Effect of pH Value and Electrolyte Concentration on the Copper Sulphide Thin Films Prepared by Chemical Bath Deposition Method

Anuar KASSIM[1♠], Saravanan NAGALINGAM[2], Tan Wee TEE[1], Khor Lea KOON[1]
Ho Soon MIN[1]

[1] Universiti Putra Malaysia, Faculty of Science, Department of Chemistry, 43400 Serdang, Selangor, Malaysia

[2] Universiti Tunku Abdul Rahman, Faculty of Engineering and Science, Department of Bioscience and Chemistry, 53300 Kuala Lumpur, Malaysia.

ABSTRACT

Thin films of copper sulphide were deposited using chemical bath deposition method. The deposition was carried out at various pH values and electrolyte concentrations. The structure, morphology and optical properties of thin films were investigated by means of X-ray diffraction, atomic force microscopy and UV-Visible spectrophotometer. X-ray diffraction patterns confirmed that the deposited materials were CuS with hexagonal phase. The films deposited using 0.05 M of copper chloride and sodium thiosulfate solutions at pH 3 showed the best crystallinity, uniform surface coverage and high absorption characteristics. The band gap was found to be 2.6 eV with p-type behaviour.

Key Words: *Copper sulphide, Chemical bath deposition, thin films, X-ray diffraction.*

1. INTRODUCTION

Copper sulphide as an important member of semiconductor family has great potential in applications such as photothermal conversion, solar cells, electroconductive electrodes and microwave shielding coatings. There are many methods to prepare copper sulphide thin films such as spray pyrolysis [1], successive ion layer adsorption and reaction method [2], photochemical deposition [3], electrodeposition [4] and chemical bath deposition [5]. Recently, chemical bath deposition method has emerged as a simple, inexpensive and low temperature method to prepare good quality thin films of sulphides [6-11] and selenides [12-16]. The principle involved in this method is control precipitation of desired compound from a solution of its constituents.

♠Corresponding author, e-mail: anuar@science.upm.edu.my

This requires that the ionic products must exceed solubility products. Thus, the formation of thin films can be achieved by ion-by-ion condensation on the surface of substrate.

In this paper, we report the preparation of CuS thin films in an acidic medium using chemical bath deposition method. The CuS thin films are deposited by using mixed aqueous solutions of copper chloride, sodium thiosulfate and hydrochloric acid where hydrochloric acid as the pH adjuster. We study the effect of pH and electrolyte concentration towards the properties of CuS thin films prepared by this method. The resulting films are characterized in terms of structure, surface morphology and optical properties using XRD, AFM and UV-Vis Spectrophotometer techniques, respectively.

2. EXPERIMENTAL

2.1 Preparation of Thin Films

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionised water (Alpha-Q Millipore). The copper sulphide thin films were prepared from aqueous solutions of copper chloride ($CuCl_2.2H_2O$) and sodium thiosulfate ($Na_2S_2O_3.5H_2O$) acted as a source of Cu^{2+} and S^{2-} ions, respectively. The indium-doped tin oxide (ITO) glass substrates were used as the substrate for the chemical bath deposition of CuS thin films. Before deposition, the glass substrates were degreased with ethanol for 10 min. Then, ultrasonically cleaned with distilled water for another 10 min and finally dried in desiccators. Deposition of CuS thin films was carried out at 25 °C for 16 hours in the following manner. 20 mL of $CuCl_2$ was taken in a 100 mL beaker. Under continuous stirring, 20 mL of $Na_2S_2O_3$ was added slowly. The cleaned glass substrate was immersed vertically into beaker. The experiments were carried out at different pH values (2, 3 and 4) and electrolyte concentrations (0.01, 0.05 and 0.1 M) in order to determine the optimum conditions for the deposition of CuS thin films. Hydrochloric acid solution was added to the chemical bath to adjust the pH under the control of a pH meter. After the completion of deposition, the films were washed with distilled water and kept for analysis.

