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# PREPARATION AND CHARACTERIZATION OF LOW RESISTIVITY CuS FILMS USING SPRAY PYROLYSIS

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CuS films were prepared by spray pyrolysis from solutions of $(NH_2)_2CS$ and $CuCl_2.2H_2O$ mixed at ratios of 3:1, 4:1 and 5:1 on glass substrates heated at 160 to 240 $^oC$. The deposition temperatures and pulsed regime of spray were controlled with the help of electronic equipments. The resistivity, phase composition, morphology, band gap energy and type of conductivity of the films were characterized using volt-ampere, XRD, SEM, optical absorption and Hall effect measurements. It was found that for all ratios of precursors the low resistivity of the films was stably obtained at substrate temperatures from 170 to 220 $^oC$. Among them the lowest sheet resistivity of the films reached value of 8 ohm/sqr. The influences of deposition temperature and material ratio on characteristics of the spray deposited CuS films were discussed.

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*Keywords*: CuS, film, low resistyvity, spray pyrolysis.

## 1. Introduction

Copper sulfides, commonly formulated as $Cu_xS$ ($1 \leq x \leq 2$), are known as attractive materials due to their interesting properties and wide application potentials. There are many structural phases with different properties possible to exist in normal condition. All phases of $Cu_xS$ are p-type semiconductor [1-7]. With rather low band gap energy and high absorption coefficients copper sulfide has been extensively studied for using in photovoltaic conversion of solar energy, optoelectronics, solar absorber, radiation filters, gas sensor and so on.

$Cu_xS$ films can be deposited on a wide variety of substrates such as metal, TCO, CdS, $TiO_2$, glass, plastic, etc., by different techniques, such as electrodeposition [8], photochemical deposition [9], AL-CVD [10], vacuum evaporation [7], MOCVD [3], chemical bath [4, 11, 12] and spray pyrolysis deposition [2, 6, 13-16]. Among them, spray pyrolysis deposition is considered as an advantageous method for preparation of large-area films without post-deposition annealing and additives.

However it was reported that the phase and property of $Cu_xS$ films prepared by spray pyrolysis strongly depended on the preparation conditions such as substrate temperature, compositional ratio of precursors and spraying regime. Product of spray pyrolysis was often mixed even intermediate phases with low crystallinity that impedes expected applications of the materials. There have been many attempts for studying influence of various technological parameters on the properties of products but obtained results are still limited.

$Cu_xS$ becomes a high electrical conductor when x=1 (CuS) [17]. The sheet resistivity of CuS was reached 154 ohm/sqr in [4]. With low deposition temperature CuS could be a promising material for conductive coating on plastic, electrodes, ohmic contact to p-semiconductor. Some authors used CuS for heterojuntion [11], dye sensitized solar cell [4], polymer electrolyte for mixed conduction [1] but the works related single CuS were still rare. The aim of this work is to

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synthesize CuS films by spray pyrolysis under close controlling deposition temperature, spraying regime and ratio of precursors for the low resistivity of the films. Besides, in this work for the first time resistivity measurement was used as a supplementary tool to identify and characterize CuS films during the deposition process.

## 2. Experimental

### 2.1. Preparation of CuS films

Spray pyrolysis deposition is a chemical reaction, which depends on substrate temperature and material feed. So in order to obtain a high performance CuS these factors must be controlled as well as possible. For this aim, a low thermal inertia furnace was prepared and powered by electronic equipment using OMRON temperature controller. The system allows presetting and keeping temperature constant during entire preparation process. The spraying apparatus comprised of compressed air system, electromagnetic gas valve and glass atomizer. The valve was managed by pulse generator. The parameters of the pulse can be adjusted to establish optimum conditions.

The precursors were $(NH_2)_2CS$ and $CuCl_2.2H_2O$, which dissolved separately into distilled water to 0.05 M solutions. Only before spraying both solutions were mixed at a predetermined ratio and stirred vigorously. The molar ratios of $(NH_2)_2CS$ to $CuCl_2$ were 3:1, 4:1, and 5:1 (denoted as R = 3, 4, and 5).

