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Two step synthesis of CuS thin films via high vacuum sulphidation

Yüksek vakumda sülfürleme ile CuS ince filmlerin iki aşamalı sentezi

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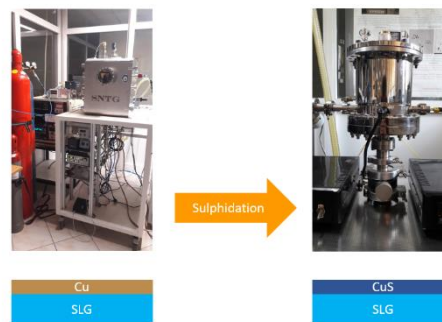
Two Step Synthesis of CuS Thin Films via High Vacuum Sulphidation

Highlights

- ❖ CuS thin films
- ❖ Vacuum Sulphidation
- ❖ Semiconductors

Graphical Abstract

CuS thin films have been synthesized via vacuum based techniques (Figure). CuS thin films have been obtained upon high vacuum sulphidation of sputter deposited Cu thin films on glass (SLG) substrates. Sputter conditions have been optimized so as to acquire small granular Cu structure for effective sulphidation.



Şekil. Two-step CuS film synthesis schematic.

Aim

In this study, two step synthesis of CuS thin films via vacuum based techniques suitable for large scale production has been aimed.

Design & Methodology

Two step synthesis is based on high vacuum sulphidation of sputter deposition of Cu thin films and post-formation of CuS thin films.

Originality

The originality of this study is utilization of all vacuum techniques for mass production of CuS thin films in two steps where pure and repeatable samples could be easily produced.

Findings

In this work, it was determined that upon optimization of sputter conditions, Cu thin film with 24 nm grains are mechanically well adhered to the substrates and by the virtue of this structure CuS thin films can be obtained at relative low sulphidation temperature of 175 °C in 60 min.

Conclusion

This work has investigated all vacuum synthesis of CuS thin films by utilizing high vacuum sulphidation of sputter deposited Cu thin films. Optimum sputter conditions for Cu thin films with good mechanical adhesion and effective sulphidation as well as high vacuum sulphidation parameters have been determined.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Two Step Synthesis of CuS Thin Films via High Vacuum Sulphidation

(This study was presented at Türk Fizik Derneği Uluslar Arası Fizik 2019 Conference.)

Research Article

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ABSTRACT

In this study, synthesis of CuS thin films on soda lime glass (SLG) substrates has been investigated. The synthesis method is based on high vacuum post-sulphidation of Cu thin films deposited by rf. magnetron sputtering. Sputtering conditions have been optimized so as to reduce grain size for better diffusion of S atoms through grain boundaries. XRD pattern of the precursor Cu sample revealed fcc structure with an average crystallite size of 24 nm. Best sulphidation was obtained at 175 °C for 60 min. The crystallite size of CuS calculated from the dominant peak of (110) planes was approximately 48 nm while average grain size observed via SEM was about 400 nm. Raman spectroscopy confirmed CuS structure by scattering peaks at around 467-472 cm⁻¹. Elemental mapping unveiled homogenous distribution of Cu and S atoms over the surface. According to EDS data, at% compositions of Cu and S were 51.6% and 48.4%, respectively. Moreover, SIMS investigation has demonstrated uniformity of S atoms through the thickness of CuS thin film. Although XRD, Raman, and EDS analysis have resulted in predominant formation of CuS structure, existence of Cu₂S phase with a strong luminescence peak located at 1.8 eV was determined by PL spectroscopy.

Keywords: CuS thin films, vacuum sulphidation, sputtering, SIMS.

