



REGULAR ARTICLE

Raman Studies in Chemically Synthesized Nanocrystalline CuS Thin Films

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This paper describes the chemical synthesis of nanocrystalline CuS thin films onto glass substrate at 40 °C. The effect of the deposition time on the Raman spectroscopy results and physical properties was investigated. X-ray diffraction pattern showed the amorphous nature of CuS thin films deposited with deposition time of 20 min and transferred to orthorhombic crystal structure for CuS thin films with deposition time of 40 min. Raman modes observed at around 273 cm⁻¹ and 475 cm⁻¹ in CuS thin films support the formation of covellite CuS phase. FESEM images taken from the surfaces of chemically deposited nanocrystalline CuS thin films shows the dense structure, smooth and relatively void-free surfaces and surface looks well adhered to the glass substrate. The optical band gap was estimated to be in the range between 2.05 eV and 2.15 eV depending on the deposition time. Finally, as a result of the analysis, we can say that the variation in deposition time can affect the structural properties of CuS thin films.

Keywords: Nanocrystalline, Thin film, Chemical synthesis, XRD, FESEM, Raman spectra.

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1. INTRODUCTION

In recent years, copper sulfide (CuS) have been extensively studied owing to its semiconducting nature and its enormous electronic as well as optical properties. CuS has emerged as a promising p-type semiconducting material for use in different optoelectronic applications because of its versatility, availability, environmental compatibility and non-toxic nature [1]. It has been widely used in the optoelectronic devices such as solar photovoltaic cell, energy storage devices, gas sensors, superconductivity, solar radiation absorber, electro conductive coatings, and catalysts etc. [2-5]. As with most chalcogenide compounds, copper sulfide forms five stable phases: covellite (CuS) in the sulphur-rich region, analite (Cu_{1.75}S), djurleite (Cu_{1.95}S) and chalcocite (Cu₂S) [6, 7]. Among these, CuS (covellite) exhibit metal-like electrical conductivity and it also possesses near-ideal solar control characteristics. Notwithstanding to this, it might even show easy current-conduction and charge-transfer mechanism [8]. There are several nanostructures of CuS have been synthesized such as nanoparticle, nanodisk, nanorod, nanotube, and nanowire etc. [9]. Such low-dimensional nanostructures have drawn significant interest owing to their variations on nanocrystal morphologies due to their most promising applications in electrical, optical and magnetic nano-devices. Such nanostructures of CuS in thin film form could be synthesized using different chemical synthesis methods. To name a few are spray pyrolysis [7], electrodeposition [10], hydrothermal method [11], spin coating [12], successive ionic layer adsorption and reaction (SILAR) [13-15], and chemical bath deposition (CBD) [16-17] etc.

In this present work, we have reporting the formation of nanocrystalline CuS thin films using chemical bath deposition method at comparatively low temperature. Physical properties of CuS thin films has been reported by correlating the crystal structure with the Raman studies and surface morphology. In CBD, physical properties depend upon the deposition parameters such as deposition time.

2. EXPERIMENTAL DETAILS

2.1 Chemical Deposition of CuS Thin Films

To fabricate nanocrystalline CuS thin films using CBD method, copper sulphate [CuSO₄·5H₂O] (M.W. 249.68 g/mol) supplied by Merck Specialties Pvt. Ltd. Worli, Mumbai) and thiourea (SC(NH₂)₂) (M.W. 76.12 g/mol. supplied by s. d. finechem limited) were used as a copper and sulphur source, respectively. Stock solutions of 10 ml 0.1 M copper sulphate, 10 ml of 0.1 M thiourea and 14 ml of 25 % aq. ammonia were prepared in deionized water. The reagents namely copper sulphate and 25 % aq. ammonia were added in 100 ml beaker under constant stirring. After 5 min, the precursor of sulphur source were added in the copper complex solution and then the total volume of the chemical bath was made 50 ml by adding deionized water. The pH value was adjusted at 10, to get uniform and homogeneous thin films of CuS on glass substrates. By several trails, the preparative parameters are optimized and reported as follows: the concentration of the reactant solutions (CuSO₄·5H₂O and SC(NH₂)₂) as 0.1 M, and pH 10. The cleaned glass substrates were kept vertically in the solution and the deposition was allowed to proceed at 40 °C

