

Structural and Morphological Properties of CuInS₂ Polycrystalline Films Obtained By Spray Pyrolysis Method

Sabiha AKSAY*

Abstract

CuInS₂ semiconductor films were prepared at three substrate temperatures on glass substrates by spray pyrolysis method. The X-rays diffraction (XRD) spectra of the films have shown that the films produced are polycrystalline and chalcopyrite in structure. The texture coefficients were evaluated for different substrate temperatures. Scanning electron microscopy (SEM) surface micrographs show different morphologies of the surface grains, which are dependent on temperature.

Key Words: CuInS₂, Chalcopyrite, Spray Pyrolysis, X-Ray Diffraction, Texture Coefficient, SEM, Substrate Temperature.

Özet

CuInS₂ yarıiletken filimleri püskürtme yöntemiyle cam tabanlar üzerine üç farklı taban sıcaklıklarında elde edilmiştir. X-ışını kırınım desenlerinden filmlerin chalcopyrite ve polikristal yapıda olduklarını saptanmıştır. Yapılanma katsayısı farklı taban sıcaklıkları için değerlendirilmiştir. SEM yüzey analizleri sıcaklığa bağlı olarak yüzey taneciklerinde farklı morfolojiler göstermiştir.

Anahtar Kelimeler: CuInS₂, Chalcopyrite, Püskürtme Yöntemi, X-Işını Kırınımı, Yapılanma Katsayısı, SEM, Taban Sıcaklığı.

* Anadolu University, Faculty of Science, Department of Physics, 26470 Eskişehir, Turkey
e-mail:saksay@anadolu.edu.tr

1. INTRODUCTION

Low temperature deposition methods for thin film photovoltaic devices are of interest to enable the use of lightweight, flexible substrates. Such devices provide a higher power-to-weight ratio and significant cost savings compared to current technologies. The National Aeronautics and Space Administration (NASA) is particularly interested in film technologies due to low launching costs, deployment and stowage options, radiation hardness, and potentially mission enabling benefits of such technologies (Christopher et al., 2005, 403-408).

The ternary compound CuInS₂ belongs to the I-III-VI₂ family of semiconductors with chalcopyrite type structure (Ortega-Lopez and Morales-Acevedo, 1998, 96-101, Krunk et al., 2002, 71-75). Due to the direct band gap of 1.3-1.5eV, high absorption coefficient (10^5cm^{-1}) (Pathan and Lokhande, 2004, 11-18) and environmental consideration, chalcopyrite compound copper indium disulfide (CuInS₂) has been considered as one of the most popular and promising candidate as absorber materials for photovoltaic applications (Hou and Choy, 2005, 13-18). CuInS₂ is nontoxic and stable under normal environmental conditions (Krunk et al., 1999, 125-130; Krunk et al., 2005, 207-214).

CuInS₂ films have been prepared using various techniques including classical thermal evaporation (Zouaghi et al., 2001, 39-46), RF reactive sputtering (He et al., 2003, 231-236), sulfurisation of metallic precursors (Antony et al., 2004, 407-417), and spray pyrolysis. Among these methods, spray method is an attractive method because large-area films with good uniformity can be grown at low cost (Ortega-Lopez and Morales-Acevedo, 1998, 96-101; Krunk et al., 2000, 61-64; Kijatkina et al., 2003, 105-109; Oja et al., 2005, 82-86).

In the present study, the effects of substrate temperature on the structural and morphological properties of copper indium disulfide CuInS₂ have been reported.

2. EXPERIMENTAL PROCEDURE

CuInS₂ films have been produced by spraying the aqueous solution of 0.01M of CuCl₂ .2H₂O, InCl₃ and CS(NH₂)₂ in a 1:1:2 (by volume) onto the microscope glass substrates (1x10x10mm³, 1x10x13mm³ and 1x13x26mm³) at various substrate temperatures of 225, 250 and 275°C. The substrate temperature was maintained to within $\pm 5^\circ\text{C}$. Deionised water was used for preparing the solutions. Prior to deposition, the substrates were cleaned in acetone.

