Optical and structural analysis of ammonia-free cooper sulphide thin films using chemical deposition method

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We report the synthesis of cooper sulphide thin films ammonia-free by chemical bath method using triethanolamine and barium hydroxide as chelating agents and were deposited on glass microscope slides at 60^0C. The use of these complexing agents improving the adhesion of the deposited films and reduces of time reaction. The structural characterization was carried out by X-ray diffraction and atomic force microscopic. The X-ray diffraction analysis showed a amorphous nature of thin film and indirect transition with a bandgap of 1.28 eV and index refraction of the 1.515.

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1. Introduction

Metal chalcogenide films have been extensively studied because of their promise in electronic, optical and superconductor devices as well as solar energy conversions and cooper sulphide (Cu_xS) is one of the most attractive. It is well known that Cu_xS in bulk form exists in five stable phases at room temperature: covellite (CuS) in the sulphur-rich region, anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite ($Cu_{1.95}S$), and chalcocite (Cu_2S) in the copper rich region [1-6]. Between some of its applications are: A.R. coating, interference filters, polarizer's, narrow band filters, solar cells, photoconductors, IR detectors, waveguide coatings, superconducting films, anticorrosive films, microelectronics devices, high temperature wear resistance films, hard coatings, etc [7]. Chemically deposited Cu_xS thin films have been found to posses near – ideal solar control characteristics: transmittance in the visible region of 20 – 50 %, low transmittance, 10 – 20 %, in the infrared region, low reflectance, < 10 %, in the visible region so as to avoid glare, and relatively higher reflectance, > 15 %, in the near–infrared region [8].

There are different techniques to deposition of these thin films, among which are: spray pyrolysis [6], electrodeposition [9], successive ionic adsorption and reaction [10], photochemical deposition [11], chemical bath deposition [12-18] and others [7]. Among them, the chemical bath deposition (CBD) has been proven to be the most suitable method to produce CuS thin films for photovoltaic applications because it is an efficient, cost-effective, and large-scale method.

Cu_xS represents an interesting class of semiconducting materials, which are attractive for large-scale applications because of the easy availability and low cost of starting materials. The preparation of thin films of CuS by chemical bath deposition is mostly based on the utilization thiourea, thioacetamide, thiosulphate and sodium sulphide are generally as sulphide precursors. Metallic precursors are metal complexed ions with ammonia ligands, for instance [7]. However, it is clear that the preparation of Cu_xS by CBD for large scale production represents a serious contamination problem because the employment of large amounts of ammonia, which is toxic and is highly volatile and harmful for the environment. Some efforts have been dedicated to the investigation of CBD processes for the synthesis of good quality Cu_xS thin films, which reduce this environmental problem. One of the main approaches is the substitution of ammonia as the complexing agent of cooper ions in the CBD process [20, 21] and others [1]. Here we report on a technique based on triethanolamine and barium hydroxide that eliminates the problems of ammonia volatility and toxicity, improving the adhesion of deposited films on the substrate and reduces the reaction time.

2. Experimental

Cu_xS thin films were deposited on glass slides substrates by means of the chemical bath method. Chemical bath used for the deposition of Cu_xS thin films were: 31 ml of H_2O, 2 ml of cooper nitrate (0.1 M), 2 ml of barium hydroxide (0.01 M), 2 ml of triethanolamine (1 M), 4 ml of thiourea (1 M) and 19 ml of H_2O.

In general, the processes that occur in the CBD solution for chalcogenide films from a metal cation like

Cu^{2+} complexed by the triethanolamine (TEA), $C_6H_{15}NO_3$ = $(HO\text{-}CH_2\text{-}CH_2)_3\text{-}N$, consist to the following steps:

1) Complexant-water equilibrium:

$$C_6H_{15}NO_3 + H_2O \rightarrow (C_6H_{16}NO_3)^+ + OH^-$$

2) Dissociation of water:

$$H_2O \rightarrow H^+ + OH^-$$

3) Displacement of ligands:

$$Cu(NO_3)_2 + Ba(OH)_2 + C_6H_{15}NO_3 \rightarrow Cu(OH)_2 + Ba(NO_3)_2 + C_6H_{15}NO_3$$

$$Cu(OH)_2 + 2(C_6H_{15}NO_3) \rightarrow [Cu(C_6H_{15}NO_3)_2]^{2+} + 2(OH)^-$$

4) Hydrolysis of Thiourea:

$$(NH_2)_2CS + (OH)^- \rightarrow HS^- + H_2O + H_2CN_2$$

$$HS^- + (OH)^- \rightarrow S^{2-} + H_2O$$

5) Total Reaction:

$$[Cu(C_6H_{15}NO_3)_2]^{2+} + S^{2-} \rightarrow CuS\ (s) + 2(C_6H_{15}NO_3)$$

The films were deposited in the substrate into solution to 60°C, they were kept into solution for 15 min. The obtained Cu_xS films were flat homogeneous, green-gray transparent and very good adherence to the substrate. The gap energy of the films was 1.26 eV for 15 minutes. Their thickness was approximately 150 nm and had a amorphous structure.

The X-ray diffraction measurements were performed using a Rigaku Ultima III diffractometer. Optical transmission spectra of the bilayer were recorded by an Ocean Optics USB4000-UV-VIS spectrometer in the 280-850 wavelength range. The index refraction was measurement with Abbe refractometer and was of 1.515. The morphology of the samples surface was investigated by Atomic force microscopy (AFM) using a JSPM-4210 scanning probe microscope (JEOL Ltd).

3. Results and discussion

The X-ray analysis of Cu_xS thin films have amorphous structure, see figure 1. This is a typical behavior previously reported, for instance in [22], but using different complexation set for the copper.

The Figs. 2 and 3 show the transmittance/absorbance, transmittance/reflectance as functions of wavelength of CuxS thin films. In these figures it can be observed that the Cu_xS thin films transmit about 70% in VIS-NIR regions of the spectrum. These films are very useful in applications of windows due to his good transparence.

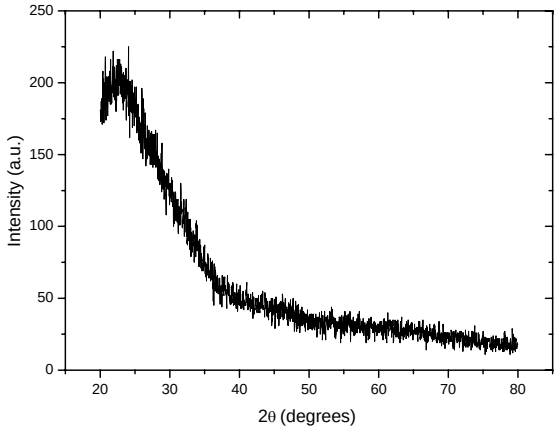


Fig. 1. X-ray diffraction pattern of Cu_xS thin films.

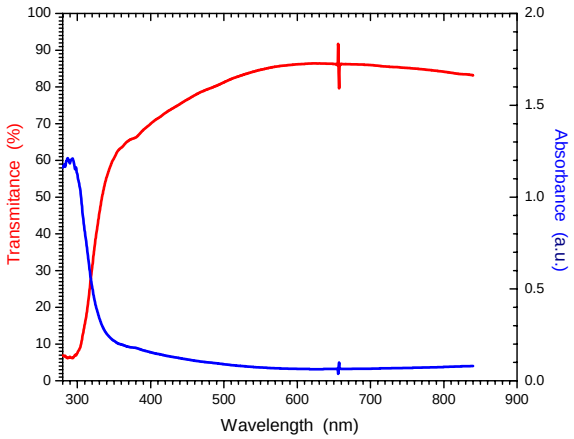


Fig. 2. Transmitance versus absorbance of Cu_xS thin films.

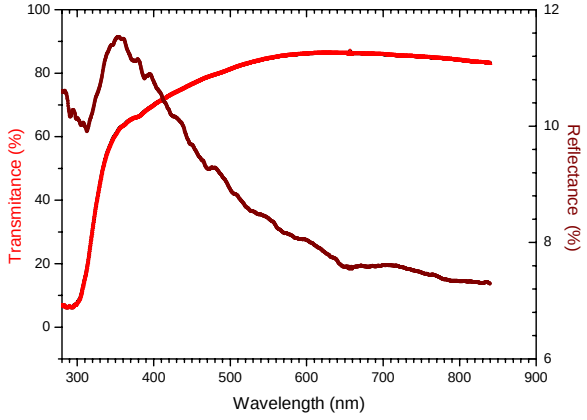


Fig. 3. Transmitance versus reflectance of Cu_xS Thin films.

