Journal of Scientific Research and Development 2 (13): 95-99, 2015
Available online at www.jsrad.org
ISSN 1115-7569

CuS P-type thin film characteristics for different copper to Sulphur molar ratios for light emitting diode application

Fayroz A. Sabah [1, 2, *], Naser M. Ahmed [1], Z. Hassan [1], Hiba S. Rasheed [1, 3]

[1]Institute of Nano-Optoelectronics Research and Technology (INOR), School of Physics, University Sains Malaysia, 11800 Penang, Malaysia
[2]Department of Electrical Engineering, College of Engineering, Al-Mustansiriya University, Baghdad, IRAQ
[3]Department of Physics, College of Education, Al-Mustansiriya University, Baghdad, IRAQ

Abstract: Spray pyrolysis deposition (SPD) used to deposit CuS thin films on glass substrates with temperature of 200 °C. This composition was consist of copper chloride and sodium thiosulfate, with 0.4 M concentration of Cu and three different molar ratios of (Cu:S). These molar ratios were (1:1), (1:2), and (1:3). The first two thin films showed mixed phases of covellite CuS hexagonal crystal structure and chalcocite Cu_2S hexagonal crystal structure, while the last thin film showed covellite CuS hexagonal crystal structure only, which was proved by X-Ray Diffraction (XRD). The morphology of the first thin film was nanoplates and hexagonal structure, while for the last two thin films these was no specific structure as shown by Field Emission Scanning Electron Microscopy (FESEM). Surface characteristics of these thin films also were measured by Atomic Force Microscopy (AFM). Electrical measurements showed the ohmic behaviour for all thin films, and the resistivity of the (1:1) molar ratio thin film was very low and this resistivity was increased with increasing sulphur concentration. Optical measurements showed that the molar ratio (1:1) CuS thin film had the lowest band gap (≈3.57 eV) and when increasing sulphur concentration, the band gap energy will be increased (≈3.74 eV) for the second thin film and (≈3.77 eV) for the third thin film. Hall effect measurements showed that these films were p-type thin films and ensured the electrical results. Also Hall effect showed that the (1:1) molar ratio thin film had the best characteristics between the other thin films; it had the lowest sheet resistivity (9.336 Ω/Sq) and the highest mobility (62.3 Cm^2/V.s).

Key words: CuS, p—type thin film; Copper to sulphur ratios; Spray pyrolysis deposition

1. Introduction

Nanostructures materials have attracted a great deal of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. A material is said to be a thin film when it is build up on a substrate by physical process or through a chemical reaction/ electrochemical with condensation controlling of the individual atomic, molecular or ionic species and it should be a thin layer (Sangamesha, 2013).

Coppers sulfide is an important semiconductor material and has received a great deal of attention because of its unparalleled physical and chemical properties (Adel, 2013). Copper sulphide has complex crystal chemistry owing to its stability to form stoichiometric compounds (Sangamesha, 2013). The properties of CuS thin films are affected by accurate stoichiometry, which depends on preparative conditions used for the thin film deposition. CuS thin films have recently received worthy attention due to various applications (Adel, 2013).

The sulphides of copper (Cu_xS) generally have five different stable phases at room temperature: covellite (CuS) in the “sulphur – rich region”, anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurlite ($Cu_{1.95}S$) and chalcocite (Cu_2S) in the “copper - rich region”. The thin films with CuS covellite phase reveal metal-like electrical conductivity and have near-ideal solar control characteristics (Mehdi, 2012).

Covellite, the stoichiometric copper-poor phase, is a green-black crystalline solid with a special hexagonal crystalline structure, containing Cu^{2+} and S^{2-} ions (Isac, 2007).

The deposition technique and parameters control the ratio of the nucleation and growth reactions, this ratio can be obtained by the crystalline structure associated with the surface morphology (L. A. Isac, 2007). Copper sulphide (Cu_2S) belongs to I-VI group compound of semiconducting material (M S Shinde, 2013).