The schematic arrangement of spray pyrolysis set-up is shown in Fig. 1. Spray pyrolysis is basically a chemical process, that is the spraying of the solution onto a substrate held at high temperature, where the solution reacts forming the desired film (Br.Patent 632256, 1942; Chamberlin and Skarman, 1966, 86-89; Lampkin, 1979, 406-416; Afify, et al., 1991, 152-156; Falcony, et al.1992, 4; Zor et al., 1997, 1132-1135; Aksay, 2001, 147-156; Nunes et al., 2002, 281-285; Aksay and Zor, 2003, 35-38; Altiookka and Aksay, 2005, 27-34). The spray rate was measured by a flowmeter. The flow rate of the solution during spraying was adjusted to be about 2.5mlmin^{-1} and kept constant throughout the experiment. The normalized distance between the spray nozzle and the substrate is 29cm. Nitrogen was used as the carrier gas. The temperature of the substrate was controlled by an Iron-Constantan thermocouple.

The thicknesses of the films was determined using the weighing-method.

Crystal structure and morphology were investigated by means of a X-ray diffraction (XRD) (Rigaku Model D/MAX 220H using $\text{CuK}\alpha$, $\lambda=1.5405\text{\AA}$) and scanning electron microscopy (SEM) using a Jeol JSM-5600LV microscope.

3. RESULTS AND DISCUSSION

3.1. Structural properties

All deposition parameters influence on the physical properties of the films. However, the substrate temperature is the most important one. Table 1 gives the optimum spray conditions which we have observed for the preparation of CuInS_2 films. The thicknesses of the samples were determined using the weighing-method. Weighing-method was employed for CuInS_2 film thickness measurements using the following relation

$$t = \frac{\Delta m}{\rho S} \quad (1)$$

where ρ is the bulk density of CuInS_2 , S is the area and Δ the mass of the film deposited. The thicknesses of the films were found in the range 1.39-1.59 μm .

Table 1

Film	Substrate Temperature (°C)	Nitrogen Gas (bar)	Flowmeter-rate (mlmin^{-1})	Spray Distance (cm)	Deposition Time (min)	Films Thickness (μm)
CuInS_2	225±5	0.2	2.5	29	55	1.59
	250±5	0.2	2.5	29	55	1.43
	275±5	0.2	2.5	29	55	1.39

From XRD for the crystal structure, it was found that the substrate temperature had great effects on the growth of polycrystalline CuInS₂ films. XRD data consisting of lattice spacing (d), angle of diffraction (2θ), relative intensity of the peaks (I/I₀), the phases identified along with (hkl) planes, crystal structures, and the texture coefficients are computed and presented in Table 2. The results of indexing of the lines obtained from the X-ray diffraction data coincide well with the pattern of CuInS₂ film reported in the standard JCPDS data file.

Table 2

Deposition Temperature(°C)	d(Å ^o)	2θ(deg)	I/I ₀ (%)	Identification with (hkl) values	Crystal Structure	TC(hkl)	JCPDS data file no
225	9.28	9.52	63	CuInS ₂	Tetragonal	1.445	270159
	3.19	27.98	100	CuInS ₂ (112)	Tetragonal	2.294	270159
	1.95	46.46	17	CuInS ₂ (220,204)	Tetragonal	0.390	270159
250	9.34	9.46	11	CuInS ₂	Tetragonal	0.417	270159
	3.20	27.90	100	CuInS ₂ (112)	Tetragonal	3.789	270159
	1.96	46.32	9	CuInS ₂ (220,204)	Tetragonal	0.341	270159
275	3.34	27.88	100	CuInS ₂ (112)	Tetragonal	4.39	270159
	1.96	46.38	4	CuInS ₂ (220,204)	Tetragonal	0.175	270159

The corresponding XRD traces of the above films are shown in Fig. 2a-c. The 2q values were varied from 5° to 45°. It may be observed from Fig. 2 that the peak corresponding to (112) plane is the strongest peak followed by other smaller peaks for CuInS₂ at ~9.5° and (220, 204) at ~46.4°. When the growth temperature increases, the (112) diffraction peak becomes progressively more dominant and at temperature 275°C the films are strongly textured with preferential orientation along the (112) axis. The X-ray diffractogram shows well-defined peaks usually associated with CuInS₂ chalcopyrite or sphalerite structure (Ortega-Lopez and Morales-Acevedo, 1998, 96-101; Kanzari and Rezig, 2000, 335-340; Krunk et al., 2002, 71-75; Marsillac et al., 2003, 125-134; Pathan and Lokhande, 2004, 11-18). The preferential orientation is found to be sensitive to substrate temperature. It may be observed that the peak intensity increased with the increasing substrate temperature. The main features of the diffraction pattern are the same but only the peak intensity is varied. It is seen that CuInS₂ films produced at 275°C substrate temperature has a better crystallinity (Fig. 2c). The

