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Phase selective growth of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and Cu_3SbS_4 thin films by chalcogenization of simultaneous sputtered metal presursors

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Abstract

In this work, we present a procedure to grow $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and Cu_3SbS_4 thin films consisting of the deposition of simultaneously sputtered metal precursors followed by an annealing treatment in a sulphur atmosphere. The selection of the ternary phase is performed by adjusting the sulphur evaporation temperature in the chalcogenization process. It is shown that for a sulphur evaporation temperature of 140 °C the predominant phase is $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ while for 180 °C the predominant phase is Cu_3SbS_4 . In order to ensure precursor composition homogeneity, the Cu-Sb metallic precursors are deposited simultaneously by RF magnetron sputtering using adjustable segmented targets. The morphological characterization of the films was made by scanning electron microscopy and the composition was analysed by energy dispersive spectroscopy. The structural analysis and phase identification were performed by X-ray diffraction and Raman scattering. The optical properties were studied on films deposited directly on bare glass and the optical bandgap energies of 1.47 eV and 0.89 eV for $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and Cu_3SbS_4 , respectively, were determined.

Keywords: Sulfosalt, Thin films, RF Magnetron sputtering, Chalcogenization

1. Introduction

The photovoltaic market is dominated by technology based on Si, with a consistent price reduction of the systems over the past few years. The energy costs in high quality Si production are still an obstacle to a further drop in production costs. Thin film solar cells (TFSC) have been identified as an alternative to overcome this problem, supported by requiring less materials, growth methods involving lower energy consumption, cheaper and more automated processes. Among the various materials tested for this technology, $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CIGS) and CdTe stand out for their high light to power conversion efficiency, with 22.9 % and 22.1 %, respectively [1]. However, these materials exhibit a significant intrinsic problem since In and Ga elements are scarce, and Cd is toxic. The scientific community has been studying materials that can replace CIGS and CdTe. Compounds like kesterites or perovskites have been intensively studied for this kind of applications, but the difficulty of growing high quality materials or device performance stabil-

ity problems, can complicate their commercial implementation on a large scale.

$\text{Cu}_x\text{Sb}_y\text{S}_z$ compounds, generally designated as Sb-based sulfosalts, have shown optical absorptions higher than 10^5 cm^{-1} and optical bandgap energies between 1.1 to 2.5 eV, inside the energy range imposed by the Shockley–Queisser limit [2]. These studies also revealed that their electronic properties, such as charge carriers density and mobility are compatible with semiconductor materials for TFSC applications [2–7]. In nature, the most common crystalline phases of this sulfosalt class are: CuSbS_2 (chalcocite), Cu_3SbS_3 (skinnerite), Cu_3SbS_4 (famatinitite) and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (tetrahedrite). A wide variety of atmospheric pressure based synthesis methods have been reported for the growth of Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. Chemical bath deposition, solvothermal, hydrothermal routes, and hydrazine based chemical routes have been used to grow thin films and nanoparticles [6–14]. Franzer *et al.* [15] presented a method to grow Cu_3SbS_4 thin film based on post annealing of magnetron sputtering precursors.

In this work, we propose a method of growing Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ thin films based on the deposition of Cu-Sb metallic precursors by RF-magnetron sputtering followed by an annealing step in a sulphur vapour atmosphere. There are significant differences between published methods [9, 15] and what is proposed in this work: 1) The published works are mainly focused on the growth of famatinitite while the one we present here

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selectively allows growing films composed mainly by famatinite or tetrahedrite. 2) The precursors are deposited differently. The mentioned works use targets already composed by Cu-Sb-S [15] or are sequentially deposited/stacked [9]. Here, we present a composed target, which allows composition control over time due to an expected behavior. Furthermore, it has advantages in terms of composition flexibility and uniformity in the composition of metals. 3) The phase to be grown can be selected accordingly to the amount of sulphur supplied to the sample during the growth process. This amount can be tuned by changing the maximum sulphur evaporation temperature. The structural, compositional and morphological characterization of the samples are presented as well as the optical analysis.

Figure 1: The target setup used for the deposition of the metal precursors.

