STUDY EFFECTS OF AMMONIUM SOLUTION ON CHEMICAL BATH AS-DEPOSITED COPPER ALUMINUM DISELENIDE THIN FILMS

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Abstract

Because of expensive nature of silicon – based solar cells, many scientists are looking for new materials that are cheap for the solar cell applications. Ternary chalcogenide materials were deposited onto microscope glass slide using simple chemical bath deposition technique. Here, we study the influence of ammonium solution (pH) on the preparation of thin films. The optical properties of deposited films have been studied using Uv-Vis spectrophotometer. The results showed that the films have absorbance, $A \approx 20\%$, transmittance, $T \approx 64\%$, absorption coefficient, $\alpha \approx 4.14x10^{5} m^{-1}$, extinction coefficient, $\kappa \approx 15.72x10^{3}$, optical conductivity, $\delta_{op} \approx 2.55x10^{13} S^{-1}$, real dielectric function, $\varepsilon_r \approx 5.33$ and energy band gap, $E_g \approx 2.52 - 2.102eV$. The pH played important role during the deposition process.

Introduction

The development of nanomaterials with special size and shape may lead to new chances to explore materials, physical and chemical properties. In recent years, semiconductor thin films have been attracting much attention due to their great potential in solar cells, optoelectronic devices, sensors, and laser materials [Kassim *et al*, 2010]. Thin films photovoltaic devices have high worldwide demand to generate an efficient, renewable and clean solar energy as fossil fuel sources will be exhausted in future [Liang *et al*, 2008]. In recent years, considerable efforts have been made to find out low cost materials such as metal chalcogenide materials for solar energy conversion applications [kassim *et al*, 2010]. There are several methods that can be used to prepare thin films such as chemical bath deposition (CBD) [Oladeji *et al*, 1999, Fajinmi *et al*., 2009, Offiah *et al*., 2012, Kassim *et al*., 2010, Osuwa *et al*., 2011 and Maria *et al*.,2009], electrodeposition [Kassim *et al*., 2009 and Liang *et al*., 2008], low-pressure metalorganic chemical- vapor deposition [Chichibu *et al*., 1995 and Yoshiyuki *et al*., 2002], travelling – heat method [Alonso *et al*., 2000], mechanical alloying technique [Rafea *et al*., 2008], Vacuum Evaporation (Prabahar *et al*, 2010) and Sulphurization (Antony *et al*, 2003). The chemical bath deposition method is preferred for its simplicity, inexpensive and capability to achieve large surface area coatings [Kassim *et al*., 2010].

CBD has been used over the years to deposit chalcogenide material thin films: mainly ZnS [oladeji *et al*., 1999], ZnCdS [Maria *et al*., 2009], NiS_2 [Osuwa *et al*., 2011 and Kassim *et al*., 2010], CuS [Offiah *et al*., 2012], CdS [Fajinmi *et al*., 2009], Cu_4SnS_4 [Kassim *et al*., 2010]. Generally, in a CBD process, ammonia (NH_3) is used as a complexing agent to bind the metallic ions so as to minimize the precipitation of corresponding bulk compounds [Oladeji *et al*., 1999]. In this method, films are deposited on substrates whether metallic or non-metallic by dipping

them into suitable solution bath containing metal salts. The metallic ions and non-metallic ions which are present in the deposited solution react with each other and become compound. The basic principle is that in order to precipitate a certain compound from solution, its ionic product (I.P) must exceed the solubility product (S.P) [Yoshida *et al*., 2009]. The Copper aluminum diselenide semiconductor is one of the wide-gap members belonging to the I – II – VI_2- type of ternary compounds that crystallize in the chalcopyrite structure [Chichibu *et al*, 1995]. Chalcopyrite Cu – III – VI_2 compounds are promising for optoelectronic applications [Shirakata *et al*, 2000 and Alonso *et al*, 2000]. In this paper, we report study effects of ammonium solution as a pH adjuster on chemical bath deposited copper aluminum diselenide thin films on microscope glass substrates by varying the volume (1 – 9 ml)**.** The optical properties of the films were investigated.