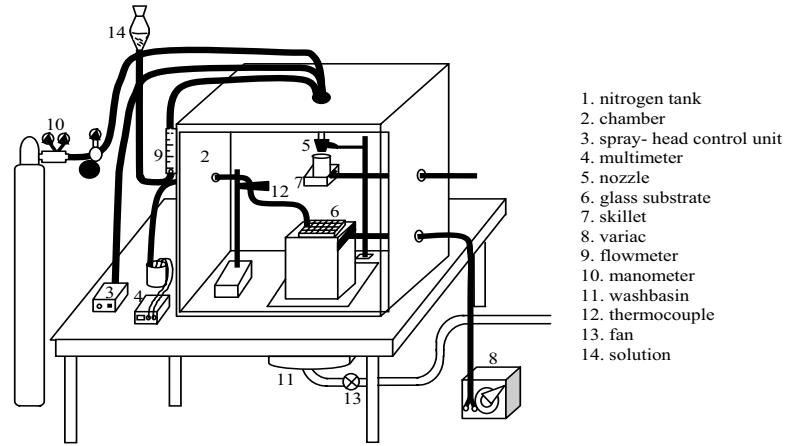


Figure 1. Schematic of the spray pyrolysis system.

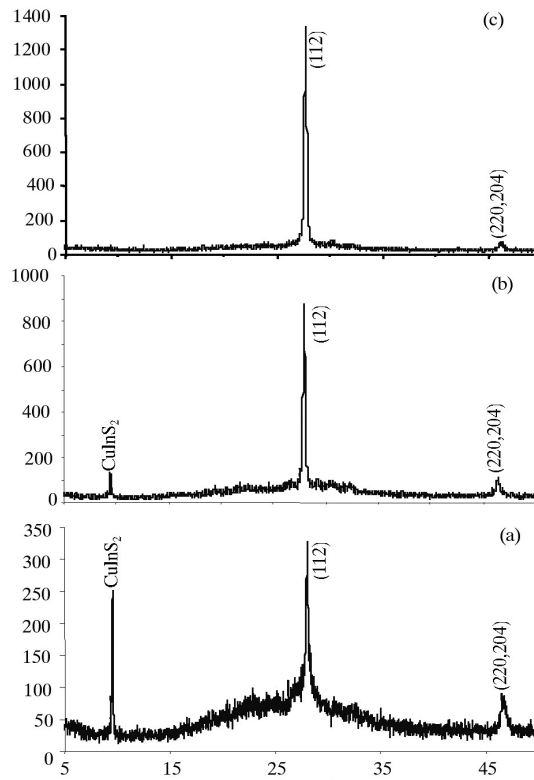


Figure 2: X-ray diffraction patterns of sprayed CuInS₂ layers for different substrate temperatures (a) 225±5°C, (b) 250±5°C, (c) 275±5°C.

deposition temperatures for these films range from 225 to 275°C. The improvement of crystallinity can be achieved by means of increasing substrate temperature within this range (Xiao, et al., 2001, 179-183; Guha, et al., 2003, 115-130). These results are similar to other reported studies dealing with the growth of CuInS₂ films obtained by different deposition techniques (Bihri and Abd-Lefdil, 1999, 5-8; He et al., 2003, 231-236; Guillen, et al., 2005, 19-23; Martinez, et al., 2004, 417-420).

The effect of preparation conditions on the orientation of the polycrystalline films was investigated by evaluating the texture coefficient TC(hkl). This factor can be calculated using the following equation (Nasser, et al., 1998, 327-335; Joseph, et al., 1999, 71-77; Bandyopadhyaya, et al., 2000, 323-339)

$$TC(hkl) = \frac{I(hkl)/I_o(hkl)}{\frac{1}{N} \sum I(hkl)/I_o(hkl)} \quad (2)$$

where I is the measured intensity, I_o is the JCPDS standard intensity and N the reflection number. The values of the texture coefficient TC(hkl) of all planes of the different substrate temperatures of CuInS₂ were calculated (Table 2). The (112) plane has the highest value of TC(hkl) for CuInS₂ film (at 275°C). This large increase in the TC value of the (112) plane could be explained as a result of preferred orientation of these films in this direction. Also TC(112) plane increase with increasing the substrate temperature of deposition.