Yüksek Vakumda Sülfürleme ile CuS İnce Filmlerin İki Aşamalı Sentezi

ÖZ

Bu çalışmada, soda kireç camı (SLG) altlıklar üzerinde CuS ince filmlerinin sentezi incelenmiştir. Sentez yöntemi, rf püskürtme tarafından biriktirilen Cu ince filmlerin yüksek vakumlu sülfürlenmesine dayanır. Büyütme koşulları, S atomlarının taneçik sınırlarından daha iyi difüzyonu için tane boyutunu küçültecek şekilde optimize edilmiştir. Öncü Cu örneğinin XRD paterni, ortalama kristalit boyutu 24 nm olan fcc yapısını ortaya çıkardı. En iyi sülfürleme koşulları 175 °C'de 60 dakikada elde edilmiştir. (110) düzlemlerinin baskın zirvesinden hesaplanan CuS kristalit boyutu yaklaşık 48 nm iken, SEM ile gözlemlenen ortalama tane boyutu yaklaşık 400 nm idi. Raman spektroskopisi, 467-472 cm⁻¹ civarındaki tepe noktaları CuS yapısını doğruladı. Elemental haritalama, Cu ve S atomlarının yüzey üzerinde homojen dağılımını ortaya çıkardı. EDS verilerine göre %'de Cu ve S bileşimleri sırasıyla %51.6 ve %48.4 idi. Ayrıca, SIMS araştırması, CuS ince filminin kalınlığı boyunca S atomlarının homojenliğini göstermiştir. XRD, Raman ve EDS analizi CuS yapısının baskın oluşumuyla sonuçlanmış olsa da, 1.8 eV'de bulunan güçlü bir lüminesans zirvesine sahip Cu₂S fazının varlığı PL spektroskopisi ile belirlendi.

Anahtar Kelimeler: CuS ince filmler, vakumda sülfürleme, püskürtme, SIMS.

1. INTRODUCTION

Studies on semiconductor structures are integral part semiconducting device technologies and the most remarkable studies in this field are mostly focused on thin film applications. Photo thermal conversion applications [1], photovoltaic applications [2], solar control coating [3] and electro conductive electrodes [4] are some of the applications where semiconducting thin films are heavily used. Since the commonly used semiconductors such as Copper Indium Gallium Sulphide (CIGS) and Cadmium Telluride (CdTe) contain toxic and rare earth elements,

new research is on the look for cheaper and non-toxic semiconductor materials. One of these materials studied is copper sulphide (Cu_xS). CuS is considered to be a good alternative in many semiconductor device technologies due to its physical properties, low cost and easy synthesis and the abundance of constituting elements. The Cu_xS structure can be present in more than one stable phase at room temperature such as covellite (CuS), anilite (Cu_{1.75}S), digenite (Cu_{1.8}S), djurleite (Cu_{1.95}S) and chalcocite (Cu₂S) [5]. The crystal structure of these phases ranges from orthogonal to hexagonal [6].

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Covellite (CuS) is a p-type semiconductor with a direct bandgap energy of 1.27 to 3 eV and indirect bandgap energy of 1 eV to 1.85 eV, absorption coefficients of around 10^4 cm^{-1} and the resistivity at room temperature (27 °C) is $10^{-4} \Omega \cdot \text{cm}$ [7-8]. As x in Cu_xS changes from 1 to 2, the resistivity increase has been shown by A. Bollero et al [9]. Based on these optoelectronic properties, while the most suitable phase for use in photovoltaic applications is considered to be Chalcocite (Cu_2S), photosensor application, optical scanners, automatic lighting controls and remote-control devices need to have Covellite (CuS) [10-11]. Therefore, controlling the formation of these phases is an important part material synthesis process.

The widely used synthesis methods are chemical bath deposition (CBD) [12-13] SILAR [8], co-evaporation [9], spray-pyrolysis [13], ion layer adsorption [14], r.f. reactive sputtering [15]. Among these methods, sputtering is usually preferred due to its suitability for large scale production and better structural control under vacuum conditions.

In this study, we have followed a two-step synthesis route [16], where post sulphidation of sputtered Cu thin films under high vacuum conditions is performed. Sputtering conditions have been adjusted to overcome the most specific adhesion problem of Cu thin film on glass substrates [17]. In order to reduce the grain size thereby increasing the adhesion, sputtering power and pressure have been optimized. Optimum deposition and sulphidation conditions have been discussed for the synthesis of CuS thin films in an all-vacuum process.

2. EXPERIMENTAL

2.1 Sample preparation.

Cu thin films were first deposited on soda lime glass (SLG) substrates by r.f. magnetron sputtering and then sulphidation of the precursor samples were performed in a high vacuum chamber. Our goal to utilize a high vacuum condition was to enable low temperature diffusion of S atoms with the help of low pressure as well as acquiring a clean environment. Prior to deposition, SLG substrates were kept in cleaning solution (potassium bichromate) for 10 minutes, acetone, alcohol and deionized water were applied respectively for 5 minutes in an ultrasonic bath, and then blown dried with N_2 . For each run, four substrates were located on the sample stage by Kapton tapes on the corners. Before the deposition, vacuum chamber was pumped down to below 10^{-6} Torr and flushed three times with 250 mTorr Ar gas so as to reduce residual gas content in the chamber. As it is very well known that mechanical adhesion of large grains is less likely as compared to small grains, sputtering power was kept low. Low sputtering power leaves smaller kinetic energy for the Cu adatoms to form larger grains. In addition to low sputtering power, relatively high pressure is required to further reduce the grain size.