Experimental

The $CuAlSe_2$ compound thin films were obtained from $CuCl_2.2H_2O$, $Al_2(SO_4)_3.14H_2O$), and Na_2SeSO_3 as sources of Cu^{2+}, Al^{3+} and Se^{2-}. All the reagents used were analytical grade. EDTA was used as a complexing agent during the deposition and ammonia solution acted as source of pH adjuster. A glass rod was used as a stirrer, mercury in glass thermometer was used to measure the bath temperature and Mac digital pH meter (MSW-552) model was used to measure the pH of the solution. The chemical baths were prepared by putting 5ml of 0.1 molar solution of copper chloride, 5mls of 0.1 molar solution of $Al_2(SO_4)_3.14H_2O$, 5ml of 0.1 molar solution of EDTA in a growth beaker were prepared and the solution was latter stirred before adding 5ml of sodium selenosulphate and 1 – 9 ml of ammonia solution respectively and deep bluish coloration was observed. When sodium selenosulphate was added, the solution did not dissolve until it was heated to temperature of 33^oC. Each bath was filled up to 50ml mark with distilled water and stirred gently and long enough to ensure uniformity of the mixture. Pre-degreased microscope glass substrates cleaned with distilled water and dried in air were then inserted vertically in the reaction bath while synthetic foam which partly covered the top of the bath. Five different mixtures using 1.0 ml, 3.0 ml, 5.0 ml, 7.0 ml and 9.0 ml of ammonia solution were prepared at room temperature of 28 ^oC and left undisturbed for twenty four hours. All the samples were further washed in distilled water and air – dried for analysis.

The substrates introduced into the reaction bath gave reaction details as hereunder stated;

$$CuCl_2.2H_2O + EDTA \rightarrow [Cu\text{-}EDTA]^{2+} + 2Cl^- + 2H_2O$$

$$[Cu - EDTA]^{2+} \rightarrow Cu^{2+} + EDTA$$

$$(Al_2(SO_4)_3 .14H_2O) + EDTA \rightarrow 2[Al\text{-}EDTA]^{3+} + 3SO_4^{2-} + 14H_2O$$

$[Al\text{-}EDTA]^{3+} \rightarrow Al^{3+} + EDTA$

$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^{2-}$

$2HSe^{2-} + 2OH^- \rightarrow 2H_2O + 2Se^{2-}$

$Cu^{2+} + Al^{3+} + 2Se^{2-} \rightarrow CuAlSe_2$

The optical characterization recorded the optical absorbance carried out with the aid of Jenway 6405 UV-Vis spectrophotometer. The instrument gives the extent of absorbance, A, of the optical spectra for the range of 300nm - 700nm. The film-coated microscope glass substrates were placed across the sample radiation pathway while the uncoated substrate was put across the reference path. The absorption coefficient,α, Photon-energy, $h\nu$, and Refractive index, n are given by Okoli [2007] as

$$\alpha = \frac{A}{\lambda} \quad (1)$$

$$h\nu = \frac{1.2eV}{\lambda} \quad (2)$$

$$n = \frac{1+R^{\frac{1}{2}}}{1-R^{\frac{1}{2}}} \quad (3)$$

Transmittance, T, reflectance R, real dielectric constant, ε_r and extinction coefficient, k, are given by Rafea [2008] as

$$T = \frac{(1-R)^2 e^{-\alpha t}}{(1-R^2)e^{-2\alpha t}} \quad (4)$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5)$$

$$\varepsilon_r = n^2 - k^2 \quad (6)$$

$$k = \frac{\lambda\alpha}{4\pi} \quad (7)$$

And films thickness, t given by Fajinmi [2009] as

$$t = \frac{In\,(1/T)}{\alpha} \quad (8)$$

was determined by optical method. The energy band gaps were determined by extrapolation of the straight portion of the graphs of α^2 against photon energy (hν) at point $\alpha^2 = 0$ (Rafea et al, 2008).

