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The Effect of Manganese percentage doping on the Thickness and Conductivity of Copper sulphide nanofilms prepared by Electrodeposition method

Okafor Patricia C., Ekpunobi Azubike J.

Abstract— Manganese doped copper sulphide nanofilms were prepared using aqueous solution of zinc chloride, manganese chloride, sodium thiosulphate and triethanolamine as a complexing agent by electrodeposition method. The experiment was carried out at room temperature and optimum deposition condition with the manganese percentage doping varied from 3% to 23%. The XRD pattern revealed that Mn doped CuS nanofilms have cubic structure with mean crystallite size of approximately 2.7937nm.The thickness and conductivity of CuS:Mn films were determined by optical method. Results from our investigation revealed that with the increasing of Mn percentage doping from 3% to 23%, the thickness of the CuS:Mn films ranged from 4.23 – 18.49nm, absorption coefficient from 0.20 x 10^5 to 1.0 x 10^5, optical conductivity from 3.0 x10^{12} to 5.50 x10^{12} and electrical conductivity from 1.53 x 10^2 to 1.58 x 10^2. Such CuS:Mn films in nanometer size range and of high conductivity could be suitable for applications in the fabrications of thin films solar cells and various optoelectronic devices.

Index Terms— Effect of manganese percentage doping, Thickness, Conductivity, Copper sulphide nanofilms, Electrodeposition

1 Introduction

COPPER sulphide as an important member of II-VI semiconductor chalcogenide family has great potential in applications such photothermal conversion, solar cells, electroconductive electrodes, microelectronic devices, optical filters, microwave shielding coatings in low temperature gas sensor [1]. Ternary copper chalcogenides like copper indium diselenide and copper indium gallium selenides, in recent times, are now widely used in the fabrication of solar photovoltaic cells. Special attention is given to copper sulphide thin films due to the discovery of the CdS/Cu_xS hetereojunction solar cell [2, 3].

Copper sulphides had been widely studied because they form complex structures, with copper atoms in a mixed valence states in some of its phases [4]. Such characteristics are responsible of very interesting physical properties such as a high electrical conductivity [4]. The compounds exhibit fast ion conduction at high temperatures and exist in wide variety of composition ranging from Cu_2S at Cu- rich sites to CuS_2 at Cu-deficient sites such as CuS [5].

- *Okafor Patricia C. is currently pursuing doctoral degree program in solid state physics in Nnamdi Azikiwe University, Nigeria. E-mail: patphysics@yahoomail.com*
- *Ekpunobi Azubike J. is currently a professor in solid state physics in Nnamdi Azikiwe University, Nigeria.*

Doping of semiconductor allowed the widespread application of such semiconductor in electronic and optic components.[6]. The process of introducing an impurity to semiconductor thin films provides control of band gap, Fermi energy and presence of charge carriers. Incorporation of dopant ions to the host semiconductor increases its carrier concentration and electrical conductivity but degrade the transparency due to the increasing free carriers absorption [7]. However, at higher doping level, increase in carrier concentration lowers mobility due to charge scattering from ionized impurities. Electrical conductivity increase with the increase of film thickness and annealing temperature [8, 9]. Annealing process improves crystallinity of the film; and this indicates low defect density. Thin films with low defect density have better electrical property [10]. Copper sulphides films are p-type substances with holes as the majority carriers [11,12]

There are various methods to prepare copper sulphide thin films such as spray pyrolysis [13], Successive ion layer adsorption and reaction method [14], photochemical deposition [15], chemical bath deposition [16] electrodeposition [17].Particularly attractive, however, is the electrodeposition because of its economy and simplicity for deposition on transparent conducting glass substrates coated with highly conducting semiconductor such as indium tin oxide (ITO). In this work, electrodeposition method has been applied. The main purpose of this study is to investigate the influence of manganese percentage doping on the thickness and conductivity of copper sulphide nanofilms.

