Studies on Synthesis and Characterization of Copper Sulfide Thin Films

S.S Dhasade[1]*, J. S. Patil[2], J.V Thombare[3], V. J. Fulari[3]

[1] Vidnyan Mahavidyalaya, Sangola

[2] K.B.P. Mahavidyalaya, Pandharpur

[3] Department of Physics, Shivaji University Kolhapur-416004

Abstract. In the present work, nanocrystalline copper sulfide thin films were deposited by electrodeposition method. Deposited films are characterized by XRD, SEM, EDAX and Optical properties. Deposited films are polycrystalline with hexagonal crystal structure. Morphology of the films strongly depends upon synthesis conditions. A magnified SEM images shows solid microspheres. EDAX analysis shows that deposited CuS films are nearly stoichiometric in nature. Typical film deposited with 0.10 M solution concentration shows optical band of about 2.37 eV. Depending upon these properties films are useful in PEC applications.

Keywords: Thin films; x-ray diffraction; morphological properties; compositional analysis; optical properties; copper sulfide

INTRODUCTION

During the past several decades, copper monosulfide (CuS) as an important semiconductor has been the focus of intense interest because of its excellent optical, electronic, and other physical and chemical properties. [1] Semiconductor chalcogenides have been of much interest because of their excellent properties and wide-range potential applications. In particular, as a p-type semiconductor with a band gap of 2.37 eV, copper sulfide (CuS) is a promising material with potential applications in solar energy conversion, catalysis, and sensing. Copper sulfides have the ability to form various stoichiometries, at least five phases of which are stable at room temperature: i.e., covellite (CuS), anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurlite ($Cu_{1.95}S$), and chalcocite (Cu_2S) [1]. Their complex structures and valence states result in some unique properties and promising applications in numerous fields, such as solar cells, optical filters, superconductors, and chemical sensors [2-5]. Many recent efforts have been devoted to the synthesis of copper sulfide micro and nanostructures with modulated morphologies and architectures [6-9].

In this paper we have discussed the preparation of copper sulfide (CuS) thin film by cathodic electrodeposition in an aqueous bath.

EXPERIMENTAL

The CuS nanograins were synthesized at room temperature by electrodeposition method. In the typical synthesis, (0.1M) copper sulfate ($CuSO_4$) and (0.1M) sodium thiosulfate ($Na_2S_2O_4$) are used as source of copper and sulfur respectively. Solutions are prepared in double distilled water. The ultrasonically cleaned stainless steel and ITO substrate are used to prepare samples. All reagents were of analytical grade and used without further purification. Electrolytic bath contains 12 ml $CuSO_4$, 12 ml $Na_2S_2O_4$ and 0.1M of TEA. Electrodeposition studies of CuS thin films were made using potentiostat (Princeton Perkin-Elmer, Applied Research Versa-stat-II; Model 250/270) in three-electrode configuration. Pure graphite plate was used as an anode, stainless steel was used as cathode and saturated calomel electrode (SCE) was used as reference electrode. Brown colored, smooth, uniform CuS thin films were obtained. In present work it is to be observed that by keeping bath conc. fixed and changing deposition time the excess of copper increases with increase in deposition time and thin films become more adhesive and stoichiometric.

RESULTS AND DISCUSSION

X-ray Diffraction

The XRD patterns (Fig. 1) of the as-prepared CuS samples with various deposition times indicate the formation of polycrystalline CuS and all of them can be indexed as the reported hexagonal CuS (JCPDS Card No. 06-0464, a=3.792 Å and c=16.34 Å). No diffraction peaks of other phases or impurities are detected, further confirming that the precursors have been completely transformed into CuS nanostructures.

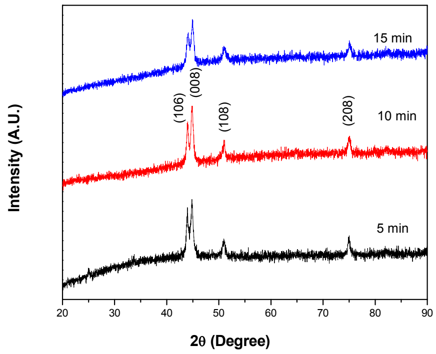

Fig. 1 XRD patterns of CuS thin films deposited with different deposition times.

Scanning Electron Micrographs

Microstructure of CuS thin films on to stainless steel substrate was analyzed by scanning electron microscope technique. SEM of CuS thin film for bath concentrations 0.10 M with deposition times (a) 5 min (b) 10 min (c) 15 min (d) 20 min are shown in Fig. 2. From the SEM images it is seen that small size grains are uniformly distributed over smooth homogenous background. The grain size increases by increasing deposition time. The well developed and matured CuS particle growth is observed in figures below.