2. Experimental Methods

2.1. Sample preparation

This work uses a 2-stage method to grow Cu-Sb-S based sulfosalt thin film. The first stage refers to the deposition of the metallic precursor layer, Cu and Sb, by RF magnetron sputtering. The chalcogen incorporation, S, and the annealing process, which enables for the crystalline phase formation, are performed in the second stage.

The sample preparation process begins with a 3×3 cm² soda lime glass (SLG) substrate cleaning, with successive ultrasound baths of acetone/alcohol/deionised water. This step ends with substrate being dried with a N₂ flow. Next, the precursor layer is deposited directly in the SLG. This step is performed using an Ar atmosphere at an operating pressure of 2×10⁻³ mbar. The target is composed by a Sb base with a thickness of 1/8 inch and 1 mm thick Cu segments placed on top as shown in Fig. 1. The radial geometry of the segments ensures a uniform distribution of metals in the sample. Both, base and segments, have a 4N purity. In order to allow adjustments in the composition of the metallic precursors, the segments were produced with a limited area. The thermal contact between base and segments is assured only by the mechanical grip using the metal ring of the sputtering gun. To avoid contamination no thermal paste is used. The power density of 0.87 W/cm² was used for the deposition of the metal precursors.

The 2nd stage was performed in a tubular furnace in a N₂ sulphur vapour atmosphere at a constant working pressure close to 500 mbar and a N₂ flow rate of 40 ml min⁻¹. Sulphur pellets with purity 5N were evaporated using a temperature controlled quartz tube source. Two different sulphur evaporation temperatures are presented, 140 °C and 180 °C. The furnace temperature profile has 3 stages: first a temperature increase of 10 °C min⁻¹, followed by a 5 min isothermal line at 480 °C and finally a natural cooling step to room temperature. The sulphur evaporator follows the same heating rate as the furnace until it reaches the maximum tested evaporator temperature. It remains in this condition until the furnace cools down to 200 °C. At this point the evaporator is switched off. These profiles are presented in Fig. 2.

Figure 2: Annealing and sulphur evaporator temperature profiles used for sulphurization process (2nd stage).

2.2. Sample characterization

The cross-sectional morphology and average composition of the samples were analysed by scanning electron microscopy (SEM) with a Hitachi Su-70 scanning electron microscope equipped with a Rontec energy dispersive spectroscopy (EDS) system operated at an acceleration voltage of 4 kV for image acquisition and 25 kV for chemical analysis. The crystalline structure was analysed by X-Ray Diffraction (XRD) with a Philips PW 3710 system, in the Bragg-Brentano configuration (θ -2 θ), using the Cu-K α line (wavelength λ =1.54060 Å) and the generator settings were 50 mA and 40 kV. A LabRam Horiba, HR800 spectrometer, equipped with a solid state laser (excitation wavelength, λ_{exc} =532 nm) was used for the Raman scattering measurements. The back-scattered radiation was analysed with a 1800 lines/mm grating. The resolution was at about 3 cm⁻¹, the wavenumber accuracy was $\pm$ 1 cm⁻¹ (calibrated with the 520 cm⁻¹ line of a Si standard reference). Absorbance measurements were done using a Shimadzu UV3600 spectrophotometer equipped with an integrating sphere. The photoluminescence (PL) measurements were performed with a Bruker IFS 66v Fourier transform infrared (FTIR) spectrom-

eter, equipped with a Ge diode detector. The samples were placed in a He gas flow cryostat. The 514.5 nm line of an Ar⁺ ion laser was used as the excitation source. The excitation power was measured at the front of the cryostat window. The correction of the spectral response of the Ge detector was performed for all spectra.

The sample naming code uses the sulphur element symbol S followed by the maximum temperature of the sulphur evaporator.

3. Results and Discussion

3.1. Compositional characterization

The main objective of this work is the growth of thin films of ternary compounds of Cu-Sb-S, namely Cu₃SbS₄ and Cu₁₂Sb₄S₁₃, and to evaluate the influence of sulphur concentration in its growth. In the course of this study several annealing/sulphurisation temperatures were tested. However, in order to keep the presentation simple, only the most relevant results, corresponding to the sulphurization temperature of 480 °C and to sulphur evaporation temperatures of 140 °C and 180 °C, are shown. Under these thermodynamic conditions, Sb₂S₃ evaporation losses are minimized, allowing the growth of only one predominant ternary crystalline phase. In addition, with these processing conditions, a better phase crystallinity is obtained compared with the ones grown at lower temperatures (not presented).