Results And Discussion

The effect of ammonia quantity (in ml) on growth of the films was examined. The quantity of ammonia in the bath varied from 1 – 9 ml increased the pH of the bath from 8.35 – 10.1. As the pH of the bath increased, the film thickness increased till at certain volume of ammonia (7 ml) before it begins to decline as seen in fig.1. The films were thick, porous, non – reflecting and weakly adhered to the substrate. At the intermediate pH values $(8.75 \leq pH \leq 9.2)$, the films are uniform, smooth, non- porous and tightly adherent to the substrate support. There was low deposition rate at pH interval of 8.35 to 8.75. This may result to non-precipitation of OH^- ions in the formation of complex, thereby lowering the concentration of metals ions required for thin films formation. When the OH^- ions participate in the formation of the complex, they stabilize

the complex leading to slow release of metal ions into the bath [Ahmed et al,2006] as in pH of interval 8.75 – 9.2. The variation of the film thickness with pH value in this region seems to be quasi – linear. We attribute the layer thickness in this region to the controlled rate of release of ions species. At higher pH values $(9.2 \leq pH \leq 10.10)$, layer thickness decreased considerably. A pH value of 9.2 was selected for good growth of the films.

In the case of absorbance of the films as in fig.2, it increases from the pH interval of 8.35 - 9.2 and dropped to a lower value. This also results from the explanation above on that film thickness versus pH. Sample A –D correspond to pH of 8.35 – 9.2. This is where the precipitation of OH^- ions occurs in the formation of the complex. The average absorbance of the films is approximately 20%. This shows that the films have poor absorbance. From the equation, $\alpha = \frac{A}{\lambda}$, it shows that absorption coefficient is directly proportional to absorbance of the films. This shows that the films have poor absorption coefficient as shown in fig. 3. The films have high average value of transmittance of 64%. The graph from fig. 4 shows that films with pH interval of 8.35 – 9.2 have high transmittance value and declined with pH value of 10.1. This x-rays those films with pH value range of 8.35 – 9.2 decrease with transmittance. Films obtained from bath having lower film thickness are most transparent and optical homogeneous. This is confirmed from the reflectance versus wavelength graph, as in fig.5, which indicates that the films have low reflectance value. Also it was said earlier that the films have low absorbance and all these contributed to high value transmittance of the films. In fig.6, the optical conductivity of the material decreases from wavelength of 380 – 800 nm/ increases from photon energy of 1.7732 – 3.2664 eV. It has low optical conductivity at near infrared. The optical conductivity of the films increases as the pH increases. The extinction coefficient of the films was examined in fig. 7. It was noticed that all the samples have low value of extinction coefficient in visible

region. This makes it a good candidate in solar cell application since its longevity in visible region is high. Increase in pH brought about increase in extinction coefficient of the films. In fig. 8, the refractive index of all the samples has nearly constant value in all the samples in the visible region. The higher the pH value the higher the refractive index. It has average refractive index of 2. The pH of the films increases alongside with the refractive index. The real dielectric function of the material as shown in fig. 9, shows that the increase in pH of the films brought about increase in the values of dielectric function. In fig. 10 – 13, they show plot of absorption coefficient squared versus photon energy. The effect of pH on energy band gap was seen to decrease it as the pH increase. The value range of energy band gap is $\approx 2.520 - 2.102$ eV. Sample D has higher energy band gap than sample E due to the extent of complex precipitation. Immediately after the peak pH (9.2), the rate of releasing complexes dropped and increasing the inter-band energy.

Conclusion

We have presented the study effects of ammonium solution on $CuAlSe_2$. The film growth is found to depend on the pH of the reaction bath. The results showed that the films have absorbance, $A \approx 20\%$, transmittance, $T \approx 64\%$, absorption coefficient, $\alpha \approx 4.14x10^5 m^{-1}$, extinction coefficient, $\kappa \approx 15.72x10^3$, optical conductivity, $\delta_{op} \approx 2.55x10^{13} S^{-1}$, real dielectric function, $\varepsilon_r \approx 5.33$ and energy band gap, $E_g \approx 2.52 - 2.102eV$. These show that $CuAlSe_2$ is a good candidate for photovoltaic applications, nonlinear optics, blue light emitting diodes.