As such, we have employed 30 and 50 Watts to the target by providing 15 mTorr Ar pressure in the chamber.

Thickness of the Cu thin film in-situ monitored via a Quartz crystal was adjusted to be about 350 nm. Sulphidation of the precursor Cu thin films was conducted in specially designed vacuum chamber shown in Figure 1. The sulphidation system can be pumped down to 2×10^{-5} Torr by turbo and mechanical pumps connected in series. While the thin film samples are heated by a 300 W ceramic plate heater, the sulphur powder placed in a ceramic crucible is heated by an 85W clamp heater. The sulphidation temperature (T_{SLP}) and the temperature of sulphur powder (T_{S}) are separately controlled by temperature controllers. Both T_{S} and T_{SLP} are measured by K-type thermocouples, pasted on the plate heater and stuck in between clamp heater and the crucible, respectively. For all sulphidation experiments, heating and cooling rates for the samples were $7 \text{ }^\circ\text{C}/\text{min}$ and T_{S} was set to $140 \text{ }^\circ\text{C}$ [16]. T_{SLP} and the sulphidation time (t_{s}) were adjusted by programming the temperature controllers using 3 zone profiles. Ramp times were determined such that two heaters reach soaking temperatures (or T_{SLP}) at the same time while maintaining $7 \text{ }^\circ\text{C}/\text{min}$ heating rate for the samples. Among the sulphidation parameters, only temperature (T_{SLP}) was changed, sulphidation time (t_{s}) was set at 60 min, sulphur amount was 0.5 g. The effects of sulphidation temperature (T_{S} : 150, 175, 200 °C) on the formation of CuS were investigated.

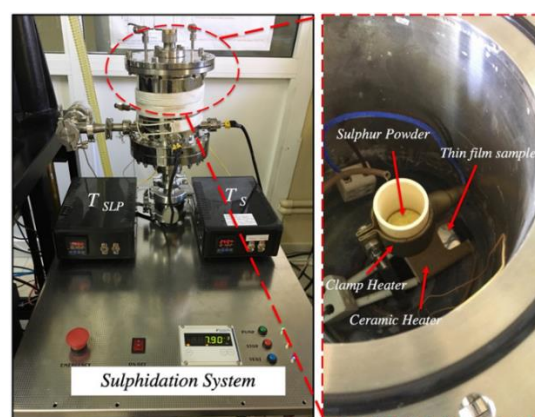


Figure 1. Picture of the sulphidation system and close-up view of the vacuum chamber. T_{S} : Temperature controller of the clamp heater. T_{SLP} : Temperature controller of the ceramic heater.

2.2. Characterization methods

X-Ray Diffraction (XRD) technique (Rigaku D-Max-B) was first used to analyze the structure of all the samples. Planar morphology and the elemental distributions of Cu and S atoms were investigated by TESCAN Gaia 3 Scanning Electron Microscope (SEM) equipped with an Energy-dispersive X-ray spectroscopy (EDS) detector. Detection of possible other binary phases that were either not detected by XRD or in amorphous form was performed by Raman scattering technique by using WITec Snom-Confocal Alpha300 System utilizing 532 nm green laser. Compositional depth profiles of the samples were extracted by using a Hidden Analytical

Secondary ion mass spectroscopy (SIMS) workstation. As for the SIMS measurements, base pressure of the chamber was kept at 10-10 mbar. Bombardment energy and the primary current for O⁻ ions were 3.85 keV, and 400 nA, respectively. The secondary ions were collected from an area of 200 μm^2 . Optical properties of the samples were determined by Photoluminescence (PL) spectroscopy by using Nanometrics RPMBlue system with 266 nm Q-switch laser.