The adjustment of the metal precursors' composition is made by placing more or less Cu segments on the Sb target base. This procedure changes the exposed area of each element to the plasma, changing the amount of sputtered metal from the target and arriving at the sample. An exhaustive study of the precursors composition with the exposed area of the metal target was made. The results of this study are shown in Fig. 3 a) and b). In Fig. 3 a), the metal composition ratio, [Cu]/[Sb], is plotted as a function of the exposed area ratio, A_{Cu}/A_{Sb} , where a polynomial fitting is used as a guide to the eye. The results show a significant Cu content increase in the precursor's composition for area ratios rising from 2.25 to 3.5. These results were attained with same Sb base but with new Cu segment for each deposition run. In order to study the reproducibility of this method, successive deposition runs were done with the same Sb base and Cu segments. The results of this study is presented in Fig. 3 b). Three sets of segments, two with the same area ratio of 1.77 for Sets 1 and 2, and a third set of segments, Set 3, with an area ratio of 1.88, were studied. The composition analyses of the precursor films shows that the content of Cu lowers at each deposition. These variations are explained by metal target interdiffusion during the deposition process and can be controlled by replacing the Cu segments by fresh ones.

Fig. 4 presents a ternary diagram with the composition of the sulphurized samples. Samples that were sulphurized using a sulphur evaporation temperature of 140 °C, samples S140, are close to stoichiometric Cu₁₂Sb₄S₁₃ phase. On the other hand, for higher S availability during the annealing process, used for the S180 samples growth, the compositions are closer to stoichiometric Cu₃SbS₄ phase. In this work, no sample approached

Figure 3: a) Metal composition ratios versus the ratios of the exposed areas of the target elements for different deposition runs. For each deposition new Cu segments were used. b) Composition ratios for successive deposition runs for same target areas using the same Cu segments. Three sets of segments are shown, Set 1 and 2 with a area ratio of 1.77 and Set 3 with 1.88.

compositions close to the two other compounds belonging to the same family, CuSbS₂ and Cu₃SbS₃. According to previous studies on phase relation in system Cu-Sb-S, for an annealing temperature of 480 °C and, depending on the exact composition, several competing phases can form [16–18]. For [Cu]/[Sb] compositions ratios close to 3, the most common phase is tetrahedrite, as this compound has an extensive formation field [17] (region 1). Higher contents of Sb lead to in solid mixtures with chalcocite. On the other hand, increasing the content of Cu, solid mixtures of tetrahedrite, covellite and famatinite are expected to form, according to these studies. When minor Sb composition increases are made together with S, the predominant phase is likely to be famatinite, but at these temperature conditions, its formation region is narrow (region 2). In our work, the growth conditions falls in regions 1 and 2, explaining why we mainly find tetrahedrite and famatinite, respectively.

3.2. Morphological and structural characterization

3.2.1. Morphological characterization

Surface morphology was studied using SEM imaging. Fig. 5 shows the results of this analysis for samples S140 and S180. Both samples show rough surfaces with an uniform distribution of aggregates. EDS point measurements on the top of these aggregates and on the background show the same compositions, with the exception of Si composition with higher contents for the background (Supplementary Information Fig. 1 and 2 and, Table 1 and 2). Comparing samples S140 with S180, the latter shows bigger aggregates on the top of the surface, with repercussions in the roughness of the films. Despite these properties, no cracks or voids were observed. Changes in the sulphurization temperature profile must be done in order to lower the film surface roughness.

Figure 4: Composition ternary diagram of the studied samples. This diagram also shows the known Cu-Sb-S ternary compounds with stoichiometric compositions.

Figure 5: Top surface SEM micrographs of S140 (on the left) and S180 (on the right) samples.