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for different time durations. Hydroxyl ions are created by ammonia when it reacts with water. These ions make a reaction with thiourea and ionized sulphur is obtained. Due to attractive forces between positive and negative ions of copper and sulphur, a CuS thin film gets deposited on the glass substrate surface. After deposition, the glass microslides were taken out from the bath, washed with deionized water to separate the loosely bounded CuS atoms, then dried in air. The films of various thicknesses were obtained by varying the deposition time. Deposited thin films of copper sulfide were further studied for various properties. Depositions longer than 40 minutes resulted in peeling of the films from the glass substrates. The change in nanocrystalline CuS thin film colour was observed with respect to deposition time was shown in the fig. 1. Photograph clearly depicts that peeling off the films was started after deposition time of 40 min.

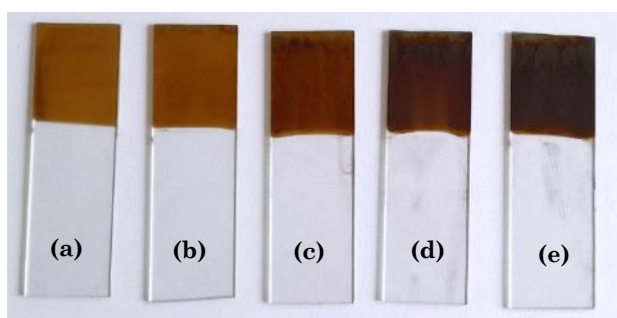


Fig. 1 – Schematic representative of nanocrystalline CuS thin film colour as a function of deposition time (a) 10 min, (b) 20 min (c) 30 min, (d) 40 min and (e) 50 min

2.2 Characterization of CuS Thin Films

X-ray diffraction (XRD) measurements were performed on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20° - 70° (2θ) using $\text{CuK}\alpha$ radiations with wavelength 1.5405 \AA . Room temperature Raman measurements were carried out using diode laser source of wavelength of 473 nm . Field emission scanning electron microscope (FESEM) images were obtained using FEI made NOVA NANOSEM 450 FE-SEM (RV). The optical properties of nanocrystalline CuS thin film were investigated by estimating the optical absorbance as a function of wavelength ranging from 400 - 900 nm was measured using a JASCO UV-Vis spectrometer (V-630).

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

Fig. 2(a-d) represents the XRD patterns of CuS thin films deposited on glass substrate by varying the deposition time by CBD method. From XRD patterns shown in Fig. 1(a-b), it is noticed that CuS films deposited with 20 min and 30 min deposition time have almost amorphous nature and at 40 min deposition time, slight improvement in crystallinity is appeared which changed to crystalline phase i.e. covellite phase of hexagonal CuS nanostructure [18]. The XRD results verified that a better crystallized CuS thin films were found at a deposition time of 40 min, which might be due to an enhancement of the rate of nucleation to form relatively thick CuS thin films. This indicates that the CuS thin films with pure

covellite phase have been synthesized by using low cost, simple chemical bath deposition method [19].