3. RESULTS AND DISCUSSION

In order to acquire a good mechanical adhesion, we aim to produce fine-grained Cu thin films. Therefore, sputtering powers were kept low (i.e., 30, 50 W) and sputtering pressures were set to be relatively high (10, 15 mTorr). Only the samples deposited with 30 W and 15 mTorr were able to pass the scotch tape test according to ASTM-D3359 test method [18]. The test result was 5A meaning there was no peeling or removal, as seen Figure 2. Therefore, post sulphidation experiments were conducted on these samples. Figure 3 demonstrates XRD patterns of Cu thin film samples deposited at 30 and 50 W under 15 mTorr Ar pressure. All the films exhibited the cubic Cu phase's typical XRD peaks located at $2\theta \sim 43^\circ$, $2\theta \sim 50^\circ$ and $2\theta \sim 74^\circ$ corresponding to (111), (200) and (220) planes, respectively. Detailed investigation of the XRD patterns was performed by Maud software implementing Rietveld refinement.



Figure 2. Scotch tape adhesion test of precursor Cu thin film deposited at 30 W.

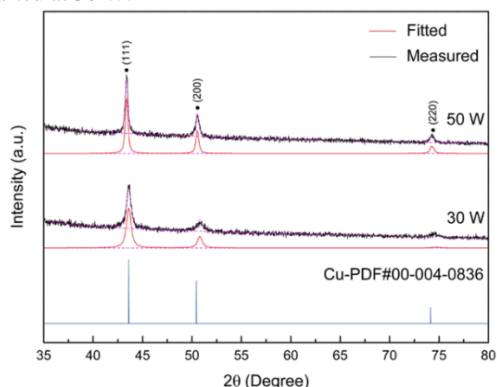


Figure 3. Measured and Rietveld refined XRD patterns of precursor Cu thin films deposited at 30 and 50 W and JPDFS card number is PDF#00-004-0836.

Structural parameters based on the Rietveld refinement fitted data are listed in Table-1. As expected, low power

sputtering with high pressure yields smaller Cu crystallites with an average size of 24 nm, resulting in good mechanical adhesion. It is also realized by Rietveld refinement that smaller crystallites acquire 0.6% lattice contraction as an indication of compressive stress. In addition, as given in Table 2, when the crystallite size is calculated for all planes separately, it is seen that the crystallite size decreases for the 30 W sample. In fact, this is due to the reduced growth rate which was measured as 0.9 $\text{\AA}/\text{s}$. Total stress in a growing film is determined by the balance between compressive and tensile stresses. For less energetic film growth, total stress becomes compressive due to dominant effects of lower growth rate and diffusivity [18]. On the other hand, 50 W sample acquires a more relaxed lattice structure driven by higher growth rate (i.e. 2.5 $\text{\AA}/\text{s}$) yielding 50 nm crystallites that could not pass the scotch tape test.

Table 1. Structural parameters of precursor Cu thin film samples calculated via Rietveld refinement.

R.f Power (W)	a (\AA)	b (\AA)	c (\AA)	Crystallite Size (nm)	Microstrain
30	3.593	3.593	3.593	23.7	0.0014
50	3.610	3.610	3.610	50.3	0.00086

Table 2. Crystal parameters of the precursor Cu thin film samples calculated by Rietveld.

R.f Power (W)	2θ (Degree)	FWHM (Degree)	(hkl)	Crystallite Size (nm)
30	43.60	0.508	(111)	17
	50.83	0.947	(200)	9
	74.42	1.28	(220)	8
50	43.38	0.316	(111)	28
	50.55	0.442	(200)	20
	74.28	0.495	(220)	21

Moreover, surface morphologies of the Cu thin films observed by SEM support the consequences of XRD investigations and mechanical tests. Particle sizes were calculated with the ImageJ program. As seen in Figure 4-5, the particle sizes of the precursor film deposited with 30 W ranged from 20 to 50 nm, while the particle sizes of the films deposited with 50 W ranged from 30 to 90 nm. Additionally, the grain boundary thicknesses were measured to be between 10 and 20 nm with a length of 450 nm for 30 W sample, while those of 50 W sample were determined to be extended up to 520 nm with an average thickness between 20 and 30 nm. One can readily notice that Cu thin film deposited at 30 W has a more uniform surface with smaller grains, Figure 4 whereas 50 W sample has cracks separating islands formed by relatively larger Cu grains Figure 5. It is also seen that 30 W sample has a loose granular structure compared to 50W, which could not only improve mechanical adhesion but also play a crucial role on effective diffusion of sulphur atoms [19].