3.2. Surface morphologies

The surface morphologies of all the films were investigated by SEM. The SEM of CuInS₂ film at three different magnifications (X1000, X2000 and X4000) is show in Fig.3(a), (b) and (c). These SEM micrographs show different morphologies of the surface grains, which are dependent on temperature. For lower substrate temperature the polycrystalline material is randomly distributed (Fig. 3(a)). The increase in the substrate temperature leads to growth of size of the crystallites (Fig. (3b)). From Fig.3(c), it can be seen that the film is relatively homogenous with visible rounded shapes due to the spray method. This behaviour is compared with the data of X-ray diffraction shown in Fig.2c. These results are in good agreement with XRD observations.

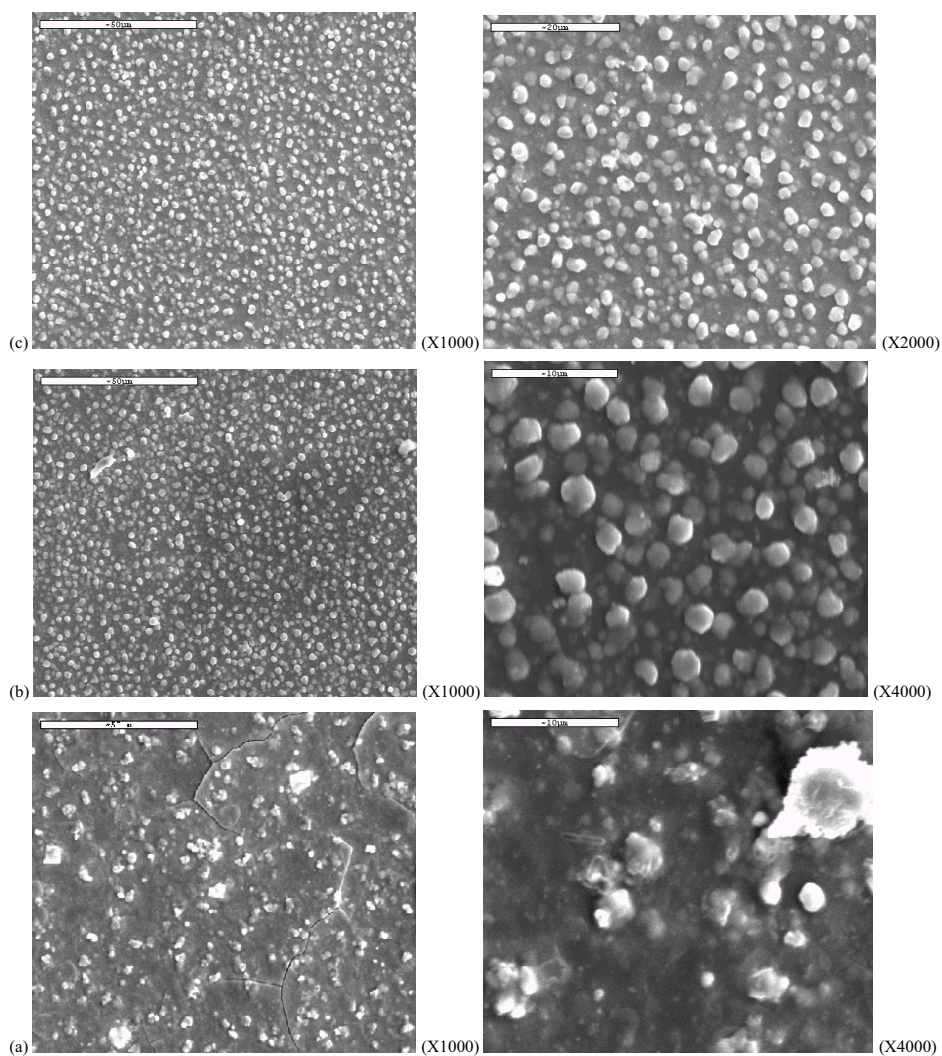


Figure 3: SEM photographs of CuInS_2 films deposited with substrate temperatures (a) $225\pm 5^\circ\text{C}$, (b) $250\pm 5^\circ\text{C}$, (c) $275\pm 5^\circ\text{C}$.