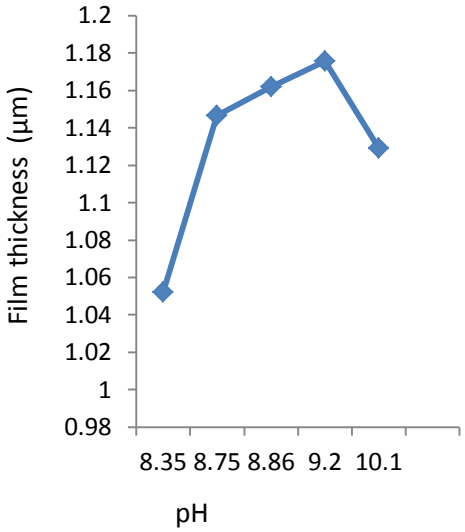

Fig. 1.Variation of average films thickness with pH for all samples

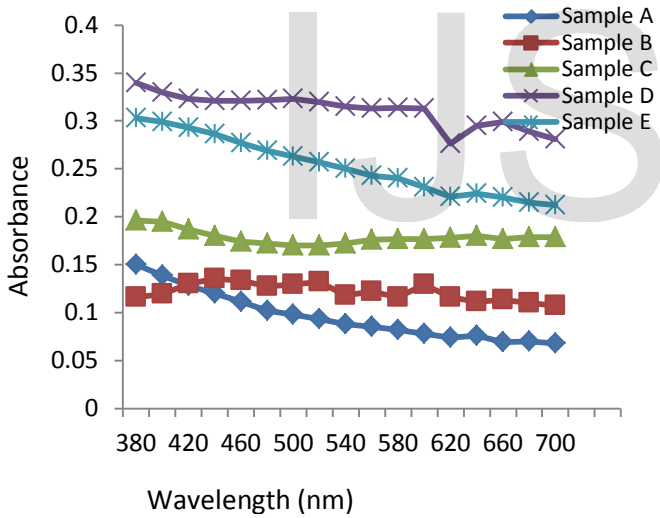

Fig. 2. Variation of films absorbance with wavelength

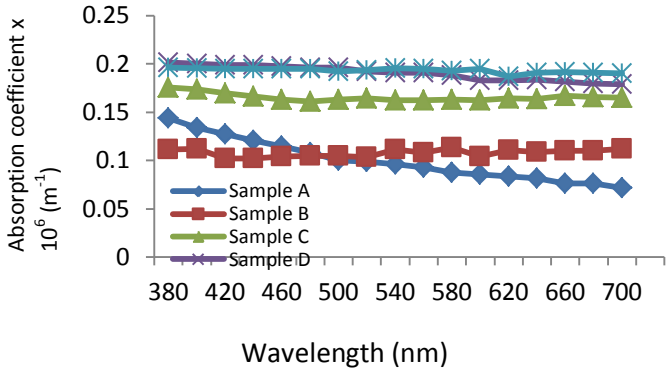

Fig. 3. Variation of films absorption coefficient with wavelength

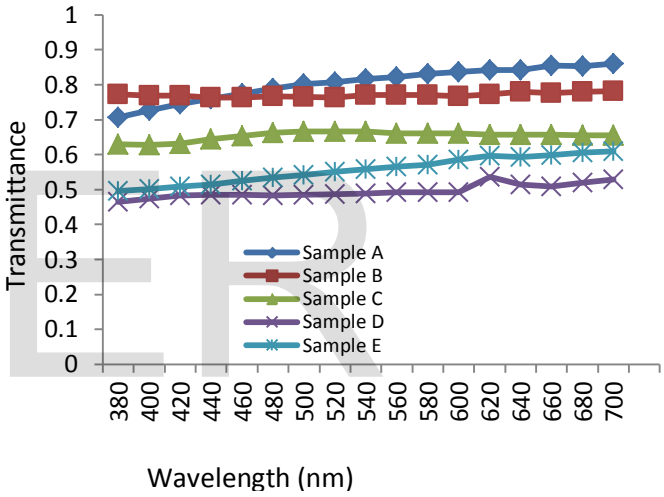

Fig.4. Variation of films transmittance with wavelength

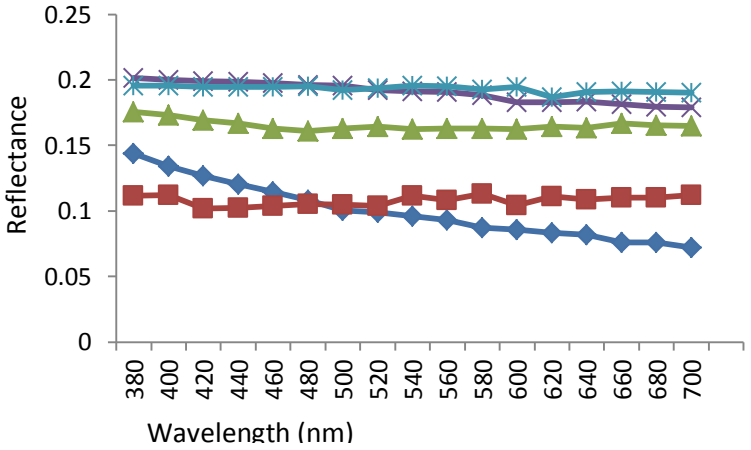