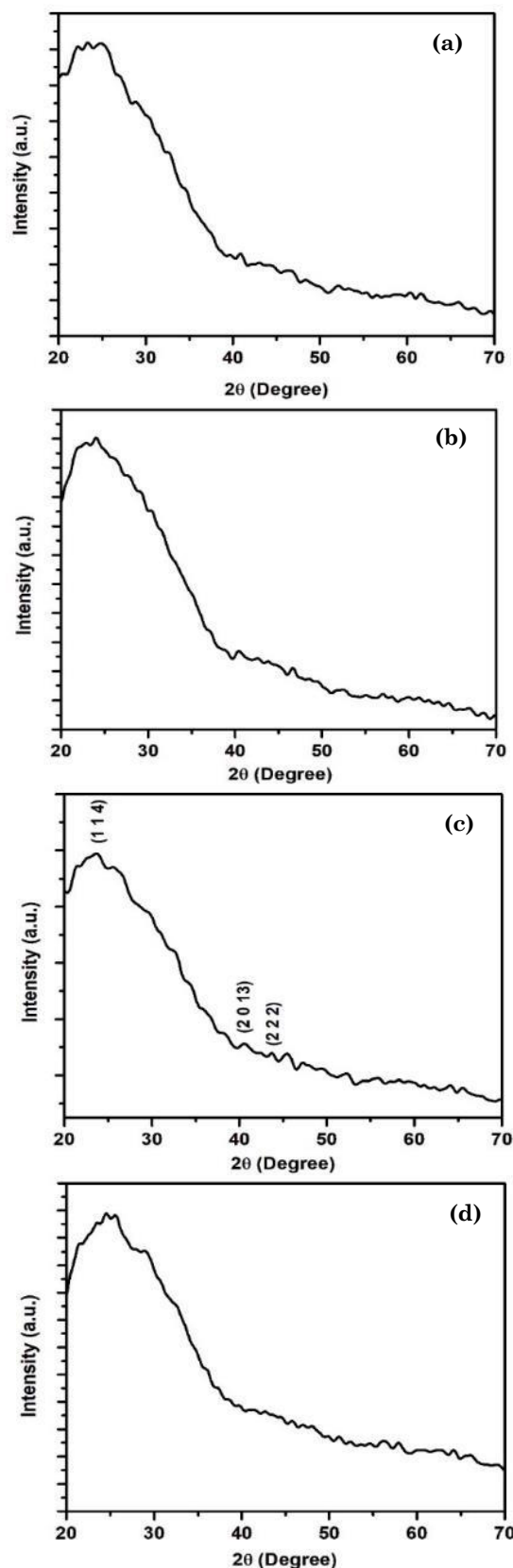


Fig. 2 – X-ray diffraction patterns for nanocrystalline CuS thin films deposited with different deposition time (a) 20 min, (b) 30 min, (c) 40 min and (d) 50 min

3.2 Raman Spectroscopy

Fig. 3 (a-d) shows the Raman spectra for CuS thin films deposited with different deposition time taken at room temperature and ambient conditions using diode laser with excitation line of 473 nm. A low intensity peak around 273 cm^{-1} and high intensity sharp peaks around 475 cm^{-1} were observed for all films. It can be seen that a strong and sharp peak observed at 475 cm^{-1} due to the vibrational modes from the covalent S-S bonds in crystalline CuS [20]. While one weak peak corresponding to 273 cm^{-1} was also observed in the Raman spectra of CuS films attributed to the Cu-S bond vibration [20]. Increase in deposition time does not shift the peak position corresponding to covellite CuS phase which indicates the excellent quality and stability of the deposited films. However, the intensity of the Raman peaks was found to be slightly enhanced for the films deposited with higher deposition time.

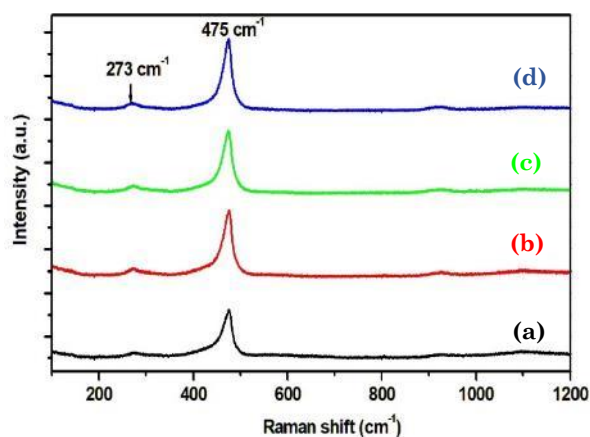


Fig. 3 – Raman spectra for nanocrystalline CuS thin films deposited with different deposition time (a) 20 min, (b) 30 min, (c) 40 min and (d) 50 min

3.3 Surface Morphology Analysis

To investigate the effect of deposition time on the surface morphology, the field emission scanning electron microscopic analysis of the synthesized CuS thin films was done. Fig. 4(a-d) indicates the surface morphology of the CuS thin films, which has the granular and dense grains with nano size are covered on the surface of the substrate uniformly. As can be seen in FESEM images, the surface of the films has no cracks, and is quite dense, compact, smooth and uniform. For optimized deposition time i.e. 40 min, surface looks well adhered to the glass substrate and substrate is coated with nanoparticles having maximum size ($\approx 120\text{ nm}$). In particular, for the applications of thin film solar cells, this kind of dense and compact morphology is essential because the leakage of photocurrent can be prevented by using such kind of surfaces [21].

