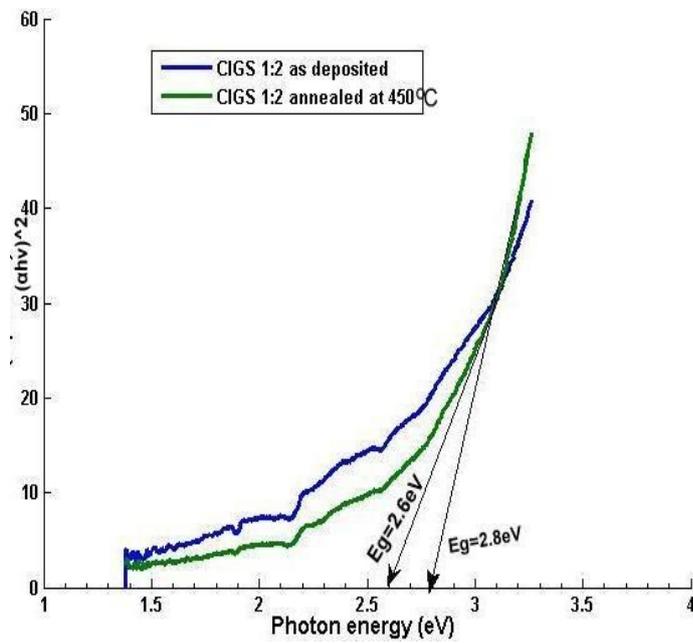


Figure 8: Graph of $(\alpha h\nu)^2$ against photon energy in eV for CIGS (1:2)

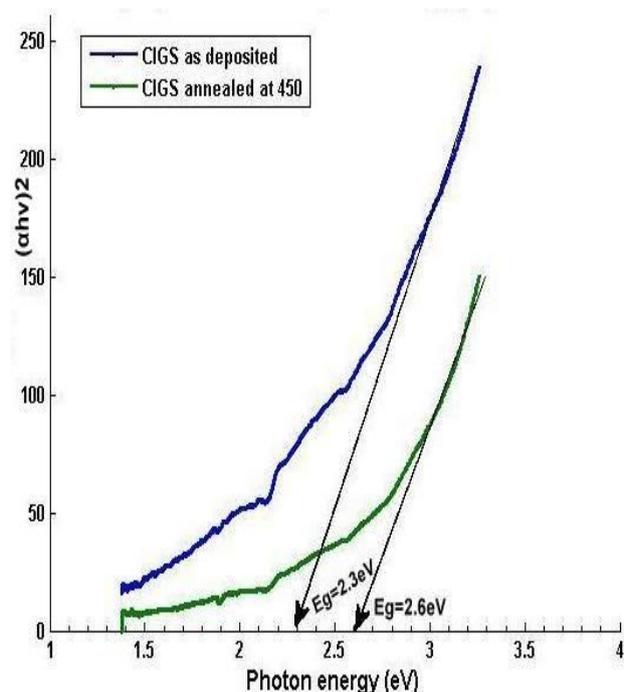


Figure 9: Graph of $(\alpha h\nu)^2$ against photon energy in eV for CIGS (1:3).