2 Materials and Methods

Manganese doped CuS:Mn nanofilms were prepared from acidic bath containing aqueous solutions of 10ml of 0.05M

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copper chloride as Cu^{+2} ions precursor, 10ml of manganese chloride (with Mn ions molar ratio varies from 3% to 23%) as Mn^{+2} ions precursor, 10ml of 0.05M sodium thiosulphate as S^{2-} ions precursor, 10ml of 0.05M tri-ethanolamine (TEA) as a complexing or capping agent. All the chemicals used for the electrodeposition were of analytical grade and all solutions prepared in de-ionized water (Alpha-Q-millipore). Prior to deposition, the ITO glass substrates were degreased with ethanol for 10 minutes; then ultrasonically cleaned with de-ionized water for another 10minutes and finally dried in a desicator. The surface of the platinum plate was thoroughly cleaned and polished. The experiment was carried out using acidic bath of PH 3, at room temperature, optimum deposition time of 60 seconds and optimum deposition voltage of 4.0 Volts with manganese percentage doping in the reaction bath varies from 3% to 23%. The reactions mechanisms for the electrodeposition involve chelating of Cu^{2+} and Mn^{2+} ions with complexing agent, tri-ethanolamine to form a complex ions,$CuMnTEA^{2+}$ and the reaction of this complex ions with the S^{2-} ions from aqueous sodium thiosulphate to form CuMnS thin layer at the surface of the cathode (ITO glass substrate). The deposited thin films were washed with de-ionized water, annealed at temperature 250˚C and kept for analysis.
The X-ray diffraction patterns of Mn doped ZnS nanofilms were recorded by X-ray Mini Diffractometer MD 10 Model with Cu-Ka radiation source of λ=0.15406nm.The thickness and conductivity were determined from the optical data obtained by JENWAY 6405 UV-Vis spectrophotometer at wavelength range of 280nm to 1100nm using the appropriate formula.

3 Results and Discussion

The XRD pattern of the CuS:Mn film sample with 8% Mn is shown in fig. 1.

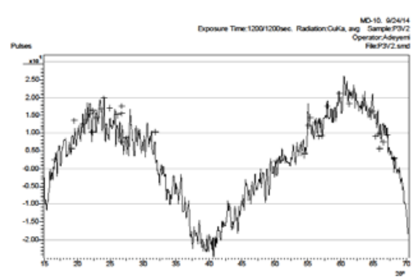

Fig. 1 XRD pattern ZnS:Mn nanofilm with 8% Mn doping

The crystals of Mn doped CuS have cubic structure with preferential growth along (400) direction and lattice constant of a = b = c = 10.087Å. The crystallite sizes of the film sample were of range, 1.17 – 5.5.1032nm with the mean crystallite size of approximately 2.7937nm. Similar cubic structure had been reported for CuS prepared by spray pyrolysis and electrodeposition [18, 19,20]. The low dislocation density value (0.3302) and low microstrain value (0.005) confirmed the good crystallinity of CuS:Mn film sample.

The variation of thickness of CuS:Mn films with manganese percentage doping is represented in Fig. 2.

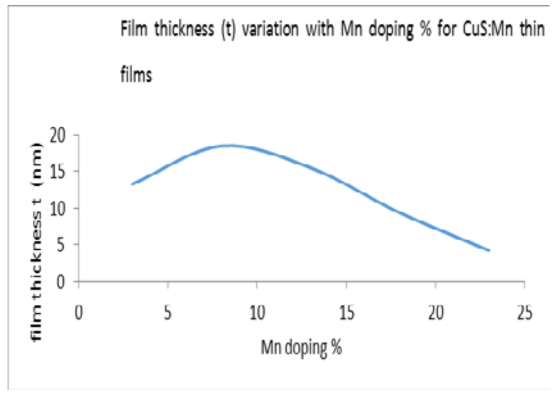

Fig. 2. Film thickness variation with manganese percentage doping for CuS:Mn nanofilms