3.2.2. XRD characterization

Fig. 6 shows the results of XRD measurements for the samples with a sulphur evaporation temperature of 140 °C. The assignment of the crystalline phases was done using the International Centre for Diffraction Data (ICDD) database [19]. According to this database, several phases can be assigned, but the best matches are Cu_3SbS_3 with a cubic structure I-43m (Space group 217), datasheet reference code number 01-075-1574, and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ with a cubic structure I-43m (Space group 217), commonly known as tetrahedrite, datasheet reference code number 04-017-1329. Using the information provided by composition analysis done by EDS, section 3.1, and the results obtained by Raman scattering characterization, shown in section 3.2.3, we concluded that the most likely crystalline phase in these samples is tetrahedrite. From this diffraction pattern, it

is shown that peaks are sharp, indicating that the samples have good crystalline quality. The diffractograms present the highest counts for the peak located at a diffraction angle, 2θ , 29.94°, corresponding to the (222) planes.

Figure 6: XRD diffractograms of the sample with a sulphur evaporation temperature of 140 °C. The phase assignment was done using the ICDD database [19].

Fig. 7 presents the diffractogram for the sample with a sulphur evaporation temperature of 180 °C. In this graph, the peak position for several crystalline phases is also presented, but in this case a clear matching is obtained. Higher sulphur content environment promotes the growth of Cu_3SbS_4 with a tetragonal structure I-42m (Space group 121), datasheet reference code number 04-006-8349, commonly named as famatinite. These results show sharp peaks indicating a good crystalline properties. The most intense reflection is located a 2θ close to 28.7°, corresponding to the (112) planes. Both XRD results, presented in Fig 6 and 7, show shifts when compared with reference peaks. Such fact can be attributed to film tension and it is a common effect in films deposited directly on substrates like SLG using high-energy deposition techniques such as sputtering.

Figure 7: XRD diffractograms of the samples with a sulphur evaporation temperature of 180 °C. The phase assignment was done using the ICDD database [19].

3.2.3. Raman scattering characterization

In Fig. 8 a) we present the results obtained for samples S140. When we compare the experimental spectrum with the Raman results of tetrahedrite mineral extracted from RUFF database, reference RRUFFID: R100204 shown in Fig. 8 b) a good agreement is attained with respect to the spectral shape and the Raman shift of the main bands, within the spectral range 250–400 cm^{-1} . Moreover, it is observed that the Raman bands presented in Fig. 8 a) are much less broader and distinguishable Raman peaks can be identified at 323 cm^{-1} , 346 cm^{-1} and 356 cm^{-1} , indicating a better crystalline quality. The findings are also in agreement with Rath *et al.* [8]. Nevertheless, other Raman bands, so far reported, are observed below 250 cm^{-1} and are peaked at 53, 66, 78, 102 and 218 cm^{-1} . Most of the published works on these systems [8–10, 20] interpret the Raman spectra based on the vibration of groups of atoms without considering the effect of crystal symmetry. Besides, in most of those cases, the presence of different crystalline phases, also identified by other complementary techniques, make it difficult to adopt an interpretation based on lattice dynamics for a single crystalline phase. The lattice dynamic is particularly relevant when the samples exhibit good crystalline quality and lower compositional disorder [21]. S. Kharbush *et al.* [22] identifies a mode between 255 cm^{-1} and 270 cm^{-1} as being a “lattice mode” of tetrahedrite. Given the fact that no other crystalline phases were detected, Raman analysis will be done considering the symmetry of the tetrahedrite. For $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ belonging to I-43m space group, the group theory predicts, at Brillouin zone center, twenty three Raman active phonon modes of distinct symmetries given by irreducible: $\Gamma_{\text{Raman}}=4A_1+6E+13T_2$ [23]. Consequently a rich first-order Raman scattering spectrum is expected for a polycrystalline sample. With this assumption in mind we attribute the Raman peaks at 53, 66, 78, 102 and 218 cm^{-1} to the tetrahedrite phase. The broadening observed in the Raman bands, particularly evident for the tetrahedrite mineral in fig 8 b), indicates that the Raman spectra are rather an overlap of multiple peaks. The crystal disorder and structural defects, likely present in the sample, usually promotes two-phonon process coupling, with the resulting peaks often corresponding to combinations of phonons from different symmetry points [24]. Thus, the measured Raman spectrum reflects both, first and second order scattering process. In order to investigate the possibility of the presence of stable phases of copper sulfide, we extend the Raman spectral region above 400 cm^{-1} (Fig. 3 Supplementary Information). However, the Raman band at 470 cm^{-1} , identified as the S-S stretching mode in the CuS covellite phase [25], was not observed. This result indicates that the main phase detected, even at the microscale, is the tetrahedrite.