The spray solution was loaded into the atomizer and sprayed by 0.2 atm. air stream for 10 minutes. Spraying equipment created pulses of 20 cycles per minute. Each spraying pulse lasted for 2 second. Distance from nozzle to substrate was 3 cm. The substrates were 1.2 mm thick microscope glass slides preheated at temperatures from 160 to 240 $^oC$. For the resistivity measurement, the films were deposited in resistor form with CuS active area of $7x7mm^2$. Electrodes of the resistors were 15 ohm/sqr $SnO_2$:F films prepared using spray pyrolysis.

### 2.2. Characterization of CuS films

All resistors of identical form were examined by volt-ampere characteristics (I-V) measurement and their resistivity was determined. The formation and characteristics of CuS films were also examined by X-ray diffraction (XRD), scanning electron microscope (SEM), optical absorption and Hall effect measurement. All characterizations were carried out under room condition.

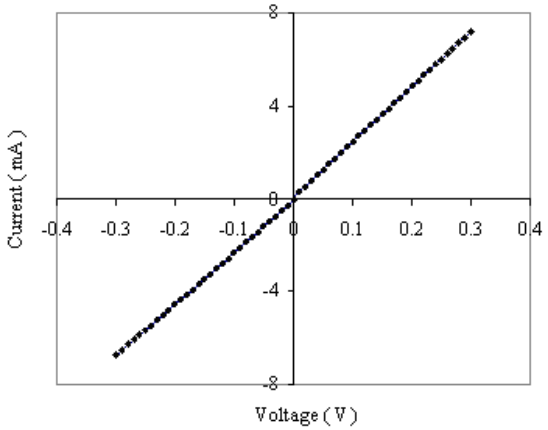


*Fig. 1. I-V characteristic of $SnO_2$:F contacts to CuS film prepared at 190$^oC$ and R=4*

## 3. Results and discussion

All obtained samples demonstrated high electrical conductivity as expected for the CuS films. Furthermore, $SnO_2$:F electrodes provide ohmic contacts to all prepared films as represented in Figure 1. This result allowed using the resistivity measurement for identification and characterization of the CuS films during preparation process.

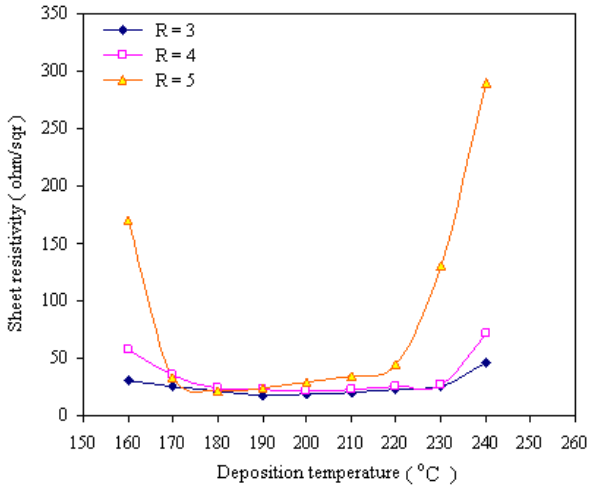


*Fig.2. Resistivity as a function of deposition temperature and R.*

The change in resistivity of CuS films versus ratios of precursors and substrate temperatures at given spraying regime is shown in Figure 2. For all R the low resistivity of the films was stably obtained at substrate temperatures from 170 to 220 °C.