The optical analyzes (reflection, transmission and absorption data) were accomplished by using Avantes UV-VIS-NIR spectrophotometer in the range 200-900 nm. Optical effects deal with transitions between bands and/or energy levels in the band gap. Therefore, optical measurements are of importance in analyzing semiconductors. Figures 2 and 3 shows the reflectance graphs of CIGS (1:2) and (1:3) thin films respectively, CIGS reflectance was found to be around 2-43 % in the wavelength region 200-900 nm. Reflectance becomes very small around 250 nm. It was observed that the annealed sample has the highest peak to the as-deposited. This is in agreement with the work of Al-Mamun, Islam and Bhuiyan (2005) who reported copper selenide thin films deposited by CBD. Similar behaviour was reported for Cu_{2-x}Se thin films prepared via CBD by Nair, Rodriguez-Lazcano and Nair in 2001. It is observed that average reflectance was below 40 % for all annealed films and below 35 % for as deposited thin films. CIGS (1:2) annealed thin films had the greatest reflectance of about 38 % than all other films. Results from the reflectance spectra show that the presence of Ga in CIGS thin films reduces reflectance of the thin films in the visible and infrared range. The reduced reflectance characteristics is so imperative since it being the window layer part of the solar cell, reflectivity is supposed to be as low as possible. From the optimized data (Figure 2), CIGS (1:2) had the least reflectance of 25 % at a wavelength 800 nm. Figures 4 and 5 showed the transmittance for CIGS (1:2) and (1:3) thin films respectively. The transmittance obtained ranged between 50-82 % and 29-70% for the CIGS 1:2 and 1:3, as-deposited and annealed respectively in the wavelength range 200-900 nm. A gradual decrease in transmittance is generally observed in the lower wavelength region (220-300 nm) and then increases steadily, this may be due to absorption by free carriers in the degenerate films. It was observed that gallium doped CIGS (1:2) thin films had a higher transmittance than CIGS (1:3). All films demonstrated transmittance above 55 % for wavelength above 400 nm. There was no difference in transmission at low wavelength below 300 nm for as-deposited and annealed films. Annealed samples had highest transmittance above 600 nm (i.e in the ultraviolet visible electromagnetic spectrum range). Below 300 nm there was a sharp fall in the percentage transmittance of the films, an indication of a strong increase in

absorption (Kim, Auyeung and Pique, 2009). This could be attributed to rapid change in the optical absorption coefficient, and is an indication that some states have been created in the region between the conduction and valence band. This could also be attributed to the increase in fundamental absorption as photon striking increases with increase in carrier concentration (Kumar and Sankaranarayanan, 2009). The band gap values increased with increase in doping concentration which could be attributed to the Burstein-Moss shift (Kim, Auyeung and Pique, 2009). This is due to increase in n-type carrier concentration as the absorption edge shifts to higher energy levels. The optimized transmittance was obtained from Figure 4 which showed that optimized transmittance with Ga doping was obtained at 0.2 Gallium concentrations. The optimized transmittance at $\lambda = 880$ nm was found to be 82%. This transmittance value of Gallium doped CIGS is good for the window material to be used in solar cells (Nadeem and Waqas, 2000). This value of high transmittance is comparable with the values for doped ZnS thin films deposited by Anthoy in 2012. Figures 6 and 7 showed the absorption spectra for CIGS (1:2) and (1:3) respectively. The films have good absorption at short wavelength region. The absorption decreased with increasing wavelength of solar radiation. From Figure 7, there was a decrease in absorbance up to a doping level 0.3 of gallium at $\lambda = 250$ nm, then a slight increase in absorption. The increase in absorption occurs when the photon energy is equal to the value of the energy gap when electronic transfers between the valence band and conduction band begin (Wanjala, Njoroge and Ngaruiya, 2016). Thin films of CIGS (1:2) had the lowest of absorbance of 2.3% at wavelength 250 nm. Figures 8 and 9 showed the extrapolated band gaps energy values for CIGS (1:2) and (1:3) for annealed and as-deposited thin films respectively. The band gap of CIGS (1:2) and (1:3) ranged from 2.6-2.8 eV and 2.3-2.6 eV respectively. But these deviate from the study of Chihi, Boujmil and Bessais (2015) who deposited CIGS by electro-deposition route on glass substrate and achieved optical energy band gap that increased from 1.12 to 1.33 eV. However, this kind of deviation was reported by Singha, Rangarib, Sanagapallia, Jayaramana and Mahendraa (2004) where CdTe film was grown and band gap energy of 2.8eV was obtained instead of 1.5eV. The increase in band gap energy makes CdTe a good material for electroluminescent display device and window layer in n-CdTe/p-CdTe homojunction device. They also obtained 2.98 eV for CdS thin film instead of 2.4 eV and it was concluded that this makes the film a better window material in an n-CdS/p-CdTe heterojunction solar cell. The primary function of a buffer layer in a hetero-junction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer. In addition, this layer should have minimal absorption losses and should be capable of driving out the photo-generated carriers with minimum recombination losses and transporting the photo generated carriers to the outer circuit with minimal electrical resistance. The band-gap of a window layer should be as high as possible and the layer should be as thin as possible to maintain low series resistance (Chopra, Paulson and Dutta, 2004). The band-gap of the synthesized thin films is high with small thickness which agrees with Chopra, Paulson and Dutta (2004). The energy band gaps of the films decreased with increase in concentration of gallium to the minimum band gap of 2.3 eV and 2.6 eV for CIGS (1:3), as-deposited and annealed films respectively. Decrease in optical band gap energy can be attributed to creation of new donor levels in the forbidden zone; and a shift in the Fermi level causing the band structure of the films. Further increase of doping concentration of gallium could result to increase of band gap. This could be attributed to absorption edge being pushed to higher energies as a result of all states close to the conduction band being populated with excited electrons from the valence band. As doping concentration was increased, more and more donor states may be produced which could push Fermi level higher in energy (Wanjala, Njoroge and Ngaruiya, 2016). This is a good observation for window layers that are required to have high transmittance properties.