4. CONCLUSION

CuInS_2 films have been deposited by the spray pyrolysis method at various substrate temperatures. XRD results showed that the films were polycrystalline with preferred orientation along (112) plane. The preferential orientation of the film is found to be sensitive to substrate temperature. SEM studies revealed nearly uniform polycrystalline

surface for film deposited at substrate temperature at 275°C. In conclusion, the spray pyrolysis method is an extremely simple and low-cost method for the preparation of films, which should be useful for different applications.

ACKNOWLEDGMENT

The author is grateful to Prof.Dr.Muhsin ZOR from Anadolu University, Science Faculty Department of Physics for his technical and scientific help.

REFERENCES

- Afify, H.H, Nasse, S.A. and Demian, S.E., Influence of Substrate Temperature on The Structural, Optical and Electrical Properties of ZnO Thin Films Prepared by Spray Pyrolysis, *J. of Mater. Sci.*, 2 (1991), pp.152-156.
- Aksay, S., The Films The Compound Semiconductors are Produced by Spray Pyrolysis, *Anadolu University Journal of Faculty of Science*, 5 (2001), pp.147-156.
- Aksay, S. and Zor, M., AC Electrical Properties of Cu(Zn,Cd)InS₂ Films Produced by The Spray Pyrolysis Method', *Anad. Uni. J. Sci. and Tech.*, 4, 1 (2003), pp.35-38.
- Altuokka, B. and Aksay, S., Optical Properties of CuInS₂ Films Produced by Spray Pyrolysis Method, *Journal of Arts and Sciences*, 3 (2005), pp.27-34.
- Antony Aldrin, A.S. Asha, Rahana Yoosuf, R. Manoj, M.K. Jayaraj, Growth of CuInS₂ Thin Films by Sulphurization of Cu-In Alloys, *Solar Energy Materials & Solar Cells*, 81 (2004), pp.407-417.
- Bandyopadhyaya, S., Chaudhuri, S., Pal, A.K., Synthesis of CuInS₂ Films by Sulphurization of Cu/In Stacked Elemental Layers, *Solar Energy Materials & Solar Cells*, 60 (2000), pp.323-339.
- Bihri, H. and Abd-Lefdil, M., Effect of An Initially Sulphurich Sprayed on CuInS₂ Thin Films, *Thin Solid Films*, 354 (1999), pp.5-8.
- Br.Patent 632256 to H.A.Mc Masters Lebley Owers Ford Glass Co., (1942).
- Chamberlin, R.R., Skarman, J.S., Chemical Spray Deposition Process for Inorganic Films, *J. Electrochem. Soc.*, 113 (1966), pp.86-89.
- Christopher V. Kelly, Michael H. C. Jin, Kulbinder K. Banger, Jeremiah S. McNatt, John E. Dickman, Aloysius F. Hepp, Parametric Study on Non-vacuum Chemical Vapor Deposition of CuInS₂ from a Single-source Precursor, *Materials Science and Engineering B* 116 (2005), pp.403-408.
- Falcony, C., Garcia, M., Ortiz, A. and Alonso, J.C., Luminescent Properties of ZnS: Mn Films Deposited by Spray Pyrolysis, *J. Appl. Phys.* 72 (1992), pp.4.
- Guha, P., Das, D., Maity, A.B., Ganguli, D., Chaudhuri, S., Synthesis of CuInS₂ by Chemical Route: Optical Characterization, *Solar Energy Materials & Solar Cells*, 80 (2003), pp.115-130.
- Guillen, C., Kerrero, J., Gutierrez, M., Briones, F., Structure, Morphology and Optical Properties of CuInS₂ Thin Films Prepared by Modulated Flux Deposition, *Thin Solid Films*, 480-481 (2005), pp.19-23.
- He, Y.B., Kramer, T., Polity, A., Gregor, R., Kriegseis, W., Österreicher, D., Hasselkamp,, Meyer, B.K., Preparation and Characterization of Highly (112)-oriented CuInS₂ Films Deposited by a One-stage RF Reactive Sputtering Process, *Thin Solid Films*, 431-432 (2003), pp.231-236.