Mixed phases are known in the moderate compositions. The copper sulfide compounds structure is complicated to a large degree. Even the structures of Cu_2S and CuS, which are supposed to be stoichiometric, are not consistent with their forming as Cu (I) and Cu (II) sulfides. Cu_xS symbolizes to the Copper sulfides with inconstant composition, have been deposited using various techniques (Sheng, 2003); Asynchronous- pulse ultrasonic spray

* Corresponding Author.

pyrolysis deposition (Sheng, 2003), Chemical Bath Deposition (CBD) (Sangamesha, 2013) and (Adel, 2013), Thermal evaporation (Ramya, 2010), successive ionic layer adsorption and reaction method (Ubale, 2014), Spray Pyrolysis Deposition (SPD) (Mehdi, 2012) and (Isac, 2007).

Among all mentioned previous techniques, SPD is the promising one, for its simplicity, the ability to cover effective large area and low cost deposition, so no need of any advanced instrumentation in this technique. By changing some deposition parameters such as, composition of precursors' solution (Cu:S molar ratio, type of solvent), or the substrate temperature; the composition, morphology, electrical and optical properties of CuS thin films were be designed and changed (Mehdi, 2012).

Electrical measurements show good electrical properties and p-type CuS semiconductors (J. Santos, 2013). CuS thin films have been playing an important role in the development of solar selective coatings, solar cells, photoconductors, sensors, IR detectors (A.U. Ubale, 2014), light emitting diodes and other optoelectronics (Adel, 2013).

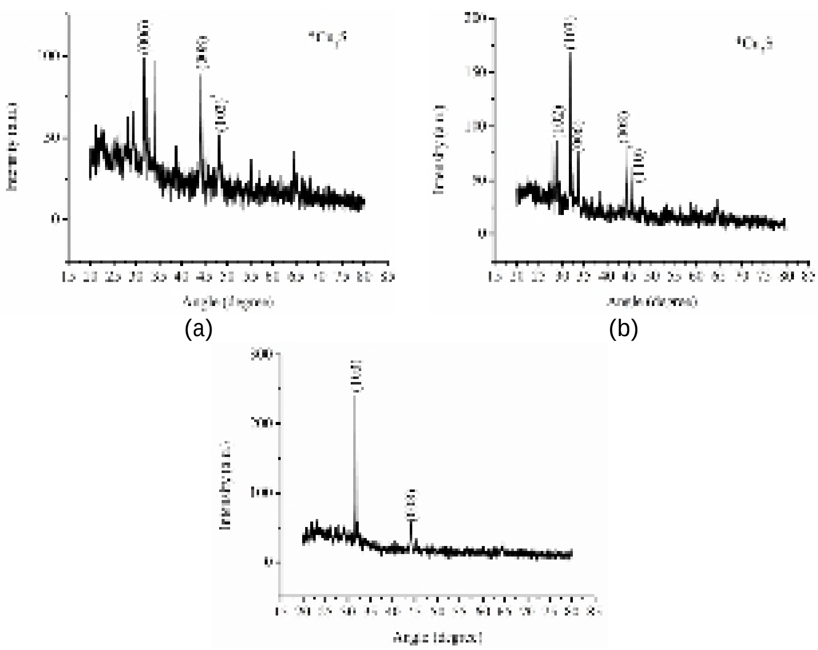
In this work; CuS thin films were deposited on glass substrate using SPD for 0.4 M concentration of Cu with three copper to sulphur molar ratios, (1:1), (1:2) and (1:3). By applying structural, electrical, optical, and Hall effect measurements for these thin films, one can find which molar ratio gives better characteristics to be used for a device performance.

2. Methodology

SPD is a simple, low cost and large cover area technique to deposit thin films on substrates. And this technique gives very good adhesion for CuS thin film that deposited on glass substrate unlike most of other techniques. The composition was prepared by mixing 0.4 M of copper chloride with three molarity concentration of sodium thiosulfate, (i.e. (Cu:S) was (1:1), (1:2) and (1:3)), to make it easy to deal with these three thin films, they can be named as s1, s2 and s3, respectively. The solvent for these materials was deionised water, the substrate temperature was 200 °C, and the spray distance was 30 cm. Spraying the solution started with 1 spray/second for 10 times then wait for a minute, after that the procedure was repeated for 6 times. This gave the thin films time to keep the temperature equilibrium and to not be cracked. After complete spray, the thin films were ready to be measured by XRD, FESEM, AFM, electrical, optical, and Hall effect measurements.