For samples annealed with a sulphur evaporation temperature of 180 °C, the Raman scattering results are presented in Fig. 9 a). When comparing with the Raman spectrum of famatinite mineral (in Fig. 9 b) extracted from RUFF database, reference RRUFFID: R110022, we concluded that within the frequency shift ranging from 200 cm^{-1} to 400 cm^{-1} the results are similar, indicating that the sample is constituted mainly by Cu_3SbS_4 .

Figure 8: a) RT Raman spectrum of samples S140; b) Raman spectrum of tetrahedrite mineral extracted from RUFF data base [Ref: PRFFID:R100204].

famatinite phase. The main Raman modes for this crystalline phase are located at 244, 273, 317 and 344 cm^{-1} , matching the values reported [9, 10]. Comparatively to the mineral reference data, the Raman spectrum of sample S180 displays narrow peaks, especially for the peaks located at 273, 317, 344 cm^{-1} , indicating better crystalline quality. The less broadening of the overall Raman spectrum indicates that the first-order scattering processes should dominate. For the Cu_3SbS_4 , belonging to I-42m space group, the group theory analysis gives sixteen distinct Brillouin zone center's modes whose symmetries are given by: $\Gamma_{\text{Raman}}=2A_1+2B_1+5B_2+7E$ [23]. Consequently more Raman peaks should be expected for a polycrystalline sample of good quality. In fact, below 250 cm^{-1} and beyond the peak at 133 cm^{-1} , also reported by Chalapaty *et al.* [9], not yet reported peaks can be observed at 58, 71, 90, 143 cm^{-1} , in good agreement with the group theory analysis. We assign these lower frequency Raman peaks to the famatinite phase. In this sample the existence of CuS phases was also examined and the Raman spectra were also acquired above 400 cm^{-1} (Fig. 4 Supplementary Information). As shown, no Raman band at 470 cm^{-1} was observed. This fact also suggests that the narrow Raman bands observed below 150 cm^{-1} cannot be associated with the CuS covellite, since it was expected that the band at 470 cm^{-1} would be the most intense.

3.3. Optoelectronic characterization

3.3.1. Absorbance characterization

The results of the absorbance measurements are shown in Fig. 10 a) and b) for sample S140 and S180, respectively. The

Figure 9: a) RT Raman spectrum of samples S180; b) Raman spectrum of famatinite mineral extracted from RUFF database, reference RRUFFID: R110022

Figure 10: a) Absorbance measurement results for sample S140 plotted versus the radiation wavelength from 400 nm to 1600 nm. b) Absorbance measurement results for sample S180 plotted versus the radiation wavelength from 400 nm to 1600 nm. c) and d) Optical absorption coefficients for S140 and S180, respectively, versus the photon energy.

measurements were performed for radiation in the visible and near IR regions, between 400 nm and 1600 nm. The S140 results show a absorbance threshold close to 700 nm.

Based on the absorbance results, Abs , and the thickness of the films, the absorption coefficient, α , can be extracted using the following expression:

$$\alpha = 2.303/d \times \log(I_0/I) = 2.303/d \times Abs \quad (1)$$

where I_0 and I are the incident and transmitted intensity, respectively, and d is the path length/film thickness. Average film thicknesses, measured by step profilometer were $1.38 \mu\text{m}$ and $1.73 \mu\text{m}$, for S140 and S180, respectively. The resulting absorption coefficient is shown in Fig. 10 c) and d), for samples S140 and S180, respectively. In both cases, the studied materials are compatible with thin film solar cells technology, presenting absorption coefficient values higher than 10^4 cm^{-1} .