Fig.5. Variation of films reflectance with wavelength

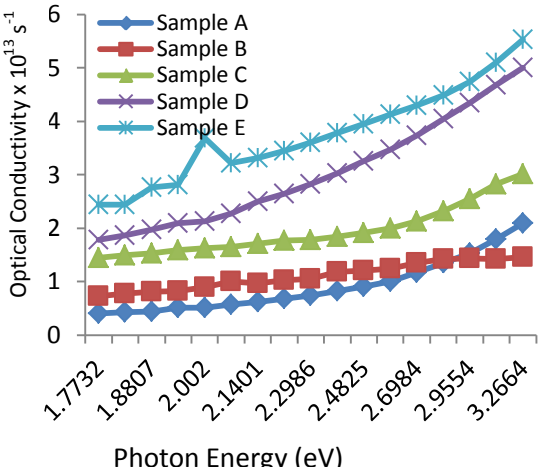

Fig.6. Variation of Films optical conductivity with photon energy

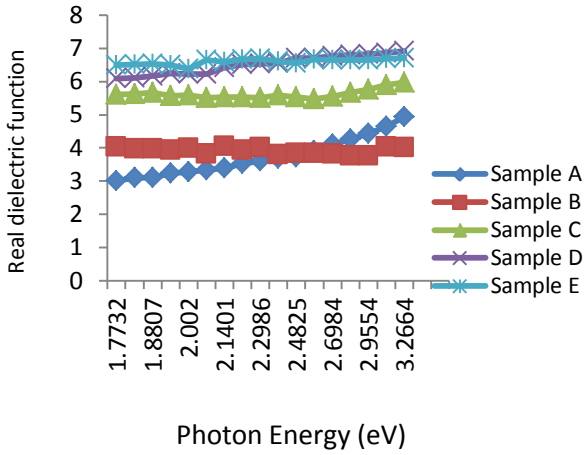

Fig.9. Variation of real dielectric function with photon energy

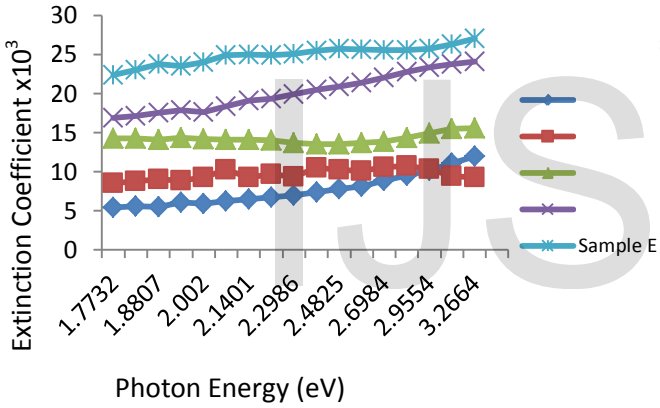

Fig.7. Variation of extinction coefficient with photon energy

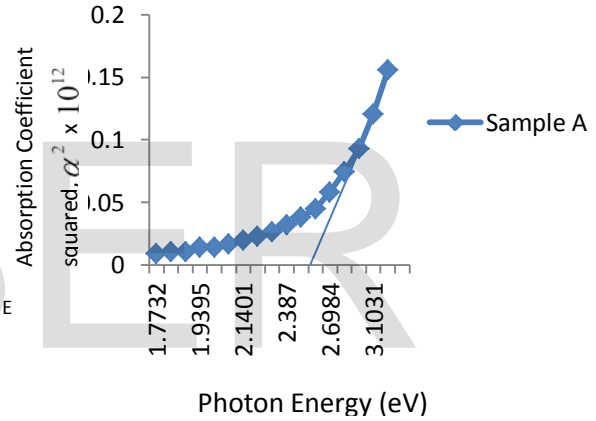

Fig.10. Variation of absorption coefficient squared with photon energy for sample A