3. Result

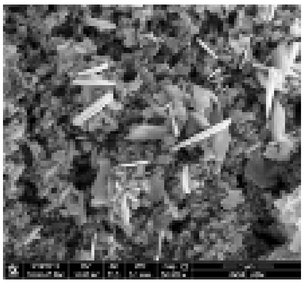
XRD results show that s1 and s2 composed of mixed phases of covellite CuS hexagonal crystal structure and one small peak of chalcocite Cu_2S hexagonal crystal structure. While s3 composed of covellite CuS hexagonal crystal structure only as shown in fig. 1. S1 has two orientations named, (006) and (008) for covellite CuS hexagonal crystal structure, and one small orientation named (103) for chalcocite Cu_2S hexagonal crystal structure. S2 has four orientations named (103), (102), (008), and (006) for covellite CuS hexagonal crystal structure, and one small orientation named (110) chalcocite Cu_2S hexagonal crystal structure. S3 has two orientations named (103) and (008) for covellite CuS hexagonal crystal structure, and there is no orientation for Cu_2S which proved that s3 is sulphur – rich thin film.

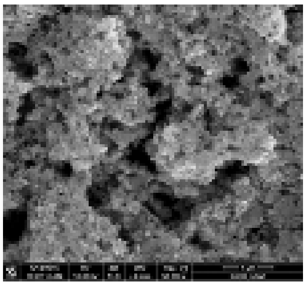


(a) (b) (c)

Fig. 1: XRD for (a) s1, (b) s2, and (c) s3

As can be seen from Fig. 2, s1 has the best structure which is mixed of nanoplates and hexagonal structure. While the other two samples are not in regular and known structure, so when the ratio of (Cu:S) is equal, it gives better structure than the other thin films.


(a)


(b)

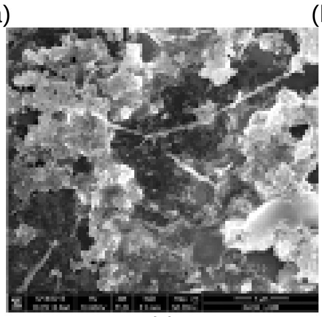
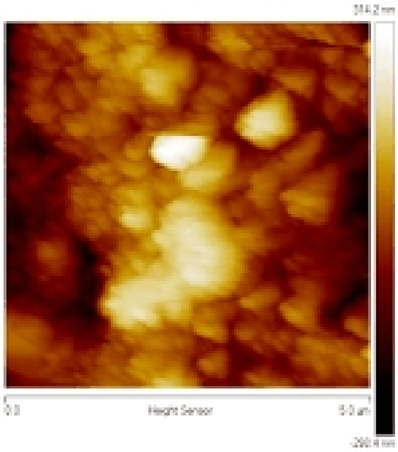
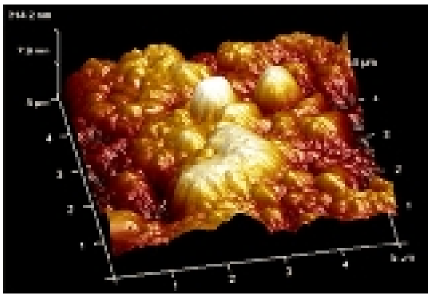
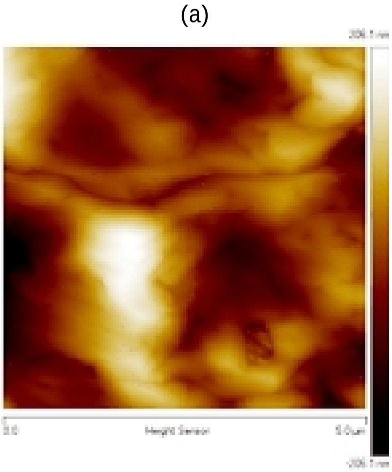