2.2. Characterization of Thin Films

The crystal structure of the films was monitored by X-ray diffraction (XRD) with a Philips PM 11730 diffractometer equipped with a CuK_α (λ=0.15418 nm)

radiation source. Data were collected by step scanning from 20° to 60° (2θ) with a step size of 0.05° (2θ) and 1s counting time per step. The surface morphology, thickness and roughness were examined by recording atomic force microscopy (AFM) images with a Q-Scope 250 in contact mode with a commercial Si_3N_4 cantilever. Values of root mean square (RMS) roughness were calculated from the height values in the atomic force microscopy images using the commercial software. Photoelectrochemical experiments were performed in $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system, by running linear sweep voltammetry between +1V to -1V versus Ag/AgCl. The halogen lamp (100 W) was used for illuminating the electrode. The optical properties of the film were measured with a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated indium tin oxide glass was placed across the sample radiation pathway while the uncoated indium tin oxide glass was put across the reference path. From the analyses of absorption spectrum, the band gap energy (E_g) was determined.

3. RESULTS AND DISCUSSION

The XRD patterns of CuS thin films deposited at various pH values using 0.05 M of copper chloride and sodium thiosulfate are shown in Figure 1. For the films deposited at pH 2, three prominent peaks observed in the diffractogram can be assigned to the (102), (104) and (110) planes, respectively of CuS (Figure 1a). The presence of these diffraction peaks indicates that the films are polycrystalline in nature. All these peaks correspond to hexagonal phase of CuS [17] are in agreement with the standard Joint Committee on Powder Diffraction Standards (JCPDS) data (Reference code: 00-065-3928). Lindroos et al. [18], He et al. [19] and Isac et al. [20] reported the hexagonal phase for the CuS films deposited using SILAR method, RF reactive sputtering and spray pyrolysis, respectively. As the pH is increased to 3, the intensities of peaks keep on increasing showing the improvement in the crystallinity of films. This is accompanied by the appearance of another five peaks of CuS that correspond to (004), (105), (106), (107) and (202) planes. However, as the pH is further increased to 4, the number of CuS peaks decreased to two indicating less favourable conditions for the formation of CuS films (Figure 1c). On the other hand, the 2θ peaks at 30.5° and 50.9° correspond to reflections from (222) and (420) planes of indium tin oxide [21] (JCPDS reference No.: 01-089-4597) can be seen for all the samples. This is due to glass substrate is used during deposition process.
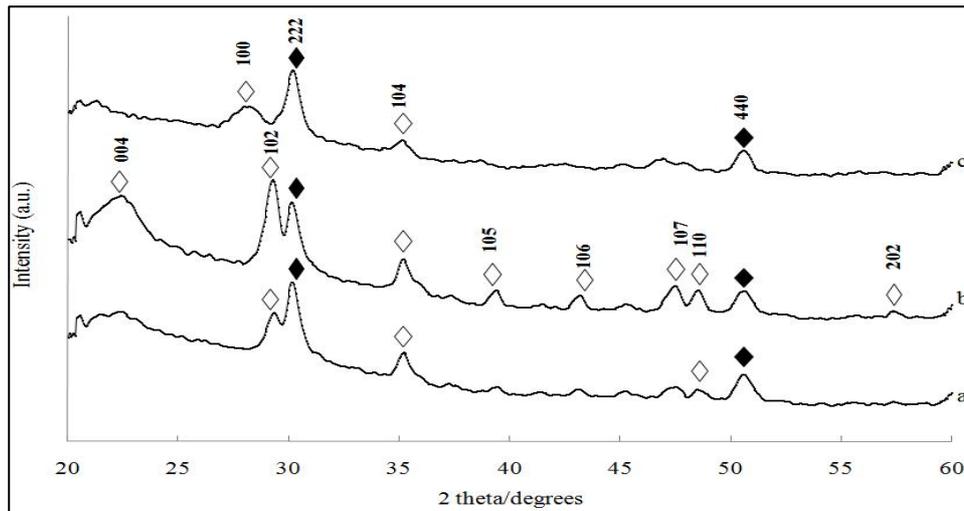
Figure 1. X-ray diffraction patterns of CuS thin films deposited using 0.05 M of copper chloride and sodium thiosulfate at various pH values. (a) pH 2 (b) pH 3 (c) pH 4.