3.4 Optical Analysis

Optical study of the CuS thin films was carried out by means of the optical absorption spectra and Fig. 5(a-d) shows the absorption spectra of CuS thin films deposited at different deposition time measured at room temperature in the range of 400-900 nm. From the graph it is seen

that absorption edge shifts towards the higher wavelength side with respect to increase in deposition time (till 40 min of deposition time) and at higher deposition time i.e. for 50 min it occurs reverses.

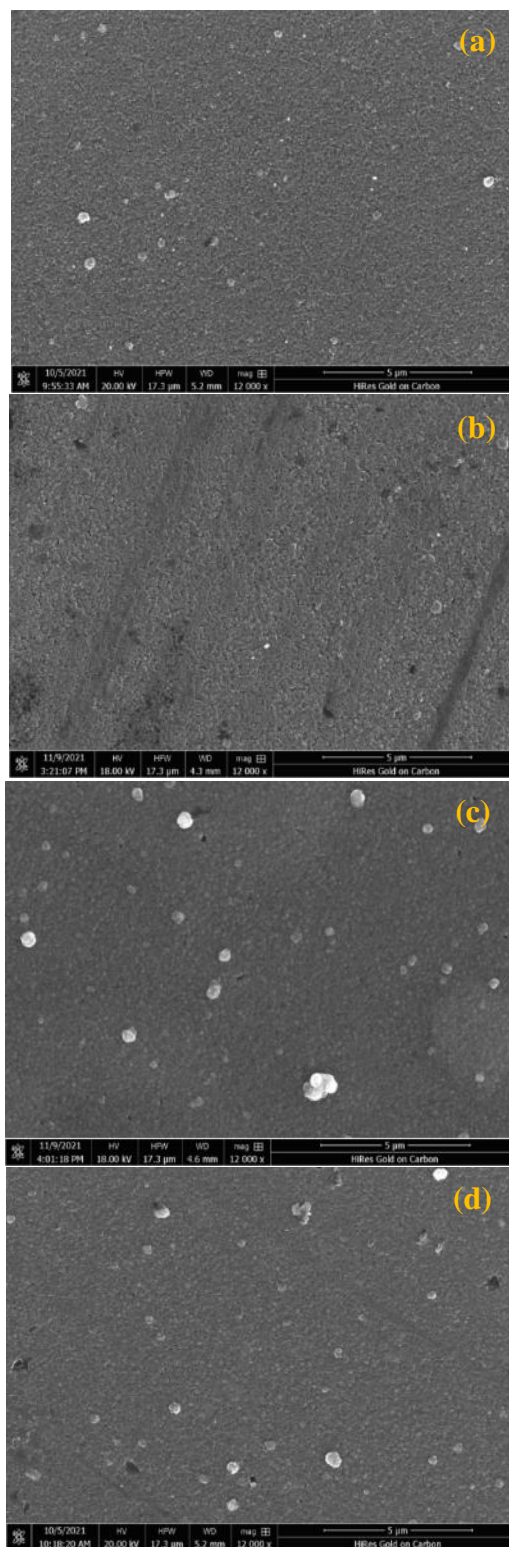


Fig. 4 – FESEM images of nanocrystalline CuS thin film synthesized at: a) 20 min, b) 30 min, c) 40 min and d) 50 min

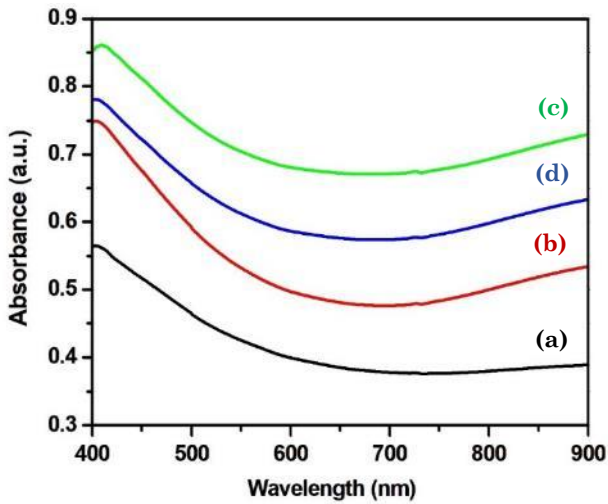


Fig. 5 – Absorbance spectra of nanocrystalline CuS thin film synthesized at: a) 20 min, b) 30 min, c) 40 min and d) 50 min