(c)

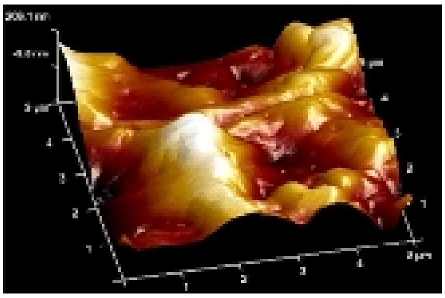
Fig. 2: FESEM for (a) s1, (b) s2, and (c) s3

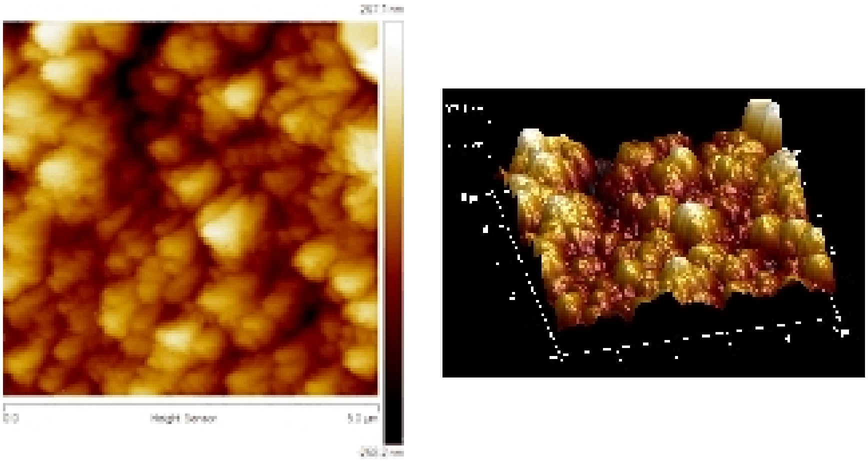
Fig. 3 represents the 2D & 3D images of AFM. The surface of these thin films is smooth as shown. The roughness for s1 is 0.0899 µm, for s2 is 0.0674 µm, and for s3 is 0.0745 µm.


(a)


(b)


(c)


(d)



(e) (f)

Fig.3: 2D and 3D AFM for (a-b) s1, (c-d) s2, and (e-f) s3

As shown in Fig. 4, all thin films have ohmic behaviour and s1 has the lowest resistance, then resistance increase with increasing the sulphur concentration. But it still low resistance for all CuS thin films.

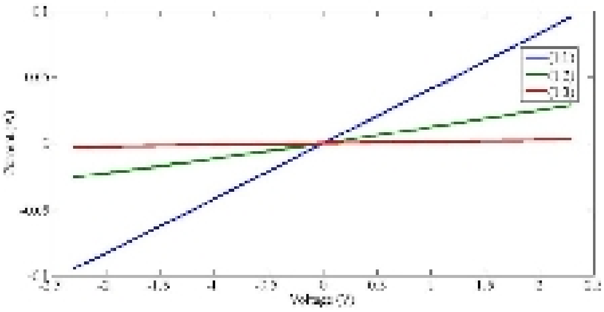


Fig. 4: Electrical characteristics of s1, s2 and s3

S1 has the lowest value of band gap energy which is ≈3.57 eV, while when sulphur concentration increased; the band gap energy will be increased to reach ≈3.74 eV for s2, and ≈3.77 eV for s3, as shown in fig. 5.

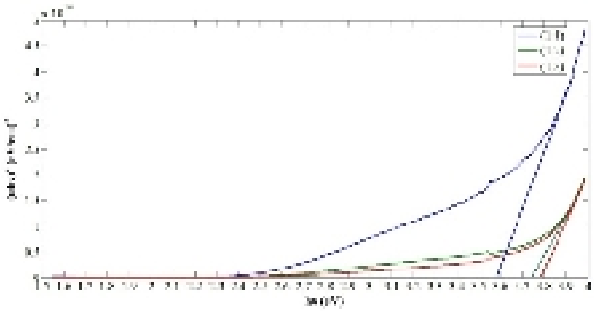


Fig. 5: Band gaps of CuS thin films

Hall effect measurements show other characteristics of CuS thin films such as; resistivity, mobility, carrier concentration, etc. From these measurements it can be found that all CuS thin films are p-type thin films and s1 is the best thin film because it has the lowest resistivity (9.336 Ω/Sq) and the highest mobility (62.3 cm2/V-s) which make the thin film very good for device performance. Also these measurements confirm the result of electrical measurements. Hall effect measurement results shown in Table 1.