(◇ CuS;   ◆ $In_{1.875}O_3Sn_{0.125}$)

Figure 2 shows the atomic force microscopy (AFM) images (5x5 μm) of CuS thin films deposited under various pH values using 0.05 M of copper chloride and sodium thiosulfate. According to AFM images, the films deposited at pH 2 and 4 reveal the grains are not distributed uniformly over the substrate surafce. The growth of grains is focused at certain nucleation centres on the surface of substrate. The size of the grains varies from one to another. From the AFM image (Figure 2b), it is clear that the films are uniform (0.4-0.5 μm) and substrate surface are well covered by spherical grains. No pinholes or cracks can be observed on the surface of these samples.
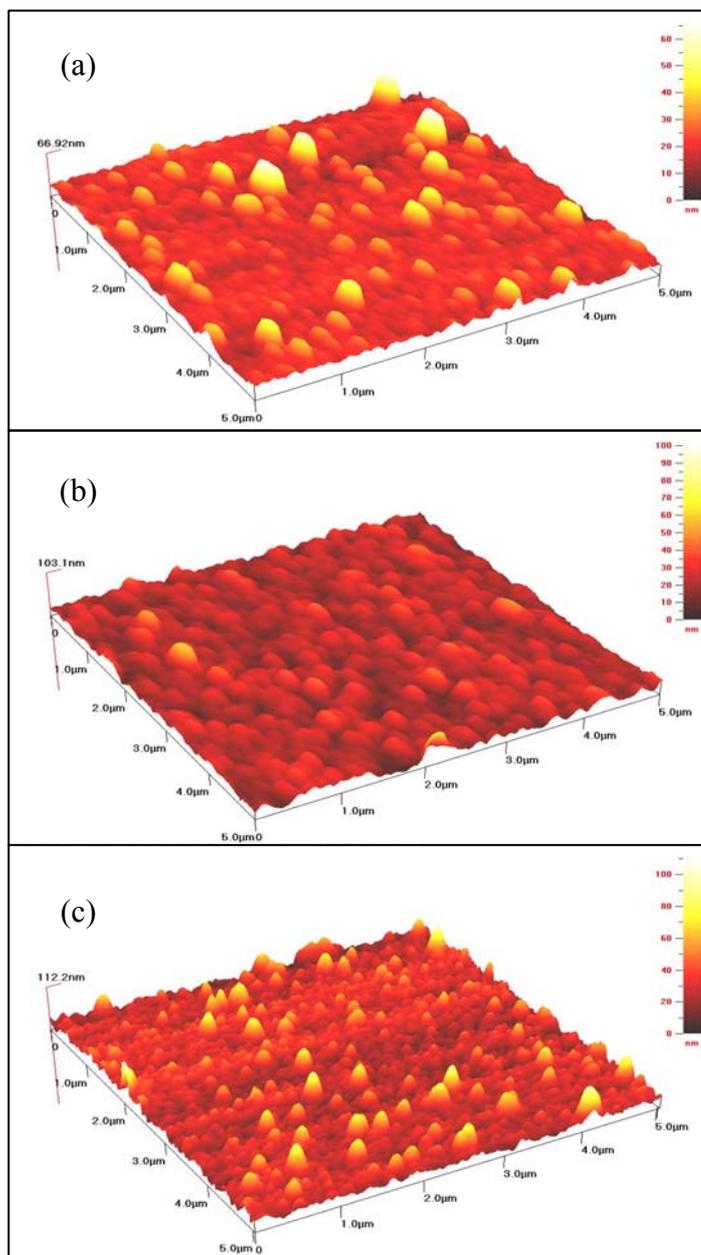
Figure 2. Atomic force microscopy images of CuS thin films deposited using 0.05 M of copper chloride and sodium thiosulfate at various pH values. (a) pH 2 (b) pH 3 (c) pH 4.

The root mean square (RMS) surface roughness and thickness of the films were studied using atomic force microscopy. Root mean square roughness is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness The surface roughness values of the films prepared at pH 2, 3 and 4 are 6.3, 6.5 and 10.2 nm, respectively. Similarly, the corresponding values of thickness are 67, 103 and 112 nm, respectively. We can conclude that increasing pH value increases the thickness and roughness of the films.