The film thickness increased from 13.27nm to 18.49nm as Mn doping % increased from 3% to 8% and then decreased to 4.23nm as Mn doping % increased to 23%. The highest film thickness value (18.49nm) was obtained from the film sample (P_3C_2) doped with 8% Mn. The results revealed that at low Mn percentage doping level, the thickness of the film increased with the increasing of Mn doping % but decreased with the increasing of Mn doping % at higher Mn percentage doping level. Similar results had been reported for Mn doped-CdS, ZnS [9, 21,22]. The decrease in the thickness of the film at higher Mn doping concentrations may be attributed to decrease in the growth rate, an indication of minimal deposition of the material on to the substrate [21]. Based on the results obtained, we conclude that electrodeposition using 8% Mn at room temperature was the best condition to prepare good quality of CuS:Mn nanofilms under the current condition. Such CuS:Mn nanofilms could find suitable for applications in various fields of nanofilms technology such nanofilms solar cells, photothermal, optoelectronic and spintronic devices. [1,2,3]
The absorption coefficient (α) spectra, optical conductivity (σ_0) spectra and electrical conductivity (σ_e) spectra of CuS:Mn nanofilms with different Mn percentage doping are shown in Fig. 2, Fig. 3 and Fig. 4 respectively.

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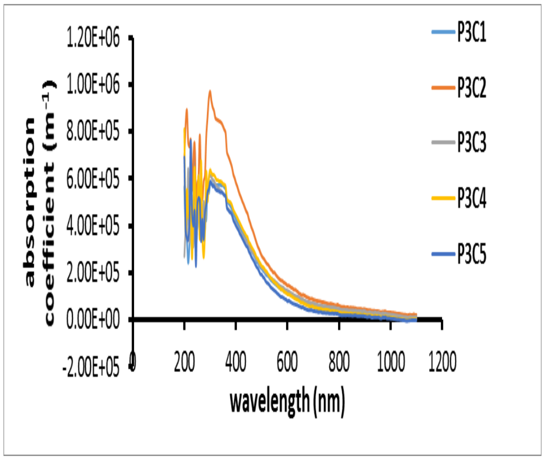

Fig. 3. Absorption coefficient spectra of CuS:Mn nanofilms

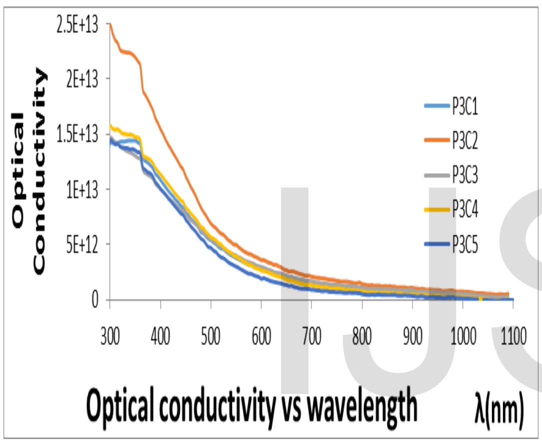

Fig. 4. : Optical conductivity spectra of CuS:Mn nanofilms

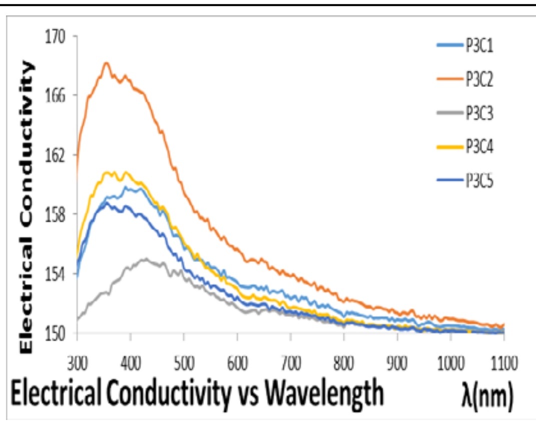

Fig. 5. : Electrical conductivity spectra of CuS:Mn nanofilms

Fig. 2 revealed that the absorption coefficient (α) of all the electrodeposited CuS:Mn nanofilms were relatively high in the wavelength range of UV region and zeroed from the wavelength of 680nm. At wavelength of 550nm in the visible region, the average absorption coefficient of the CuS:Mn films increased from 0.50 x 10^5 to 1.0 x 10^5 as Mn doping % increased from 3% to 8% and then decreased to 0.20 x 10^5 as Mn doping % increased to 23%. The highest absorption coefficient value (1.0 x 10^5) was obtained from the film sample (P_3C_2) doped with 8% Mn. The results revealed that the absorption edge of all the deposited CuS:Mn films are blue shifted towards the shorter wavelength range 290nm - 300nm and this could be attributed to the influence of Mn dopant ions. The obtained absorption coefficient of magnitude 10^5 compares well to 10^6 reported for FeCuS thin films [23] and 10^6 -10^{-} required for semiconductor thin film solar cells [24]. Such films with high absorption coefficient could be employed in the fabrication of thin films solar cells and various optoelectronic devices.