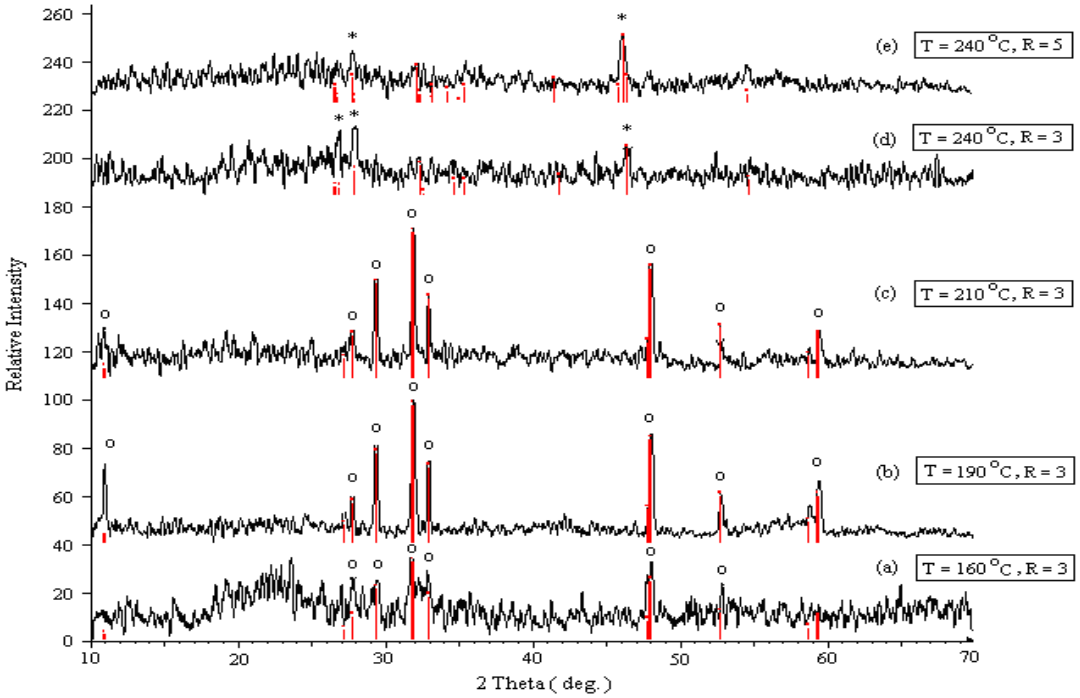


*Fig. 3. XRD of CuS films prepared at different T and R*
(°): CuS, (*): $Cu_7S_4$

XRD characterizations revealed that all films prepared at temperatures from 160 to 220 °C were CuS as representatively shown in Figure 3a,b,c taken from samples prepared at temperatures of 160, 190 and 220 °C and R=3. As it's seen, in all of the films, single crystalline CuS was deposited. No peak from other compound was detected. However crystallinity of the films depended on the substrate temperature. The film prepared at 160 °C (Figure 3a) even comprised of an amorphous phase. At temperature of 240 °C crystalline $Cu_7S_4$ was deposited and an amorphous phase appeared again (Figure 3d). At this temperature the same result was obtained with R=5 (Figure 3e).

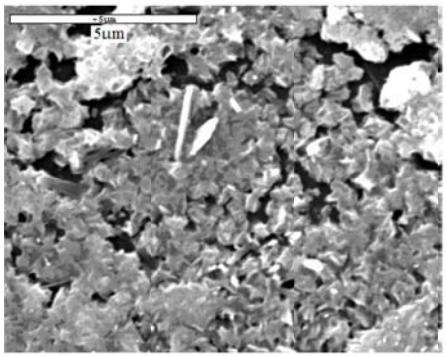


*Fig. 4. SEM of sample prepared at 160 °C*

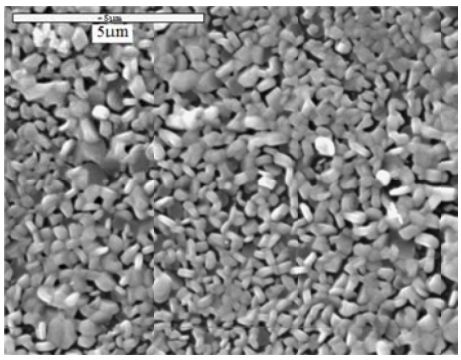


*Fig. 5. SEM of sample prepared at 210 °C*

Morphology of CuS films was examined by SEM. Figure 4 shows the SEM of film prepared at 160 °C and R=3. As can see, this film was inhomogeneous with different contrast indicating multiphase structure. With the same R morphology of film prepared at 210 °C became more homogenous with uniform grains as shown in Figure 5.