The XRD patterns of CuS thin films deposited under various electrolyte concentrations at pH 3 are shown in Figure 3. According to XRD patterns, only single peak is detected for the films deposited using 0.01 M of copper chloride and sodium thiosulfate (Figure 3a). As the concentration is increased to 0.05 M, the number of peaks increased to eight peaks. These peaks are well matched with the JCPDS for CuS (Reference code: 00-065-3928). This indicates that an increase of concentration improves the crystallinity of samples. However, as the concentration is further increased to 0.1 M, the intensities of all the peaks are reduced accompanying with the disappearance of (202) plane (Figure 3c).
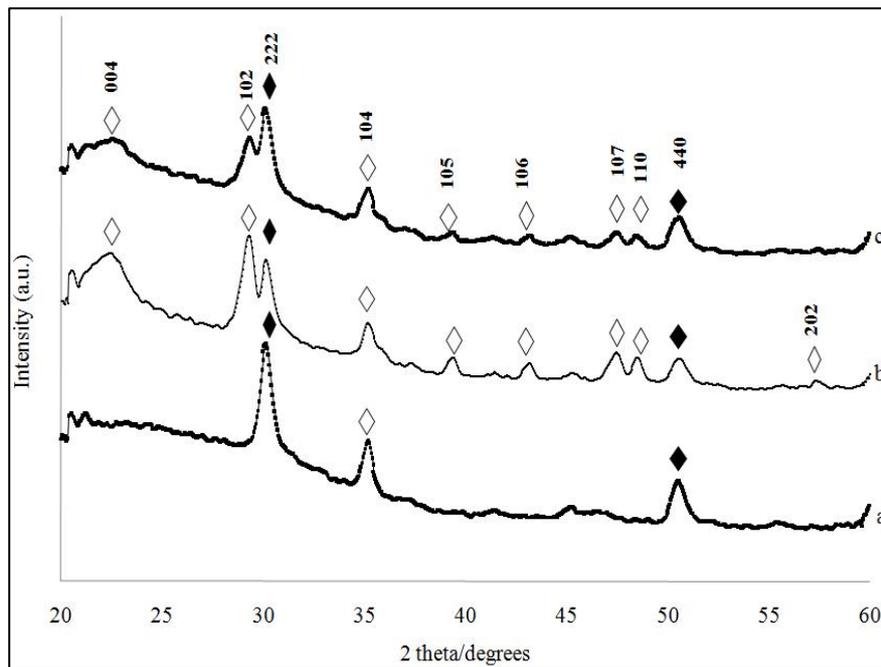
Figure 3. X-ray diffraction patterns of CuS thin films deposited at pH 3 under different electrolyte concentrations. (a) 0.01 M (b) 0.05 M (c) 0.10 M (◇ CuS; ◆ $In_{1.875}O_3Sn_{0.125}$).
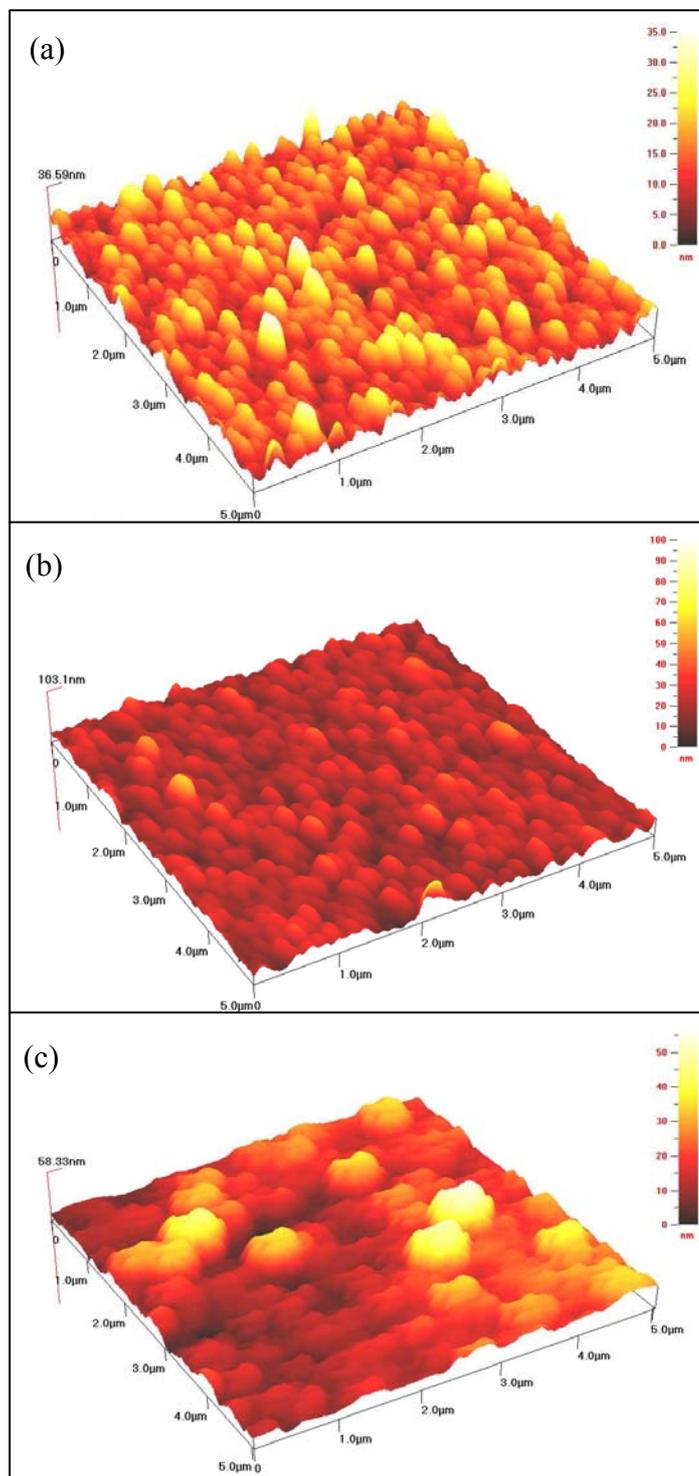
Figure 4. Atomic force microscopy images of CuS thin films deposited at pH 3 under different electrolyte concentrations. (a) 0.01 M (b) 0.05 M (c) 0.10 M.