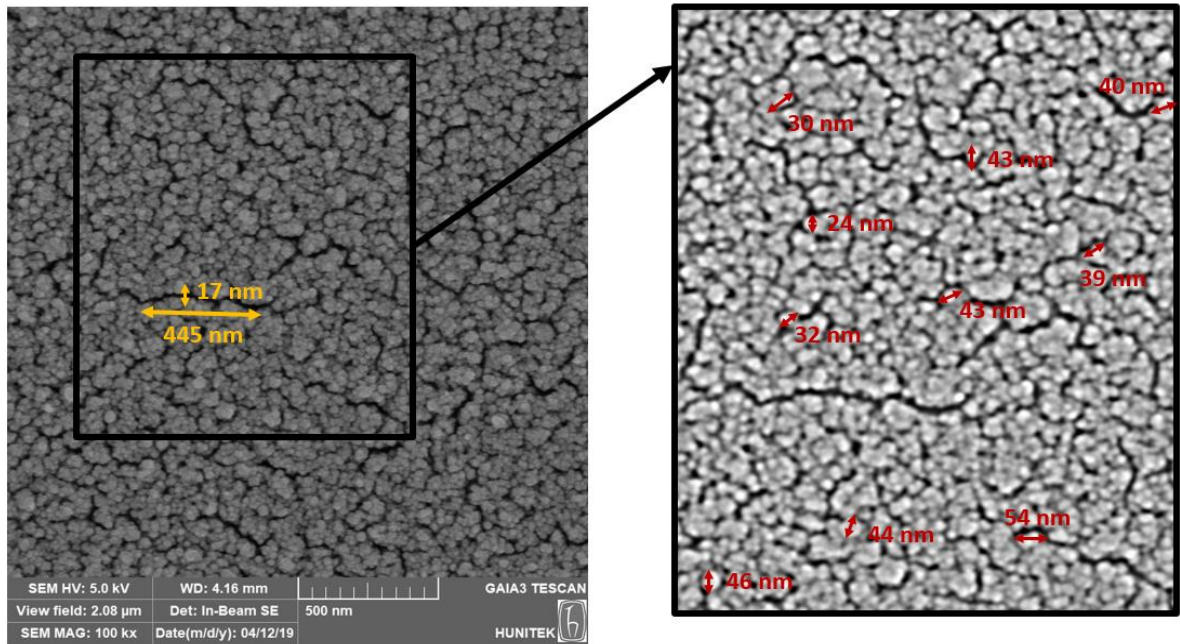


Figure 4. SEM and ImageJ images of Cu thin films deposited at 30 W.