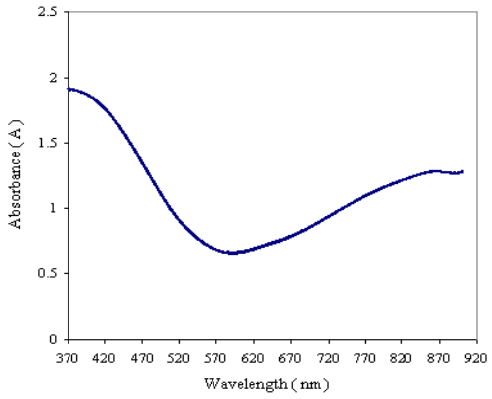


*Fig. 6. UV-Vis absorption spectrum of film prepared at 190 °C and R=3*

The semiconducting behavior of the films was determined via optical absorption and Hall effect measurements. The UV-Vis absorption spectrum of CuS film prepared at 190 °C and R=3 presents in Figure 6. The band gap energy of the film can be estimated from the absorption spectrum using the Tauc's equation described as follows [5]:

$$\alpha h\nu = A\,(h\nu - E_g)^m$$

By plotting $(\alpha h\nu)^{1/m}$ versus photon energy then extrapolating plot to $\alpha=0$, the band gap energy of CuS film prepared at 190 °C was estimated to be 2.37eV with m=1/2 for direct transition (Figure 7a) and Eg=1.5eV for indirect transition with m=2 (Figure 7b). These values shown to be in agreement with previously reported ones [1, 2, 5, 6, 11].

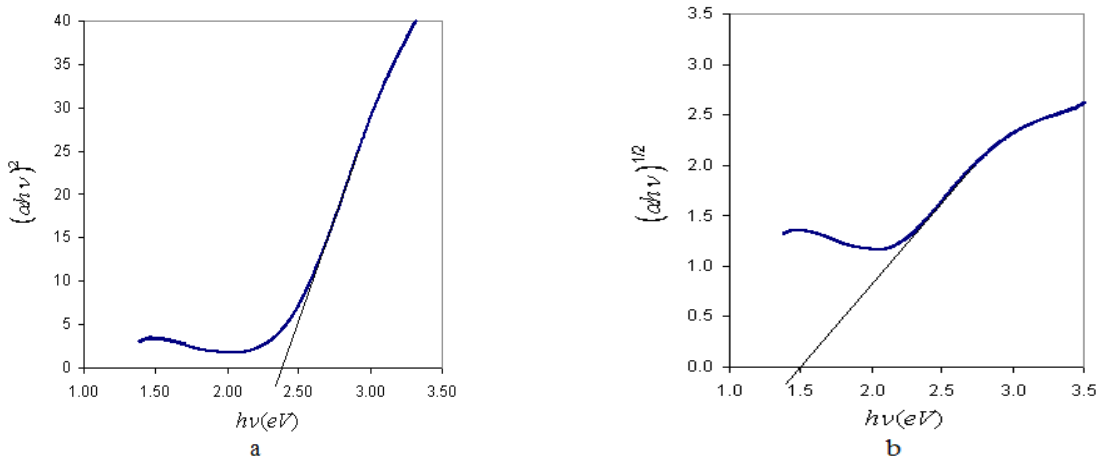


*Fig. 7. Graphical determination of the band gap energy*
*(a): direct transition, ( b): indirect transition*

The type of conductivity and carrier's mobility of CuS films were determined by Hall effect measurement using Lake Shore 665 at magnetic field density scanned from 1 to 10 kG. It was determined that obtained CuS films exhibited p-type conductivity. The film prepared at 190 °C had average Hall mobility of 3.5 $cm^2/Vs$, sheet carrier's concentration of $2.25.10^{17}$ $(1/cm^2)$ and sheet resistivity of 8.0938 Ω/sqr (at 1kG). The obtained Hall mobility was comparable with the value of 7.24 $cm^2/Vs$ [4]. The sheet resistivity of 8.0938 Ω/sqr was considered as the real value of the CuS film because it was excluding the influence of $SnO_2$:F contacts.

The formation and growth of CuS films were resulted from many different processes simultaneously took place on substrate. They were mainly hydrolysis of $(NH_2)_2CS$, reaction to form and grow CuS crystal, evaporation of solvents and intermediate products. In this complicated situation the balance between processes plays a decisive role. Chemical reactions and crystal growth were unfavourable at low temperature that led to the low-ordered CuS crystals and existence of amorphous phase from incomplete processes. Increase in substrate temperature facilitated the formation and growth of crystalline CuS films. However the high substrate temperature also accelerated evaporation of solvents and sub-products that prohibited crystal growth and even destructed CuS crystals. Furthermore, CuS by itself begins decompose at 220 °C to form Cu-rich phase as reported in [2, 15]. The high resistivity $Cu_7S_4$ together with amorphous phase as can see in Figure 3d,e, taken from the films prepared at 240 °C were attributed to dramatical increase in resistivity of the films deposited at temperature higher than 220 °C. Interval of substrate temperature from 170 to 220 °C could be optimal, where the low resistivity CuS films have been deposited .