Fig. 3 revealed that the optical conductivity of the CuS:Mn nanofilms were relatively high in UV region and low in NIR region. At wavelength of 550nm, the average optical conductivity of CuS:Mn films increased from 4.50 x10^{12} to 5.50 x 10^{12} as Mn doping % increased from 3% to 8% and then decreased to 3.0 x10^{12} as Mn doping % increased to 23%. The highest optical conductivity value (5.50 x 10^{12}) was obtained from the film sample (P_3C_2) doped with 8% Mn. The obtained results revealed that all the CuS:Mn film samples exhibited high average optical conductivity of magnitude 10^{12} showing that they have good photo response. The difference in the average optical conductivity values of CuS:Mn film samples may be ascribed to the effect of different Mn percentage doping. Such CuS:Mn films are good candidate materials for the fabrication of thin films solar cells. The films could also be employed as photoconductors to generate photocurrents in optoelectronics devices.

Fig. 4 revealed that electrical conductivity (σ_e) of CuS:Mn nanofilms were high throughout UV-Vis-NIR. At wavelength of 550nm in the visible region, the average electrical conductivity of CuS:Mn nanofilms increased from 1.55 x 10^2 to 1.58 x10^2 as Mn doping % increased from 3% to 8% and then decreased to 1.53 x 10^2 as Mn doping % increased to 23%. The highest electrical conductivity value (1.58 x 10^2) was obtained from the film sample doped with 8%. The results showed that at low doping region, electrical conductivity increased with the increasing of Mn percentage doping. The decrease in electrical conductivity observed at higher doping region may be attributed to decrease in carrier mobility due to impurity scattering [8]. The magnitude of average electrical conductivity 10^2 for the CuS:Mn nanofilm samples is within the electrical conductivity range of 10^{-13} to 10^2 of semiconductors [24]. The difference in the peak values of electrical conductivity of the CuS:Mn film samples may be attributed to the effect of variation in Mn percentage doping. Such CuS:Mn films with high electrical conductivity could be employed in the manufacture of the thin films solar cells and in various optoelectronics devices.

4 Conclusion

Manganese doped CuS nanofilms with different Mn percentage doping have been successfully deposited on ITO glass substrates by electrodeposition method. The XRD studies revealed that CuS:Mn nanofilms have cubic structure with crystallite size of approximately 2.7937nm.. The thickness and conductivity of the films were determined by optical method. Results from optical analysis showed that with the increasing of Mn percentage doping from 3% to 23%, the thickness of the CuS:Mn nanofilms ranged from 4.23nm to 18.99nm, absorption coefficient from 0.20 x 10^5 to 1.0 x 10^5, optical conductivity from 3.0 x 10^{12} to 5.50 x 10^{12} and electrical conductivity from 1.53 x 10^2 to 1.58 x 10^2. The difference in the thickness and average conductivity values of the CuS:Mn films shows that the both parameters are significantly influenced Mn percentage doping. Such CuS:Mn thin films with thickness in nanometer range and of high conductivity are promising candidate materials for thin films solar cells fabrications and various optoelectronic devices applications.

References

[1] Alaric, D.S. and Kalita, P.K. (2012); "Chemical synthesis of metal doped copper sulphide nanoparticles in PVA matrix"; International Journal of Chemical Science and Technology, 2(4), 57-60

[2] Das, S.R. (1978); "The preparation of Cu_xS films for solar cells;" Thin solid films 51, 257-264

[3] Pathan, H.M; Salunke, P.V; Sankapal, B.R. and Lokhande C.D. (2001); "Photoelectrochemical investigation of Ag_2S thin films deposited by SILAR method". Materials Chemistry and Physics, 72, 105-108

[4] Cruz-Vazquer C; Inoue M.B. (1999); "Characterization of new copper sulphide materials"; Superfices y Vacio 9, 219 -221.