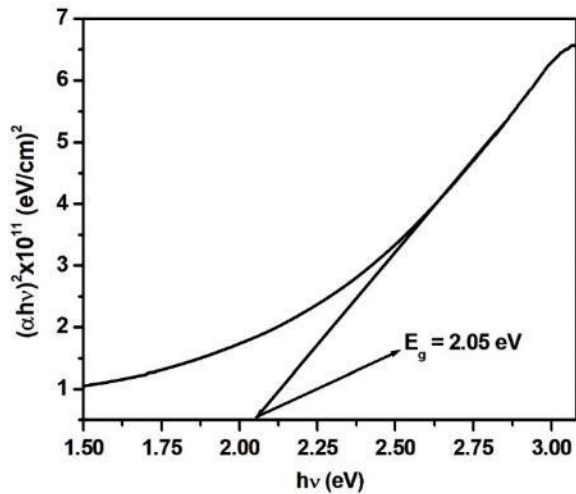


Fig. 6 – Typical plot of $(\alpha hv)^2$ versus $h\nu$ for nanocrystalline CuS thin films deposited at deposition time of 40 min

To obtain the band gap values, we used the theory of optical absorption, which gives the relation between the absorption coefficient ‘ α ’ and the photon energy ‘ $h\nu$ ’, for direct allowed transition as [22]:

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (1)$$

Where ‘ $h\nu$ ’ is the photon energy, ‘ E_g ’ is the optical band gap, ‘ A ’ is a constant. In the present study, the value of the optical bandgap energy E_g is calculated by extrapolating the linear region of $(\alpha hv)^2$ versus $h\nu$ plot. Fig. 6 shows plot of $(\alpha hv)^2$ versus $h\nu$ for nanocrystalline CuS thin films deposited at 40 min while Fig. 7 shows variation of energy bandgap as a function of deposition time. The calculated band gap energy values vary slightly; i.e. 2.15 eV, 2.13 eV, 2.05 eV, and 2.10 eV for the deposition times of 20 min,

30 min, 40 min, and 50 min, respectively. The obtained band gaps of CuS nanocrystalline thin films are closely matched with reports in which authors reported the fabrication of CuS films by using hydrothermal method with flower and wall-like morphologies [22].

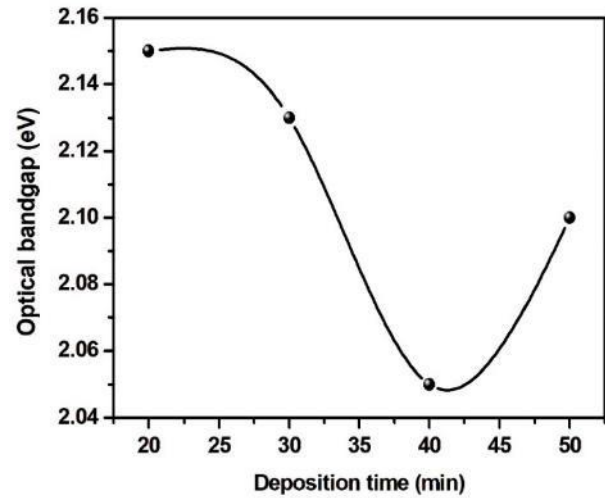


Fig. 7 – Variation of energy bandgap as a function of deposition time

4. CONCLUSION

Nanocrystalline CuS thin films by varying deposition time have been successfully synthesized by using low cost chemical bath deposition method. Structural analysis revealed that the crystal structure is effectively modified by varying the deposition time. XRD measurements revealed that film was in crystalline form for CuS thin films deposited with deposition time of 40 min. Raman analysis show that the low cost chemical bath deposition method is good one for fabrication of a nanocrystalline CuS thin films and confirm that the main component of the deposited thin film are copper and sulfur. Uniform surface morphology with fine spherical grains covering the entire substrate surface is seen through the FESEM studies. It is also found that the deposition time affects the size of the spherical grains. Optical band gap values have been deduced from absorption spectra and it varies between 2.05 eV to 2.15 eV depending on the film deposition time.