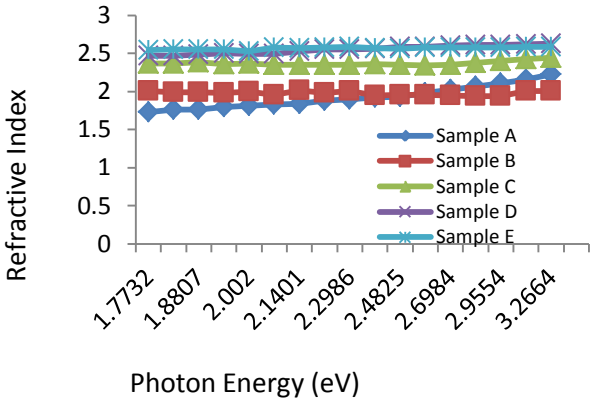

Fig.8. Variation of refractive index with photon energy

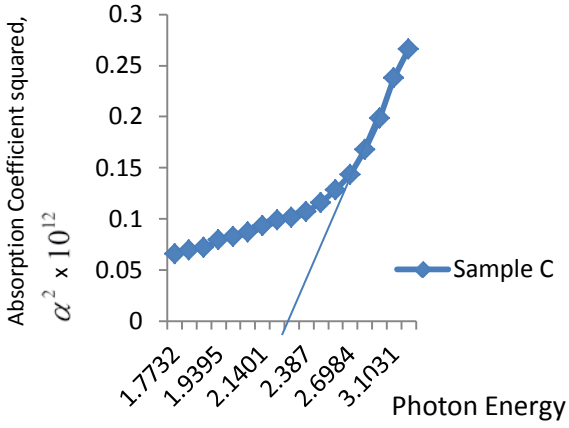

Fig.11. Variation of absorption coefficient squared with photon energy for sample C

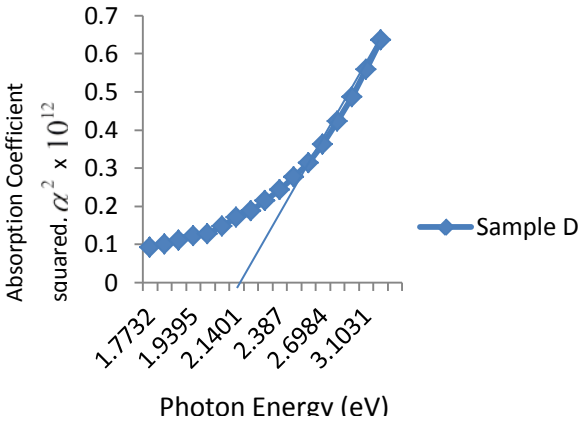

Fig.12. Variation of absorption coefficient squared with photon energy for sample D

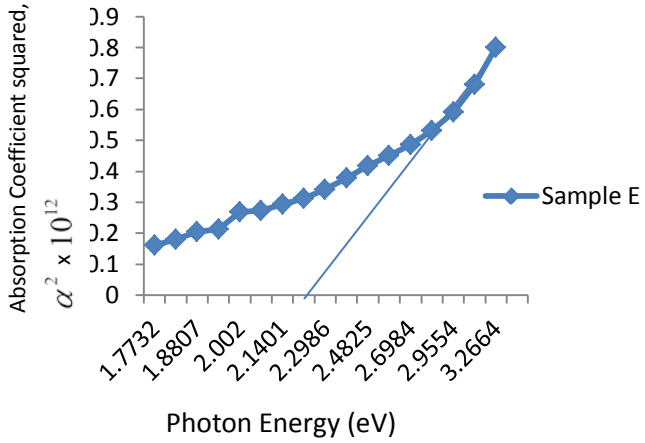

Fig.13. Variation of absorption coefficient squared with photon energy for sample E

References

Ahmed A.D and Ibanga E.J; (2006): Structural and surface compositional characterization of silver thin films prepared by solution growth technique, *Nigeria Journal Physics,* properties of $CuAlSe_2$, *Journal of Applied Physics* vol. 88, No. 4, 1923 – 1927.