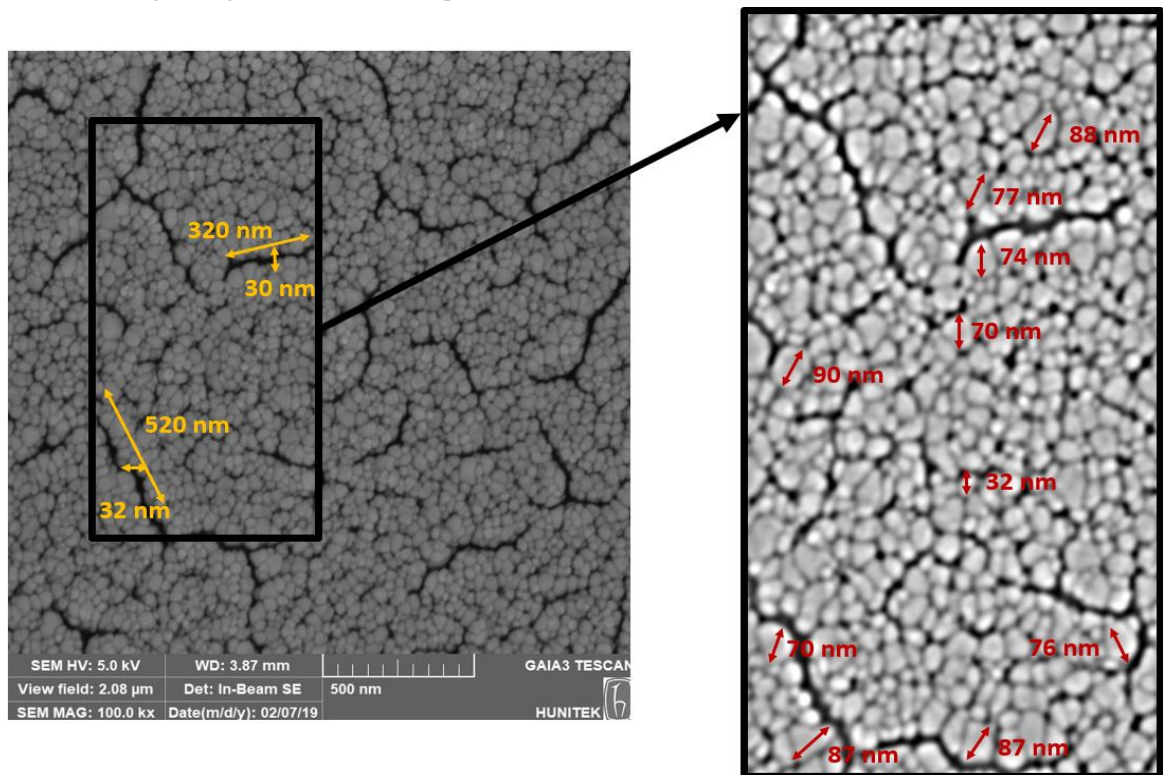


Figure 5. SEM and ImageJ images of Cu thin films deposited at 50 W.

Having reached to mechanically intact precursor Cu thin films, sulphidation optimization was conducted. As opposed to conventional tube furnace sulphidation, we have utilized high vacuum sulphidation, where low pressure environment enables lower sulphidation temperatures. Phase diagram of Cu-S system obtained by thermodynamic calculations points that phase relations are obtained above 200 °C [21]. Accordingly, experimental studies use TSLP ranging between 200 and 350 °C in order to synthesize low temperature phases i.e. $\text{Cu}_{1.75}\text{S}$ anilite (An), $\text{Cu}_{1.95}\text{S}$ djurleite (Dj), a- Cu_2S low-chalcocite (aCh) and b- Cu_2S high-chalcocite (bCh) [22-23-24]. The most important observation is that phase relations are dominated by metastable phases of $\text{Cu}_2\text{-xS}$ forming upon decomposition of the stoichiometric CuS above 500°C. Moreover, self-limitation of sulphidation due to passivation effect of CuS_x formation on Cu surface at around 150°C is another issue experienced under low vapor pressure conditions [25]. Therefore, complete formation of a stable CuS structure without metastable phases has been a great challenge for experimental studies. Based on literature information, sulphidation temperatures of the precursor Cu thin films under high vacuum has been determined as 150°C, 175°C, and 200°C. XRD patterns of the CuS samples are presented in Figure 6.

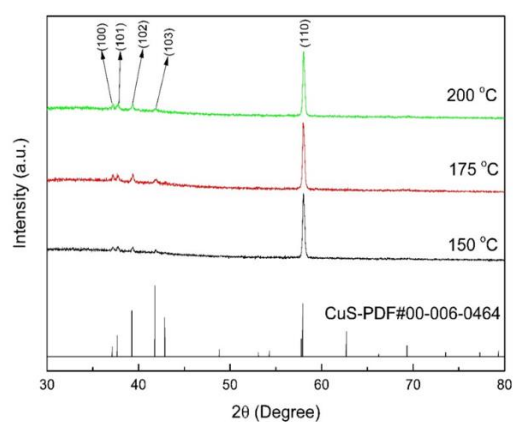


Figure 6. XRD patterns of CuS thin films sulphurised at 150, 175 and 200 °C

All samples manifest a preferential growth of CuS covellite phase (PDF#00-006-0464) perpendicular to (110) plane of hexagonal wurtzite structure. The average crystallite sizes of CuS thin films were calculated as 33.8, 47.8 and 56.8 nm at 150, 175 and 200 °C, respectively. Other lattice parameters of these samples are given in Table 3. As expected, the crystallite size increases as thermal energy enables long range arrangement of crystal planes of the CuS grains. Peak positions of the CuS samples were determined to be 27.1°, 27.7°, 29.3°, 31.8°, and 47.9° for (100), (101), (102), (103), and (110), respectively.

Table 3. Structural parameters of CuS thin film samples calculated via Rietveld refinement.