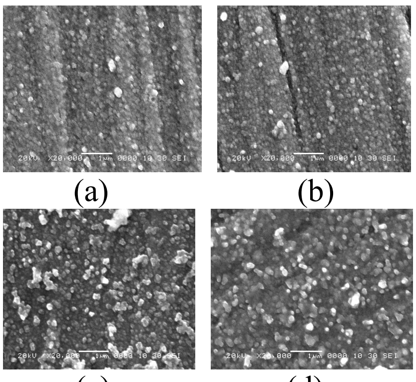

Fig. 2 scanning electron micrographs of CuS thin films (a) 5 min (b) 10 min (c) 15 min (d) 20 min

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The compositional analysis of copper sulfide is as shown in Fig. 3. Chemical composition for bath conc. 0.10 M and 20 min. deposition time was carried out by Energy-Dispersive X-ray analysis. The ratio between the copper and sulfur peaks should be nearly equal to one for higher deposition time. From the graph, it is noted that for deposition time of 20 min. the atomic percentage of copper is 56.87, while that of sulfur is 43.13.

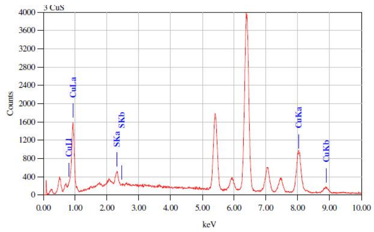

Fig. 3 EDAX of CuS thin film

Optical Study

The Fig. 3 shows the variation of $(\alpha h\nu)^2$ versus hν of typical CuS thin film deposited with 0.1M solution concentration. It is seen that, the plot is linear; indicating the mode of transition is of direct nature. Extrapolation of these curves to zero absorption coefficient value, gives the optical band gap energy 'E_g'. Optical absorption study of the film deposited on ITO coated glass substrate is carried out using UV-VIS spectrometer. The optical band gap energy value of CuS thin film with deposition time of 20 min. is 2.37 eV which is comparable to reported value [10].

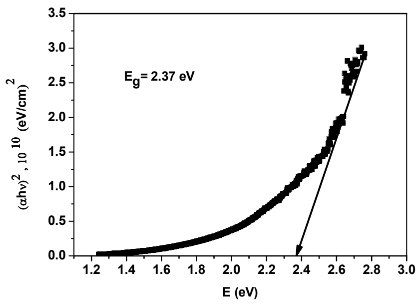

Fig. 4 Optical band gap of CuS thin film

CONCLUSIONS

X-ray diffraction studies confirmed the deposited materials are polycrystalline in nature having hexagonal crystal structure. Surface morphology reveals the hexagonal crystals of CuS covellite. The Optical band gap is of optimized CuS thin film is about 2. 37eV. The optical properties of such films make them suitable for solar control coatings and photovoltaic devices. There is a tendency that more copper-rich thin films have higher deposition time.

REFERENCES

1. J. Gao, Q. Li, H. Zhao, L. Li, C. Liu, Q. Gong, and L. Qi, Chem. Mater., Vol. 20, 19, (2008)
2. Yu, X.; Cao, C.; Zhu, H.; Li, Q.; Liu, C.; Gong, Q. AdV. Funct. Mater. 17, 1397. (2007).

3. Johansson, J.; Kostamo, J.; Karppinen, M.; Niinisto, L. J. Mater. Chem., 12, 1022. (2002)
4. Feng, X.; Li, Y.; Liu, H.; Li, Y.; Cui, S.; Wang, N.; Jiang, L.; Liu,X.; Yuan, M. Nanotechnology 2007, 18, 145706.
5. Yao, Z.; Zhu, X.; Wu, C.; Zhang, X.; Xie, Y. Cryst. Growth Des., 7, 1256, (2007)
6. Cao, H.; Qian, X.; Wang, C.; Ma, X.; Yin, J.; Zhu, Z. J. Am. Chem. Soc., 127, 16024, (2005)
7. Jiao, S.; Xu, L.; Jiang, K.; Xu, D. AdV. Mater. 2006, 18, 1174. Wu, C.; Yu, S.; Antonietti, M. Chem. Mater.,18, 3599, (2006)
8. Li, B.; Xie, Y.; Xue, Y. J. Phys. Chem. C, 111, 1218, (2007)
9. Wan, S.; Guo, F.; Shi, L.; Peng, Y.; Liu, X.; Zhang, Y.; Qian, Y. J. Mater. Chem., 14, 2489. (2004)
10. 27. H. M. Pathan, S. S. Kale, C. D. Lokhande, Ju-Hyun Ahn, Sung-Hwan Han, O. Joo, Mater. Res. Bull. 42 , 1565, (2007).