Figure 4 shows the atomic force microscopy (AFM) images of CuS thin films prepared under various electrolyte concentrations at pH 3. The small grains with different sizes can be obtained for the films deposited at lower concentration (0.01 M). From this AFM image, it can be seen that the grain size of the thin films are estimated to be about 0.2-0.3 μm. With an increase of concentration, the surface morphology of the films

become relatively uniform. From the Figure 4b, it is clear that the grains are well defined, speherical and of almost equal size. However, at higher concentration (0.1 M), the morphology of the films changed as shown in Figure 4c. The grain size of CuS materials are much bigger with diameter of about 0.6 to 0.8 μm.

On the other hand, the film thickness is increased from 37 to 103 nm as the concentration is increased from 0.01 to 0.05 M. However, film thickness reduced to 58 nm when the concentration is further increased to 0.1 M. This is indication of minimal deposition at higher concentration

of copper chloride and sodium thiosulfate. This statement is also supported by the data obtained from XRD (less peaks as compared with the films deposited using 0.05 M). The surface roughness values of the films were measured using AFM technique. From the AFM analysis, as the concentration is increased from 0.01 M (5 nm), 0.05 M (7 nm) to 0.1 M (9 nm) , an increasing in the surface roughness can be observed. The surface roughness of the films is unavoidable since grains were grown with different sizes and spherical in shapes.
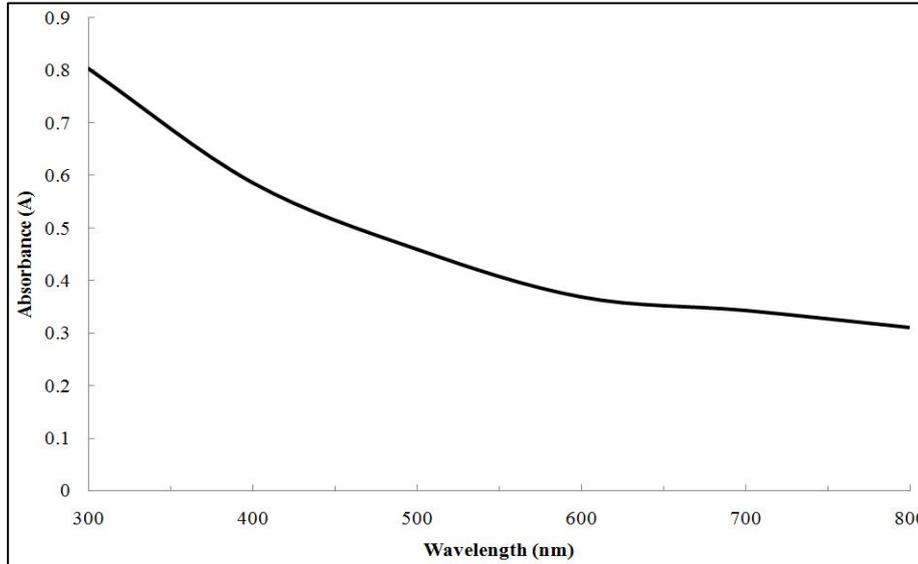