Table 1: Hall effect results of 0.4 M CuS thin films

Parameters	S1	S2	S3
Sheet resistivity (Ω/Sq)	9.336	125.8	5.217E+04
Bulk resistivity (Ω-cm)	0.009336	0.1258	52.17
Hall coefficient (m2/C)	0.0582	0.0286	52
Mobility (cm2/V-s)	62.3	2.27	9.98
Sheet concentration (/cm2)	1.07E+16	2.18E+16	1.20E+13
Bulk concentration (/cm3)	1.07E+19	2.18E+19	1.20E+16

4. Conclusion

In conclusion, s1 reveals the best characteristics to be the best thin film for device performance, as it has the lowest resistivity (9.336 Ω/Sq), the highest mobility (62.3 cm2/V-s), the lowest band gap energy (≈3.57 eV), and the best structure.

So it can be used for solar cell, gas sensor or LED implementations.

Acknowledgment

We gratefully acknowledge the support of the University Sains Malaysia and Grant number; FRGS 203/PFIZIK/6711353.

References

A.U. Ubale, M.V. Bhute, G.P. Malpe, P.P. Raut, K.S. Chipade, S.G. Ibrahim, "Physical properties of nanostructured $(PbS)_x(CuS)_{1-x}$ composite thin films grown by successive ionic layer adsorption and reaction method", Journal of Saudi Chemical Society (2014), pp. 1-10, article in press.

Adel H. Omran Al-khayatt, Mustafa D. Jaafer, "Annealing effect on the structural and optical properties of CuS thin film prepared by Chemical Bath Deposition (CBD)", Journal of Kufa – Physics, Vol. 5, No. 1, (2013), pp. 79-90.

J. Santos Cruz, S. A. Mayén Hernández, F. Paraguay Delgado, O. Zelaya Angel, R. Castanedo Pérez, and G. Torres Delgado, "Optical and electrical properties of thin films of CuS nanodisks ensembles annealed in a vacuum and their photocatalytic activity", International Journal of Photoenergy, Volume 2013, Article ID 178017, 9 pages.

L. A. Isac, A. Duta, A. Kriza, I. A. Enesca, M. Nanu, "The growth of CuS thin films by spray pyrolysis", Journal of Physics: Conference Series 61, (2007), pp. 477-481.

M S Shinde, D R Patil & R S Patil, "Ammonia gas sensing property of nanocrystalline Cu_2S thin films", Indian Journal of Pure & Applied Physics, Vol. 51, October 2013, pp. 713-716.

M. A. Sangamesha, K. Pushapalatha, G. L. Shekar, "Effect of concentration on structural and optical properties of CuS thin film", International Journal of Research in Engineering and Technology, Volume: 02, Issue: 11, Nov. 2013, pp. 227-234.

M. Ramya and S. Ganesan, "Annealing effects on resistivity properties of vacuum evaporated Cu_2S thin films", International Journal of Pure and Applied Physics, Volume 6, Number 3 (2010), pp. 243-249.

Mehdi Adelifard, Hosein Eshghi and Mohamad Mehdi Bagheri Mohagheghi, "An investigation on substrate temperature and copper to sulphur molar ratios on optical and electrical properties of nanostructural CuS thin films prepared by spray pyrolysis method", Applied Surface Science, 258, 2012, pp. 5733-5738.

Sheng- Yue Wang, Wei Wang, Zu- Hong Lu, "Asynchronous- pulse ultrasonic spray pyrolysis deposition of Cu_xS (x=1,2) thin films", Materials Science Engineering B103 (2003) 184-188