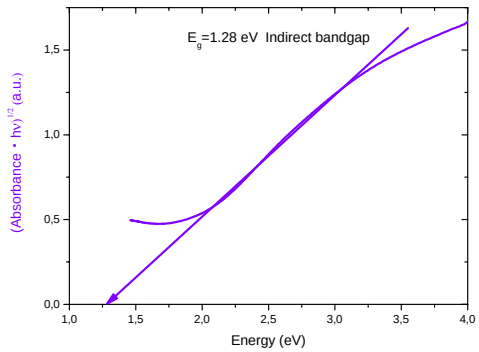
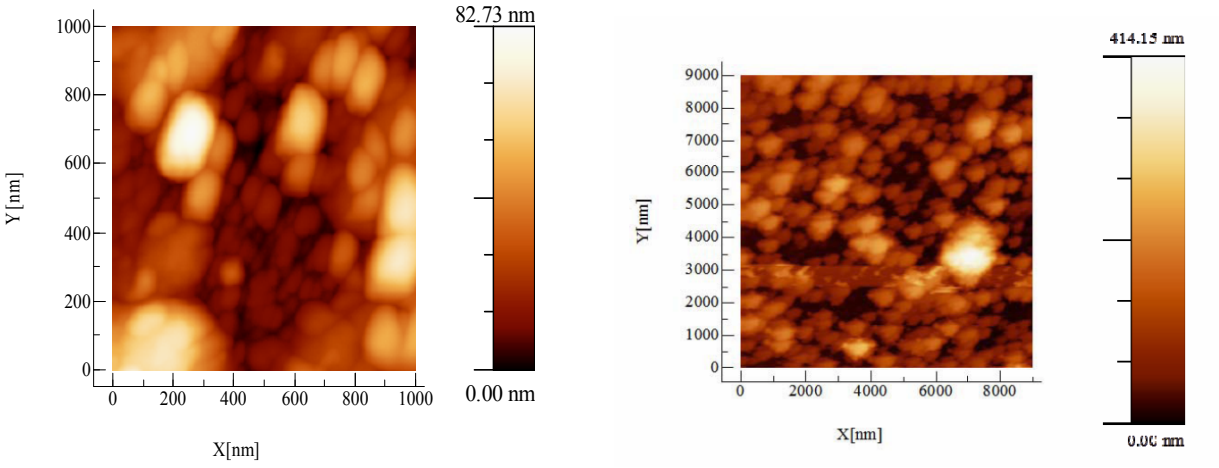


Fig. 4. Plot of square of optical absorption multiplied by square energy versus energy for the Cu_xS thin films.

A plot of square of optical absorption multiplied by square energy versus energy for the Cu_xS thin films is shown in figure 4. The energy gaps are obtained by extrapolating the linear portion of the curve to the energy axis. The indirect bandgap was found to be 1.28 eV. The optical band gap of Cu_xS varies in the range of 1.2–2.5 eV.

The Fig. 5 shows surfaces morphologies, in two [a)] and three [(b)] dimensions, which are representative across the overall sample extension. These images were obtained with an AFM system. Our sample show that the maximum grain size is about 400 nm, but the average is between 100 and 200 nm.

a)



b)

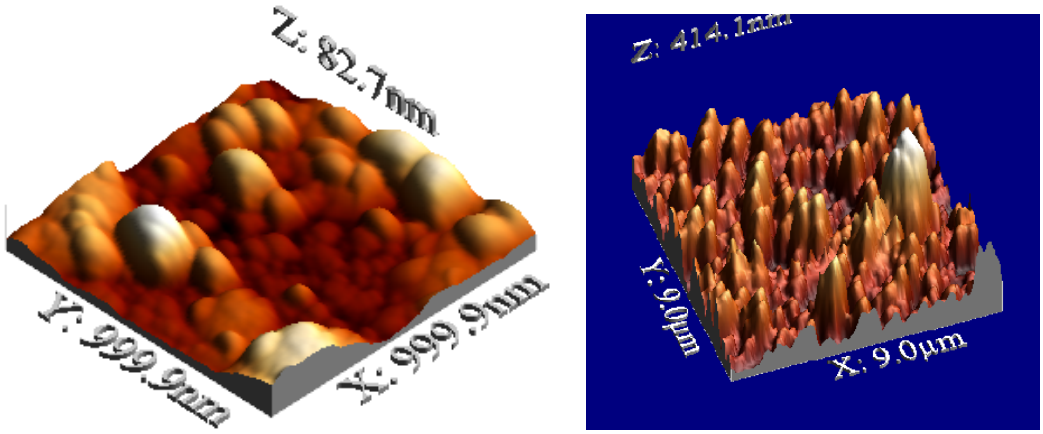


Fig. 5. AFM images of Cu_xS thin film: a) Top view of a representative area, showing its nanometric grains sizes and b) Perspective view of the same representative area, showing its nanometric grains sizes.