Figure 5. Optical absorption spectrum of CuS thin films deposited at pH 3 using 0.05 M of copper chloride and sodium thiosulfate.

Optical properties of CuS thin films were studied by UV-Vis spectrophotometer in the range of 300-800 nm (Figure 5). The copper sulphide thin films are deposited onto ITO glass substrate using 0.05 M of copper chloride and sodium thiosulfate at pH 3. The films show gradual

absorption starting at 650 nm downward. The high absorbance value in the visible region indicates that these films can be used as photoactive materials and photoelectrochemical cell.
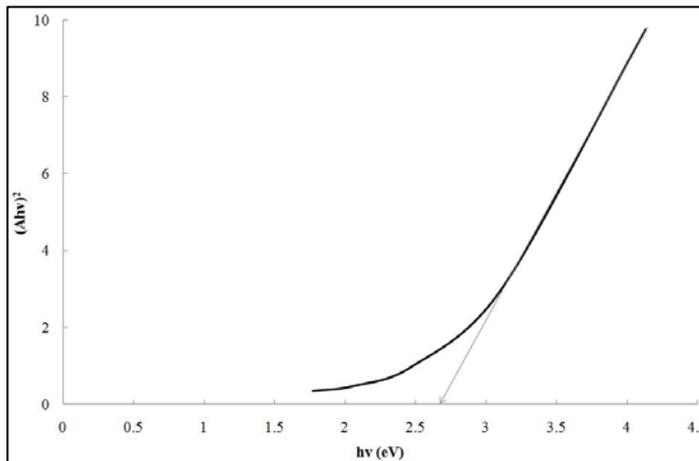

Figure 6. The plot of $(Ah\nu)^2$ versus $h\nu$ of CuS thin films deposited at pH 3 using 0.05 M of copper chloride and sodium thiosulfate

In order to determine the band gap of thin films, the equation of Stern [22] was used.

$$A = \frac{[k(h\nu - E_g)^{n/2}]}{h\nu}$$

(1)

where v is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The $n=1$ for direct transition and $n=4$ for indirect transition semiconductor. Figure 6 shows the plot of $(Ahv)^2$ versus hv for the CuS thin films deposited at pH 3 using 0.05 M of copper chloride and sodium thiosulfate. The linear nature of the plot indicates the existence of direct transition semiconductor. The band gap energy is obtained by extrapolating the linear portion of $(Ahv)^{2/n}$ versus hv to the energy axis at $(Ahv)^{2/n} = 0$. The band gap energy obtained is about 2.6 eV which is in agreement with that reported by Sartale and Lokhande (2.36 eV) [23].
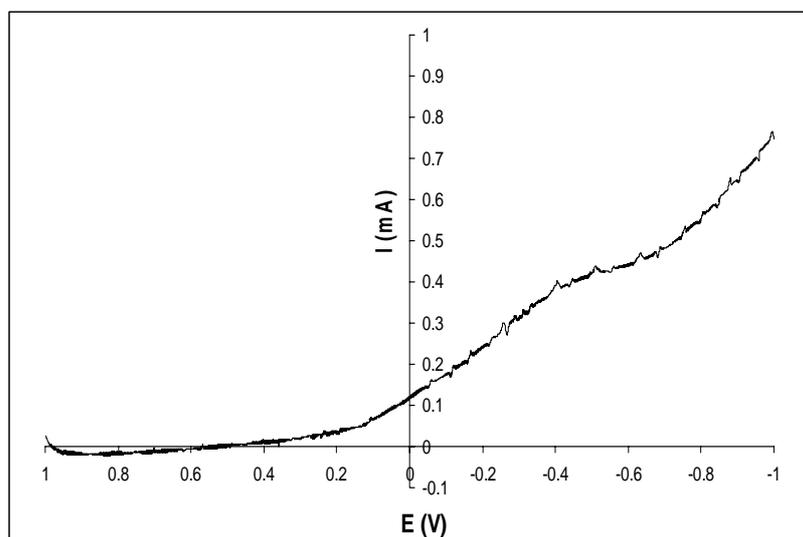

Figure 7. Photoresponse of CuS thin films deposited at pH 3 using 0.05 M of copper chloride and sodium thiosulfate.