From Table 2, the resistivity of the CIGS (1:2) thin films for as-deposited and annealed at 450 °C are $1.73 \times 10^{-4} \Omega\text{m}$ and $2.42 \times 10^{-3} \Omega\text{m}$ while for the CIGS (1:3) films are $3.77 \times 10^{-4} \Omega\text{m}$ and $1.33 \times 10^{-3} \Omega\text{m}$ respectively. This showed that high resistivity was recorded for the annealed samples. This agrees with the report of Al-Mamun, Islam and Bhuiyan, (2005) for similar films. It has been suggested that the resistivity of this type of material should not be too high or low due to the inevitable defects in solar cells fabrication during production processes (Ikihiyoa, 2015). It was observed that resistivity decreased with increase in Ga ion concentration and it ranged between $1.73 \times 10^{-4} \Omega\text{m}$ to $2.42 \times 10^{-3} \Omega\text{m}$ and $3.77 \times 10^{-4} \Omega\text{m}$ to $1.33 \times 10^{-3} \Omega\text{m}$ for as-deposited and annealed samples respectively. The low sheet resistance obtained was due to the Ga substitution of In in the grain boundaries leaving additional electrons acting as donors. At higher doping concentration, segregation of Ga takes place resulting in the increase of resistance. Though the film resistivity increases, it can be used for photovoltaic applications with adjustments on resistivity either by further doping with dopants that reduce resistivity or introducing low resistivity grids. The respective conductivities for as-deposited and annealed films are $4.132 \times 10^2 \Omega\text{m}^{-1}$ and $5.780 \times 10^3 \Omega\text{m}^{-1}$ for CIGS (1:2), $2.652 \times 10^3 \Omega\text{m}^{-1}$ and $7.520 \times 10^2 \Omega\text{m}^{-1}$ for CIGS (1:3). Similar sheet resistivity measurements for ZnS were obtained using Van der Pauw technique in the order of $10^{-1} \Omega\text{cm}$ to $10^{-2} \Omega\text{cm}$ and electrical conductivity of 10^2 to $10^3 (\Omega\text{cm})^{-1}$ (Wanjala, Njoroge and Ngaruiya, 2016).

CONCLUSION

The results of this study make chemical bath deposition more preferable to other methods for its large areas coating in a reproducible and low cost way. Also, the thin films deposited through this technique were found to have high absorbance in UV-VIS-NIR regions while the films absorbance increases as the thickness increased, thus they could find applications in solar radiation absorbers for solar cell applications. The high transmittance of the films also made the films good candidates for solar cell absorbers. The high band gap properties indicate that the films can be used as a window layer in the fabrication of thin film heterojunction solar cell and other optoelectronic devices. In addition, the low reflectance properties make them good materials for antireflection coatings, solar cell absorbers, thermal control and photosynthetic coatings. Conclusively, high energy band gap thin films have been generated for the design of photovoltaics/solar cells.

Compliance with Ethical Standards:

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