The fact that CuS films obtained in the temperature range from 160 to 220 °C at various R proved a weak influence of precursor ratios on the CuS formation. Thioure is easily decomposed so it needed to take in excess over molar equivalence (R=1) to compensate for the material loss. However the excess also intensified evaporation that negatively affected the performance of crystals and consequent resistivity of CuS films.

## 4. Conclusions

The low resistivity CuS films were successfully prepared by spray pyrolysis from the mixed solution of thioure and $CuCl_2$. Minimum resistivity of them reached ca. 8 ohm/sqr.

It can confirm that in spray pyrolysis deposition of CuS, substrate temperature plays a decisive role. Single phase CuS could be deposited up to 220 $^{o}$C. Beyond this temperature the films became a rich-Cu copper sulfide and crystallinity may be decreased due to enhanced evaporation. The excess of thioure over compensative need also intensified evaporation that negatively affected performance of CuS crystals.

The low resistivity of CuS films were achieved as a result from both factor: the purity of CuS phase and its high crystallinity. By controlled spray pyrolysis as conducted in this work, the temperature interval from 170 to 220 $^{o}$C and molar ratio of precursor equal 3 were shown to be the optimum conditions for preparation of the low resistivity CuS films.

Performance of as-prepared CuS films shows worthiness for advanced applications and the described technique can be developed for other single $Cu_xS$ or similar films.

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## References

[1] M. Kumar, A. Chandra, Ionics, **16**, 849 (2010), DOI: 10.1007/s11581-010-0474-6.
[2] C. Naşcu, I. Pop, V. Ionescu, E. Indrea, I. Bratu, Materials Letters, **32**, 73 (1997).
[3] R. Nomura, K. Miyawaki, T. Toyosaki, H. Matsuda, Chem. Vap. Deposition, **2(**5), 174 (1996).
[4] K. D. Yuan, J. J. Wu, M. L. Liu, L. L. Zhang, F. F. Xu, L. D. Chen, F. Q. Huang, Applied Physics Letters, **93**, 132106 (2008).
[5] A. E. Pop, V. Popescu, M. Danila, M. N. Batin, Chalcogenide Letters, **8**(6), 363 (2011).
[6] L. A. Isac, A. Duta, A. Kriza, M. Nanu, J. Schoonman, J. Optoelectron. Adv. Mater, **9**(5), 1265 (2007).
[7] R. Hill, Solid-State and Electron Devices, **2**, 49 (1978).
[8] K. Anuar, Z. Zainal, M. Z. Hussein, H. Ismail, Journal of Materials Science: Materials in Electronics, **12,** 147 (2001).
[9] J. Podder, R. Kobayashi, M. Ichimura, Thin Solid Films, **472,** 71 (2005).
[10] L. Reijnen, B. Meester, A. Goossens, J. Schoonman, Materials Science and Engineering C, **19,** 311 (2002).
[11] F. I. Ezema, D. D. Hile, S. C. Ezugwu, R. U. Osuji, P. U. Asogwa, Journal of Ovonic Research, **6**(3), 99 (2010).
[12] A. Kassim, H. S. Min, L. K. Siang, S. Nagalingam, Chalcogenide Letters, **8**(7), 405 (2011).
[13] L. A. Isac, A. Duta, M. Nanu, J. Schoonman, J. Optoelectron. Adv. Mater., **9**(10), 3072 (2007).
[14] J. Madarasz, M. Okuya, S. Kaneko, Journal of the European Ceramic Society **21,** 2113 (2001).
[15] S. Y. Wang, W. Wang, Z. H. Lu, Materials Science and Engineering B, **103,** 184 (2003).
[16] I. Popovici, L. Isac, A. Duţă, Bulletin of the *Transilvania* University of Braşov, **2**(51), 193 (2009).
[17 V. Krylova, R. Ivanauskas, Materials Science (Medziagotyra), **13**(2), 127 (2007).