The photoactivity of copper sulphide thin films was studied when lights were shone and chopped at an almost constant frequency during the photoelectrochemical (PEC) test. Figure 7 shows the photoresponse of the CuS thin films deposited at pH 3 using 0.05 M of copper chloride and sodium thiosulfate in contact with $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system. When the sample is illuminated, the current increases [24] while the current flow decreases as the light is interrupted by chopping process. This situation exhibits semiconductor behaviour of the materials. The photocurrent phenomenon can be explained by the fact that once transition of electron occurs, holes are left in valence band with a lifetime adequate for them to participate in the electrochemical reaction at the electrode/electrolyte interface [25]. In this study, the photocurrent occurs on negative potential region which indicative of the reduction at the electrode surface being enhanced under illumination. This implies that the light energy which affects the generation of minority carriers, promotes the generation of electrons. Thus, the films are p-type substances with holes as the majority carriers. Grozdanov and Najdoski [26], Johansson et al. [27] and De Tacconi et al. [28] have also reported that the copper sulphide thin films prepared are of p-type.

4. CONCLUSION

The CuS thin films were successfully deposited on indium tin oxide glass substrates using chemical bath deposition technique from acidic medium. This technique was simple, economic and offered a possibility for large area depositions. Deposition at pH 3 using 0.05 M of copper chloride and sodium thiosulfate solutions was found to be the best deposition parameters to prepare good quality thin films under the current conditions. The thin films produced were found to be polycrystalline with hexagonal structure. The thin films obtained showed uniform surface coverage according to AFM images. These films exhibited high absorption characteristics in the visible region. The band gap was found to be 2.6 eV with p-type behaviour.

REFERENCES

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

[2]   Zhuge, F.W., Li, X.M., Gao, X.D., Gan, X.Y., Zhou, F.L., "Synthesis of stable amorphous Cu_2S thin film by successive ion layer adsorption and reaction method", **Mater. Lett.,** 63: 652-654 (2009).

[3]   Podder, J., Kobayashi, R., Ichimura, M., "Photochemical deposition of Cu_xS thin films from aqueous solutions", **Thin Solid Films**, 472: 71-75 (2005).

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

[5] Gadave, K.M., Lokhande, C.D., "Formation of Cu_xS films through a chemical bath deposition process", *Thin Solid Films*, 229: 1-4 (1993).

[6] Goudarzi, A., Aval, G.M., Sahraei, R., Ahmadpoor, H., "Ammonia-free chemical bath deposition of nanocrystalline ZnS thin film buffer layer for solar cells", *Thin Solid Films*, 516: 4953-4957 (2008).

[7] Karimi, M., Rabiee, M., Moztarzadeh, F., Tahriri, M., Bodaghi, M., "Controlled synthesis, characterization and optical properties of CdS nanocrystalline thin films via chemical bath deposition (CBD) route", *Curr. Appl Phys.*, 9: 1263-1268 (2009).

[8] Krishnan, B., Arato, A., Cardenas, E., Roy, T.K.D., Castillo, G.A., "On the structure, morphology and optical properties of chemical bath deposited Sb_2S_3 thin films", *Appl. Surf. Sci.*, 254: 3200-3206 (2008).

[9] Mnari, M., Kamoun, N., Bonnet, J., Dachraoui, M., "Chemical bath deposition of tin sulphide thin films in acid solution", *Comptes Rendus Chimie*, 12: 824-827 (2009).

[10] Song, W.C., Lee, J.H., "Growth and characterization of $Zn_xCd_{1-x}S$ films prepared by using chemical bath deposition for photovoltaic devices", *J. Korean Phys. Soc.*, 54: 1660-1665 (2009).