$T_{(\text{SLP})}$ (°C)	a (Å)	b (Å)	c (Å)	C. Size (nm)	Microstra in
150	3.791	3.791	16.26 3	33.8	0.00024
175	3.789	3.789	16.25 9	47.8	0.00023
200	3.784	3.784	16.24 0	56.8	0.00023

Although XRD pattern of 150 °C sample show formation of CuS covellite phase without any metallic Cu peak, incomplete sulphidation has been noticed from the back side of the sample where metallic Cu is visible. However, increasing the process temperature has led to complete sulphidation. Elemental compositions obtained by EDS along with SEM images presented in Figure 7 have revealed that 175 °C adequately formed CuS structure (51.6%Cu and 48.4% S) with relatively smooth surface (Figure 7a) with a broad size distribution of CuS grains whereas 200 °C sulphidation resulted in Cu-rich (52.2% Cu and 47.8% S) structure with a rough surface (Figure 7b). Cu and S mapping images (Figure 8(b and c)) from the very same area manifest homogenous sulphidation supporting XRD results. Therefore, 175 °C for 60 min sulphidation has been determined as the optimum temperature for a 350 nm thick Cu thin film from which CuS structure could be successfully synthesized via high vacuum sulphidation.

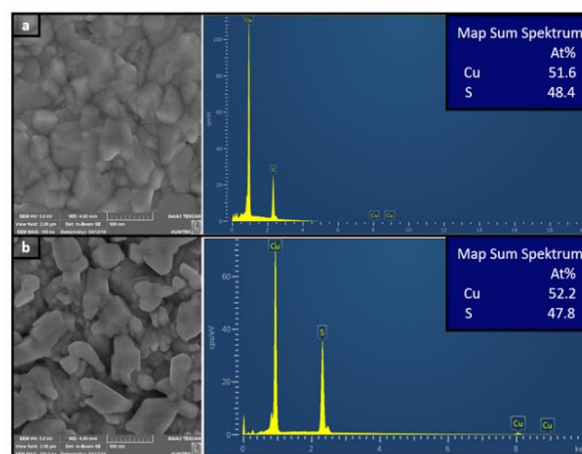


Figure 7. SEM images and EDS spectra of CuS thin films sulphurised at a) 175 °C b) 200 °C.

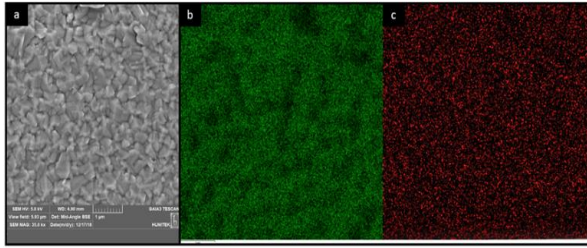


Figure 8. a) SEM image of the CuS thin film sulphurised at 175 °C, elemental mapping images of b) Cu, and c) S atoms.

Here in this work, we have employed a two-step synthesis route which involves diffusion of S atoms into Cu thin film under high vacuum conditions. Although via various tools we have shown the structural quality of the CuS thin films it is complementary to investigate the variation of atomic concentration of Cu and S through the thickness of the sample synthesized under optimum conditions. SIMS profile shown in Figure 9 demonstrate that uniform S diffusion has been accomplished through the film thickness. Therefore, based on SEM and SIMS analyses we conclude that three-dimensional uniformity of S atoms within the CuS has been successfully materialized by sulphidation under high vacuum conditions. Atomic structure of the CuS samples is further investigated by Raman spectroscopy due to the fact that low concentration amorphous phases cannot be detected by XRD and distinguished by SEM or SIMS. Raman spectra of the samples presented in Figure 10 have also confirmed the formation of stoichiometric CuS by a strong and sharp peak at 473 cm^{-1} corresponding to S-S stretching mode [26]. Here we note that increasing T_{SLP} does not result in a noticeable change on either the peak width or the position. In order to understand the optical response of the CuS samples as well as determining energetic position of possible defect levels in the band gap, Photoluminescence (PL) measurements have been performed at ambient conditions by using 266 nm Q-switch laser. The PL spectra of the samples are given in Figure 11. All samples commonly manifest a similar spectrum where an intense blue peak at 1.8 eV along with a broad green peak at 2.4 eV. Studies report varying band gap value for CuS thin films as well as CuS nanoparticles [27] depending on the stoichiometry and morphology. Although bulk CuS is known to have a direct band gap around 2.5 eV, size reduction leads to slight blue-shift of the emission peak due to quantum confinement [28]. Broad nature of the peak results from combined effect of small and large grains whose sizes range between 50-400 nm. In the literature 1.8 eV PL peak is reported for Cu_2S [29]. Although, neither XRD nor Raman analysis have led to a clue for the existence of this phase in our samples, there could be two possible explanations for a copper rich phase determined by PL spectroscopy. First is that surface grains might have S deficiency due to volatility of S atoms and the second is the laser induced local transformation of CuS to Cu_2S . The reason that a surface technique, Raman spectroscopy could not detect Cu_2S is because of indistinguishability