[5] Bague S.V. (2007); Growth and Characterization of Cu_xS (x = 1.0; 1.76 and 2.0) thin films grown by solution growth"; Journal of Physics and Chemistry of Solids, 68, 1623-1629

[6] Sze S.M. (1981); "Physics of Semiconductor devices"; Wiley-Interscience New York, 2nd ed.

[7] Maity R.C. (2006); "Synthesis and characterization of aluminium doped CdO thin films by Sol-gel process"; Sol. Energy Mater. & Sol. Cell, 90, 597-606.

[8] Al-Shammari A.S; Mulla A.F and Dhafiri A.M (2005); "Preparation and characterization of chlorine doped Cadmium sulphide thin films and their applications"; M.Sc Thesis, King Saud University, College of Science, Department of Physics and Astronomy, Saudi Arabia

[9] Gode F. and Gumus C. (2009); Influences of copper and manganese concentrations on the properties of polycrystalline ZnS:Cu and ZnS:Mn thin films"; Journal of Optoelectronics and Advanced Materials, 11(4), 426-436

[10] Choi J.Y; Kang-Jin K; Yoo J.B. and Donghawan K; (1998); "Properties of Cadmium sulphide thin films deposited by ultrasonication"; Sol.Energy 64(1-3), 41-47

[11] Grozdanov I; Najdoski M; (1995); "Optical and electrical properties of copper sulphide of variable composition"; J. Solid State Chem; 114, 469-475

[12] Johansson J; Kostamo J; Karppinen M; Niinisto L; (2002); "Growth of conductive copper sulphide thin films by atomic layer deposition"; J. Mater. Chem; 12, 1022-1026

[13] Nascu C; Pop I; Ionescu V; Indrea E; Bratu I; (1997); "Spray pyrolysis deposition of CuS thin films"; Mater. Lett; 32, 73-77

[14] Zhuge F.W; Li X.M; Gao X.Y; Zhou P.L (2009); (Synthesis of stable amorphous Cu_2S thin films by successive ion layer adsorption and reaction method; Mater. Lett; 63, 652-654

[15] Podder J: Kobayashi R; Ichimura M. (2005); Photochemical deposition of Cu_xS thin films from aqueous solutions"; Thin solid films, 71 – 75

[16] Anuar K; Ho S.M; Mohd J.H. and Saravanan N.(2011); "Preparation of thin films of copper sulphide by chemical bath deposition"; International Journal of Pharmacy and Life Sciences (IJPLS), 2 (11), 1190-1194

[17] Anuar K; Zainal Z; Hussein M.Z; Saravanan N; Haslina I; (2002); "Cathodic electrodeposition of Cu_2S thin film solar energy conversion"; Sol. Energy Mater. Sol. Cells, 73, 351-365

[18] Nascu C.; Horea J; and Popescu V (1998); CuS thin films obtained by spray pyrolysis"; Rev. Chem. (Bucharest) 49, 535

[19] Thanikaikara-San S; Mahalingam I; Kathalingam A; Moon H. and Yong D.K; (2009) "Characterization of electrodeposited CuS thin films"; Journal of New Materials for electrochemical systems" 29-33

[20] Sagade A. and Sharma R; 2005); "Copper Sulphide (Cu_xS) as an ammonia gas sensor working at room temperature"; Sensors and Actuators B, 133 (1), 135-143

[21] Alvan S.H; Abdulhadi K.J; Attalia B.H. (2010); "Optical electrical and structural properties of Mn doped CdS prepared by CBD method; Journal of College of Education 1(1), 76-90

[22] Ozutok F; Erturk K; and Bilgin V. (2012); Growth electrical and optical study of ZnS:Mn thin films", ACTA, Physical Polonica A, 121 (1), 221-223

[23] Babatunde B. and Uhuegbu C.C. (2009); "Spectral Selectivity Characteristics of FeCuS thin films and its possible Solar energy applications"; Gobal Journal of Engineering and Technology 2 (1), 93-100

[24] Ilenikhena P.A: (2008); "Comparative studies of improved chemical bath deposited copper sulphide (CuS) and zinc sulphide (ZnS) thin films at 320K and possible applications" African Physical Review 2 (7), 59-67