[11] Anuar, K., Tan, W.T., Atan, M.S., Dzulkefly, K.A., Jelas, M.H., Ho, S.M. and Saravanan, N., "Preparation and characterization of chemically deposited Cu_4SnS_4 thin films", *J. Ultra Chem.*, 5: 21-26 (2009).

[12] Esparza-Ponce, H.E., Hernandez-Borja, J., Reyes-Rojas, A., Cervantes-Sanchez, M., Vorobjev, Y.V., Ramirez-Bon, R., Perez-Robles, J.F., "Growth technology, X-ray and optical properties of CdSe thin films", *Mater. Chem. Phys.*, 113: 824-828 (2009).

[13] Bari, R.H., Ganesan, V., Potadar, S., Patil, L.A., "Structural, optical and electrical properties of chemically deposited copper selenide films", *Bull. Mater. Sci.*, 32: 37-42 (2009).

[14] Hankare, P.P., Chate, P.A., Sathe, D.J., Chavan, P.A., Bhuse, V.M., "Effect of thermal annealing on properties of zinc selenide thin films deposited by chemical bath deposition*", J. Mater. Sci -Mater. Electron.*, 20: 374-379 (2009).

[15] Chaudhari, J.B., Deshpande, N.G., Gudage, Y.G., Ghosh, A., Huse, V.B., Sharma, R., "Studies on growth and characterization of ternary $CdS_{1-x}Se_x$ alloy thin films deposited by chemical bath deposition technique", *Appl. Surf. Sci.*, 254: 6810-6816 (2008).

[16] Bhardwaj, A., Varadarajan, E., Srivastava, P. and Sehgal, H.K., "Structural, optical and electrical properties of chemically grown $Pb_{1-x}Fe_xSe$ nanoparticle thin films", *Solid State Commun.*, 146: 53-56 (2008).

[17] Takeuchi, Y., Kudoh, Y., Sato, G., "The crystal structure of covellite CuS under high pressure up to 33 kbar", *Z. Kristallogr.*, 173: 119-128 (1985).

[18] Lindroos, S., Arnold, A., Leskela, M., "Growth of CuS thin films by the successive ionic layer adsorption and reaction method", *Appl. Surf. Sci.*, 158: 75-80 (2000).

[19] He, Y.B., Polity, A., Osterreicher, I., Pfisterer, D., Gregor, R., Meyer, B.K., Hardt, M., "Hall effect and surface characterization of Cu_2S and CuS films deposited by RF reactive sputtering", *Physica B*, 308-310: 1069-1073 (2001).

[20] Isac, L.A., Duta, A., Kriza, A., Enesca, I.A., Nanu, M., "The growth of CuS thin films by spray pyrolysis", *J. Phys.: Conf. Ser.*, 61: 477-481 (2007).

[21] Nadaud, N., Lequeux, N., Nanot, M., Jove, J., Roisnel, T., "Structural studies of tin-doped indium oxide (ITO) and $In_4Sn_3O_{12}$", *J. Solid State Chem.*, 135: 140-148 (1998).

[22] Stern, F., "Elementary theory of the optical properties of solids", *Solid State Phys.*, 15: 299-408 (1963).

[23] Sartale, S.D., Lokhande, C.D., "Growth of copper sulphide thin films by successive ionic layer adsorption and reaction (SILAR) method", *Mater. Chem. Phys.*, 65: 63-67 (2000).

[24] Ali Yildirim, M., Ates, A., Astam, A., " Annealing and light effect on structural, optical and electrical properties of CuS, CuZnS and ZnS thin films grown by the SILAR method", *Physica E*, 41: 1365-1372 (2009).

[25] Fonash, S.J., Solar Cell Device Physics, *Academic Press*, Sydney, (1981).

[26] Grozdanov, I., Najdoski, M., "Optical and electrical properties of copper sulfide films of variable composition", *J. Solid State Chem.*, 114: 469-475 (1995).

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

[28] De Tacconi, N.R., Rajeshwar, K., Lezna, R.O., "Study of copper sulfide film formation by voltammetry combined with electrochemical quartz crystal microgravimetry/coulometry and optical spectroscopy," *J. Phys. Chem.*, 100: 18234-18239 (1996).