of Cu_{2-x}S phases from $x=0$ to $x=2$ due to unaffected S-S stretch modes [30-31]. As for the strong intensity of 1.8 eV PL peak, Cu_2S is known to have a strong fluorescence at around 2 eV due to excess holes in the top of the valence band [32-33]. Therefore, this near infrared PL peak could be induced by plasmonic resonance with a 0.2 eV red shift which could very possibly be resulted from effective size and morphology of Cu_2S grains [34].

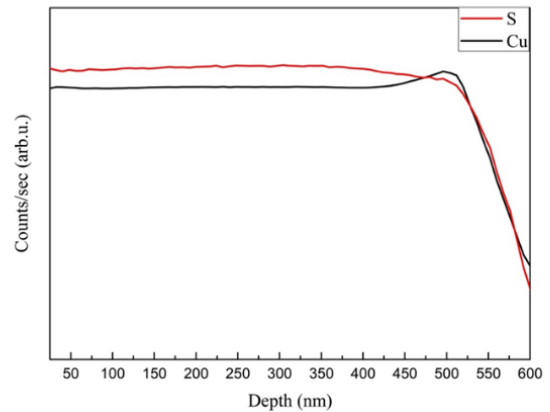


Figure 9. SIMS profile of the CuS thin film sulphurised at 175 °C.

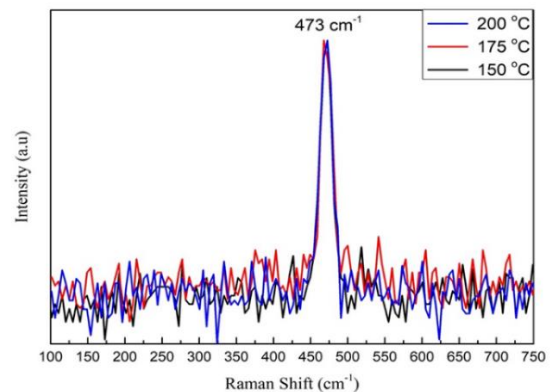


Figure 10. Raman spectra of the CuS thin films sulphurised at 150, 175 and 200 °C.

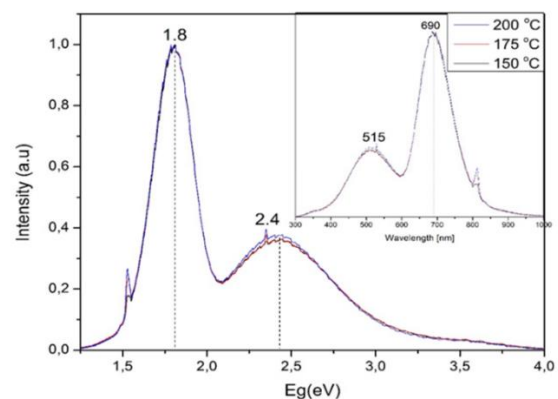


Figure 11. Photoluminescence spectra of the CuS thin films sulphurised at 150, 175 and 200 °C.

4. CONCLUSIONS

In conclusion, this work has investigated all vacuum synthesis of CuS thin films by utilizing high vacuum sulphidation of sputter deposited Cu thin films. Sputter conditions have been optimized to acquire Cu thin films with good mechanical adhesion on SLG substrates. It has been understood that low sputtering power (30 W) and relatively high sputtering pressure (15 mTorr) enable Cu thin films with smaller granular structure. Additionally, optimum sulphidation conditions have been determined for 350 nm thick Cu thin films. While the structural characterizations have manifested that 60 min sulphidation at 175 °C adequately forms well defined CuS, PL spectroscopy has revealed existence of Cu₂S phase most likely on the surface of the samples. Although the possible reasons of Cu₂S phase have been speculated as volatility of S atoms during and laser induced variation of the local structure during PL, further studies and characterization are required for a complete understanding of the Cu₂S formation mechanisms.

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DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission..

AUTHORS' CONTRIBUTIONS

Ali Rıza Yıldırım: Performed the experiments and analyse the results.

Abdullah CEYLAN: Wrote the manuscript.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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