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REFERENCES

1. P. Roy, S.K. Srivastava, *CrystEngComm* **17**, 7801 (2015).
2. F. Kari, A. Kothari, *Nano Express* **2**, 010003 (2021).
3. F. Li, T. Kong, W.T. Bi, D.C. Li, Z. Li, X.T. Huang, *Appl. Surf. Sci.* **255**, 6285 (2009).
4. J. Liu, D.F. Xue, *J. Crystal Growth* **311**, 500 (2009).
5. P.J. Sebastian, O. Gomez-Daza, J. Campos, L. Banos, P.K. Nair, *Sol. Energy Mater. Sol. C.* **32**, 159 (1994).
6. H.M. Pathan, J.D. Desai, C.D. Lokhande, *Appl. Surf. Sci.* **202**, 47 (2002).
7. M. Adelifard, H. Eshghi, Mohamad M.B. Mohagheghi, *Appl. Surf. Sci.* **258**, 5733 (2012).
8. M. Froment, H. Cachet, H. Essaïdi, G. Maurin, R. Cortes, *Pure Appl. Chem.* **69**, 77 (1997).
9. P. Roy, S.K. Srivastava, *Mater. Lett.* **61**, 1693 (2007).
10. S.S. Dhasade, J.S. Patil, J.H. Kim, S.H. Han, M.C. Rath, V.J. Fulari, *Mater. Chem. Phys.* **137**, 353 (2012).
11. J. Kundu, D. Pradhan, *New J. Chem.* **37**, 1470 (2013).
12. Y. Lin, Y. Lin, J. Wu, X. Zhang, B. Fang, *Appl. Phys. A* **122**, 609 (2016).
13. Y. Yücel, E. Yücel, D. Gökhan, *J. Mater. Sci: Mater. Electron.* **26**, 4105 (2015).
14. H. Kovacı, Y. Akaltun, Ali Fatih Yetim, Y. Uzund, A. Çelik, *Surf. Coat. Technol.* **344**, 522 (2018).
15. T.Ç. Taşdemirci, *Opt. Quant. Electron.* **51**, 245 (2019).
16. H.-J. Kim, J.-H. Kim, CH.S.S. Pavan Kumar, D. Punnoose, S.-K. Kim, Chandu. V.V.M. Gopi, S. Srinivasa Rao, *J. Electroanal. Chem.* **739**, 20 (2015).
17. R. Sahraei, S. Noshadia, A. Goudarzi, *RSC Adv.* **5**, 77354 (2015).
18. JCPDS card no. 02-0820.
19. S.H. Chaki, M.P. Deshpande, J.P. Tailor, *Thin Solid Films* **550**, 291 (2014).
20. R.A. Ismail, A.-M. E. Al-Samarai, A.M. Muhammed, *J. Mater. Sci.: Mater. Electron.* **30**, 11807 (2019).
21. C. Gao, H. Shen, L. Sun, Z. Shen, *Appl. Surf. Sci.* **257**, 7529 (2011).
22. T. Marimuthu, N. Anandhan, R. Paneerselvam, K.P. Ganesan, A. Amali Roselin, *Nano-Structures & Nano-Objects* **17**, 138 (2019).

Раман-дослідження в хімічно-синтезованих нанокристалічних тонких плівках CuS

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У статті представлені результати хімічного синтезу нанокристалічних тонких плівок CuS на скляній підкладці при 40 °C. Було досліджено вплив часу осадження на результати раманівської спектроскопії та фізичні властивості. Рентгенівська дифракційна картина показала аморфну природу тонких плівок CuS, нанесених з часом осадження 20 хв, і перенесених на орторомбічну кристалічну структуру для тонких плівок CuS з часом осадження 40 хв. Моді комбінаційного розсіювання, що спостерігаються приблизно при 273 см⁻¹ і 475 см⁻¹ у тонких плівках CuS, підтверджують утворення фази кovelіту CuS. Зображення FESEM, отримані з поверхонь хімічно осаджених нанокристалічних тонких плівок CuS, показують щільну структуру, гладкі та відносно вільні поверхні, а поверхня має гарну адгезію зі скляною підкладкою. Ширина забороненої зони лежить в діапазоні від 2,05 eV до 2,15 eV залежно від часу осадження. Результати досліджень свідчать, що зміна часу осадження може вплинути на структурні властивості тонких плівок CuS.

Ключові слова: Нанокристалічний, Тонка плівка, Хімічний синтез, XRD, FESEM, Раманівські спектри.