- Hou, Xianghui and Choy Kwang-Leong, Synthesis and characteristics of CuInS₂ films for photovoltaic applications, *Thin Solid Films*, 480-481 (2005), pp.13-18.
- Joseph, B., Gopchandran, K.G., Thomas, P.V., Koshy, P., Vaidyan, V.K., A Study on The Chemical Spray Deposition of Zinc Oxide Thin Films and Their Structural and Electrical Properties, *Materials Chemistry and Physics*, 58 (1999), pp.71-77.
- Kanzari, M. and Rezig, B., Effect of Deposition Temperature on The Optical and Structural Properties of as-deposited CuInS₂ Films, *Semicond. Sci. Technol.*, 15 (2000), pp.335-340.
- Kijatkina, O., Krunk, M., Mere, A., Mahrov, B., Dloczik, L., CuInS₂ Sprayed Film on Different Metal Oxide Underlayers, *Thin Solid Films*, 431-432 (2003), pp.105-109.
- Krunk, Malle, Olga Bijakina, Tiit Varema, Valdek Mikli, Enn Mellikov, Structural and Optical Properties of Sprayed CuInS₂ Films, *Thin Solid Films*, 338 (1999), pp.125-130.
- Krunk, M., V. Mikli, O. Bijakina, H. Rebane, A. Mere, T. Varema, E. Mellikov, Composition and Structure of CuInS₂ Films Prepared by Spray Pyrolysis, *Thin Solid Films*, 361-362 (2000), pp.61-64.
- Krunk, M., Kijatkina, O., Rebane, H., Oja, I., Mikli, V., Mere, A., Composition of CuInS₂ Thin Films Prepared by Spray Pyrolysis, *Thin Solid Films*, 403-404 (2002), pp.71-75.
- Krunk, M., Kijatkina, O., Mere, A., Varema, T., Oja, I., Mikli, V., Sprayed CuInS₂ Film Grown Under Cu-rich Conditions as Absorbers for Solar Cells, *Solar Energy Materials & Solar Cells*, 87 (2005), pp.207-214.
- Lampkin, Curt M., Aerodynamics of Nozzles Used in Spray Pyrolysis, *Prog. Crystal Growth Charact.*, 1 (1979), pp.406-416.
- Marsillac, S., Zouaghi, M. C., Bernede, J. C., Ben Nasrallah, T., Belgacem, S., Evolution of The Properties of Spray-deposited CuInS₂ Thin Films with Post-annealing Treatment, *Solar Energy Materials & Solar Cells*, 76 (2003), pp.125-134.
- Martinez, A.M., Arriaga, L.G., Fernandez, A.M., Cano, U., Band Edges Determination of CuInS₂ Thin Films Prepared by Electrodeposition, *Materials Chemistry and Physics*, 88 (2004), pp.417-420.
- Nasser, S.A., Afify, H.H., El-Hakim, S.A., Zayed, M.K., Structural and Physical Properties of Sprayed Copper-Zinc Oxide Films, *Thin Solid Films*, 315 (1998), pp.327-335.
- Nunes, P., Fortunato, E., Tonello, P., Braz Fernandes, F., Vilarinho, P. and Martins, R., Effect of Different Dopant Elements on The Properties of ZnO Thin Films, *Vacuum* 64 (2002), pp.281-285.
- Oja I., M. Nanu, A. Katerski, M. Krunk, A.Mere, J. Randoja, A. Goossens, Crystal Quality Studies of CuInS₂ Films Prepared by Spray Pyrolysis, *Thin Solid Films*, 480-481 (2005), pp.82-86.
- Ortega-Lopez Mauricio, Arturo Morales-Acevedo, Characterization of CuInS₂ Thin Films for Solar Cells Prepared by Spray Pyrolysis, *Thin Solid Films*, 330 (1998), pp.96-101.
- Pathan, H.M. and Lokhande, C.D., Chemical Deposition and Characterization of Copper Indium Disulphide Thin Films, *Applied Surface Science*, 239 (2004), pp.11-18.
- Zor, M., Aksay, S., Kul, M. and Aybek, A.Ş., DC and AC Properties of The Compound Semiconductors Prepared by Spray Pyrolysis, *Balkan Phys. Lett.*, 5 (1997), pp.1132-1135.
- Zouaghi, M.C., T. Ben Nasrallah, S. Marsillac, J.C. Bernede, S.Belgacem, Physico-chemical Characterization of Spray-deposited CuInS₂ Thin Films, *Thin solid Films*, 382 (2001), pp.39-46.
- Xiao, J., Xie, Y., X., Tang, R., and Qian, Y., Synthesis and Characterization of Ternary CuInS₂ Nanorods via a Hydrothermal Route, *J. of Solid State Chemistry*, 161 (2001), pp.179-183.