Antony A, Asha A. S., Yoosuf R; Manoj R., and Jayaraj M.K. (2004): Growth of $CuInS_2$ thin films by sulphurization of Cu-In alloys, *Solar Energy Material and Solar Cells* vol. 81: 407 – 417.

Chichibu S, Shirakat S, Isomura S, Harada Y, Uchida M, Matsumoto S and Higuchi H, (1995): Photoluminescence studies in $CuAlSe_2$epilayers grown by low-pressure metalorganic chemical – vapor deposition, *Journal of Applied Physics* Vol. 77, No. 3: 1225 – 1231.

Cui F., Wang L., Xi Z., Sun Y., and Yang D; (2009): Fabrication and characterization of $CuInS_2$ films by chemical bath deposition in acid solutions, *Journal of Materials Science: Materials in Electronics*, Vol. 20, No. 7: 609 – 613.

G.R Fajinmi and J.S.A. Adelabu, (2009): Preparation and characterization of chemically deposited cadmium Sulphide thin films. *The Pacific Journal of Science and Technology*, Vol 10, No 2:817 – 822.

Honeyman W.N, (1969): Preparation and Properties of Single Crystal $CuAlS_2$ and $CuAlSe_2$, *Journal of Chemistry and Physics of Solids*, Vol. 30, No 8, 1935 – 1942.

I.O. Oladeji and L. Chow, (1999): A study of the effects of ammonium salts on chemical bath deposited zinc sulfide thin films. *Thin solid films,* 339: 148 -153.

J.C Osuwa and P.U Uwaezi, (2011): Effects of annealing on optical and solid state properties of NiS_2 thin films. *Chalcogenide Letters*, Vol. 8, No. 9: 587 – 594.

Kassim A, Kuang Z., Sharif A, Haron M.J, Tee W.T and Ho Soon Min. (2009): Effects of deposition potential on Cu_4SnS_4 thin films prepared by electrodeposition technique, *The Arabian Journal for Science and Engineering* vol. 35, No.1A: 83 – 91.

Kassim A, Wee T.T, Abdullah A. H, Nagalingam S, and Ho Soon Min, (2010): Deposition and characterization of Cu_4SnS_4 thin films by chemical bath deposition method, *Macedonian Journal of Chemistry and Chemical Engineering*, vol. 29, No. 1: 97 – 103.

Liang T. S, Zainal Z, Tee W.T and Hamadneh I., (2008): Potentiostatic deposition of copper indium disulfide thin films: Effect of cathodic potentials on the optical and photoelectrochemical properties, *The Malaysian Journal of Analytical Sciences*, Vol. 12, No. 3: 600 – 608.

Maria Stefan, Ioan Baldea, Rodica Grecu, Emil Indrea and Elisabeth-Jeanne Popovici, (2009): Growth and characterization of Zinc-Cadmium Sulphide thin films with special optical properties. *Studia Universitatis Babes-Bolyai, Chemia*, Liv, 3: 203 -211.

Megali O, Bouraiou A, and Attaf N; (2008): Characterization of $CuInSe_2$ thin films elaborated by electrochemical deposition, *Revue des Energies Renouvelable,* Vol. 11, No. 1: 19 – 24.

Okoli D.N, (2007): Growth and characterization of Ternary compound thin films and their possible applications, *Ph.D Thesis NAU*.

Prabahar S, Balasubranian V, Suryanarayanan N, and Muthukumarasamy N, (2010): Structural characterization of vacuum evaporation of copper indium diselenide thin films. *Journal of Ovonic Research,* Vol. 6, No. 1: 45 – 50.

Rafea A. M and Roushdy (2008): Preparation and characterization of $CuInSe_2$ – $CuAlSe_2$ and ZnS nanopowder by mechanical alloying technique, *Chalcogenide Letters*, Vol. 5. No. 10: 219 -227

Shirakata S, Chichibu S, Miyake H. and Sugiyama K,(2000): Optical properties of $CuGaSe_2$ and $CuAlSe_2$ layers epitaxially grown on Cu $(In0.04\ Ga0.96)Se_2$ substrates, *Journal of Applied Physics* Vol.87, No. 10: 7294 - 7302.