4. Conclusions

Cu_xS thin films using Triethanolamine and barium hydroxide as chelating agents were prepared from CBD and are amorphous nature. It's know that the annealing conditions of the deposition bath can be affect the crystallinity [22] and the phase of the deposition film at increasingly higher temperatures in an inert atmosphere, the stoichiometry of the films could be controlled [20]. These experiments are coming to do. The use of these

complexing agents eliminates the problems of ammonia volatility and toxicity, improving the adhesion of deposited films on the substrate and reduces the reaction time. Optical and structural analyses of the films have been carried out and present an indirect bandgap of 1.28 eV and 1.515 of the index refraction.

References

[1] X. Jiang, Y. Xie, J. Lu, W. He, L. Zhu, Y. Qian, Journal of Materials Chemistry, **10**, 2193 (2000).

[2] I. Grozdanov, M. Najdoski, Journal of Solid State Chemistry, **114**, 469 (1995).

[3] S. Y. Wang, W. Wang, Z. H. Lu, Materials Science & Engineering, **B103**, 184 (2003).

[4] U. K. Gautam, B. Mukerjee, Bull. Mater. Sci., **29**(1)**,** 1 (2006).

[5] S. Lindroos, A. Arnold, M. Leskela, Applied Surface Science **158**, 75 (2000).

[6] C. Nascu, I. Pop, V. Ionescu, E. Indrea, I. Bratu, Materials Letters, **32**, 73 (1997).

[7] R. S. Mane, C. D. Lokhande, Materials Chemistry and Physics **65**, 1 (2000)

[8] M. T. S. Nair, P. K. Nair, Semicond. Sci. Technol. **4**(7), 599 (1989)

[9] R. D. Engelken, H. E. McCloud, J. Electrochem. Soc. **132**(3), 567 (1985)

[10] K. Anuar, Z. Zainal, M. Z. Hussein, N. Saravanan, I. Haslina, Sol. Energy Mater. Sol. Cells **73**, 351 (2002).

[11] F. Zhuge, X. Li, X. Gao, X. Gan, F. Zhou, Mater. Lett. **63**, 652 (2009)

[12] J. Podder, R. Kobayashi, M. Ichimura **472**, 71 (2005).

[13] K. M. Gadave, C. D. Lokhande, **229**, 1 (1993).

[14] A. Goudarzi, G. M. Aval, R. Sahraei, H. Ahmadpoor, Thin Solid Films **516**, 4953 (2008).

[15] M. Karimi, M. Rabiee, F. Moztarzadeh, M. Tahriri, M. Bodaghi, Curr. Appl Phys. **9**, 12631268 (2009).

[16] B. Krishnan, A. Arato, E. Cardenas, T. K. D. Roy, G. A. Castillo, Appl. Surf. Sci., **254**, 3200 (2008).

[17] M. Mnari, N. Kamoun, J. Bonnet, M. Dachraoui, Comptes Rendus Chimie **12**, 824827 (2009).

[18] W. C. Song, J. H. Lee, J. Korean Phys. Soc. **54**, 1660 (2009).

[19] K, Anuar, W. T. Tan, M. S. Atan, K. A. Dzulkefly, M. H. Jelas, S. M. Ho, N. Saravanan, J. Ultra Chem. **5,** 21 (2009).

[20] M.T.S Nair, Laura Guerrero, P.K. Nair Semicon, Sci. Technol. **13**, 1164 (1998).

[21] C.D. Lokhande, Eun-Ho Lee, Kwang-Deog Jung, Oh-Shim Joo, Materials Chemistry and Physics **91**, 200 (2005)

[22] H. Grijalva, M. Inoue, S. Boggavarapu, P. Calvert. Journal of Materials Chemistry **6**, 1157 (1996).

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