The relation between the absorption coefficient and the nature of the optical transition can be defined by the following expression [26, 27]:

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

where A is a constant, m defines the nature of the transition, $h\nu$ is the photon energy and E_g is the band gap energy. The value of the power m is $1/2$ (allowed) or $1/3$ (forbidden) for indirect transitions and 2 (allowed) or $2/3$ (forbidden) for direct transitions. To estimate which types of transitions generate the absorption edges shown in Fig. 10 c) and d), the values of α^m were plotted against the photon energy. For the power values mentioned previously, the best results were obtained for $m = 2$,

which means that the nature of the transition was direct allowed. As presented in Fig. 11, extrapolating the results of α^2 to zero the band gap energies point to values close to a) $1.47 \pm 0.07 \text{ eV}$ for S140 and close to b) $0.89 \pm 0.01 \text{ eV}$ for S180. These values are in agreement with previously reported values for the tetrahedrite and famatinite phase, respectively [7–9, 11].

3.3.2. Photoluminescence characterization

The PL spectra at low temperature, for both samples, are shown in Fig. 12. For S140 no luminescence was measured in the entire detection range of the Ge detector. We ascribe this result to the existence of non-radiative recombination channels that capture free charge carriers, blocking their radiative recombination. In the case of S180, a broad and asymmetric band is observed from 0.76 to 0.89 eV. This energy range is compatible with the estimated bandgap value, 0.89 eV (see Fig. 10). Thus, we ascribe the luminescence to radiative recombination channels in the Cu_3SbS_4 crystalline phase. The high full width at half maximum of the luminescence suggests a large density of defects, in accordance with PL results for other semiconductors [28–30]. Despite the low signal-to-noise ratio, the asymmetry of this band suggest the presence of two components. However, more PL measurements are required to clarify this issue. The intensity of PL emission is usually connected with good optoelectronic properties. When a material has very low PL emission or it does not emit, it usually means that its qualities are poor for optoelectronic devices. The reasons for this be-

Figure 11: Tauc's plots of the samples a) S140 and b) S180, showing the estimated energies values for direct transitions.

haviour can be attributed to a high number of non-radiative defects. The used detector has a range of operation optimized for energy values above the Ge bandgap region, where both samples should emit. Hence, we have some degree of confidence that the observed results indicates that a high number of defects are present in sample S140. However, we note that the emission of both samples is very low with high noise. Thus, we ascribe the high noise to the existence of non-radiative recombination channels that are quite competitive with the radiative ones for both samples.

Figure 12: PL spectra measured at 5 K for samples S140 and S180, with 514 nm excitation wavelength.

4. Conclusion

In this work we describe a 2-step method to grow selectively $\text{Cu}_{12}\text{Sb}_4\text{S}_{14}$ and Cu_3SbS_4 thin film by changing the sulphur supply during the sulphurization/annealing process. The metallic precursors are deposited simultaneously by RF magnetron sputtering using a target composed by Cu segments and a Sb base. By controlling the sulphur evaporation temperature during the sulphurization/annealing process, two different crystalline phases are obtained. The crystalline phase identification was performed using structural characterization using XRD and Raman scattering techniques. For a sulphur evaporation temperature of 140 °C the prominent crystalline phase is tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{14}$, with a cubic structure. For a sulphur evaporation of 180 °C the main phase is famatinite Cu_3SbS_4 with a tetragonal structure. Optical analysis allowed the estimation of the band gap energies. For the bandgap values were 1.47 eV and 0.89 eV for $\text{Cu}_{12}\text{Sb}_4\text{S}_{14}$ and Cu_3SbS_4 , respectively, both with direct allowed transitions. PL measurement show a broad peak centered close to 0.83 eV for sample S180. No PL signal is detected for sample S140.

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Highlights

- $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and Cu_3SbS_4 thin films using different sulphur evaporation temperature;
- Simultaneous metal precursors using RF sputtering and segmented Cu-Sb targets;
- Crystalline phase identification by XRD, Raman scattering and EDS;
- $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and Cu_3SbS_4 show direct band gap with 1.47 eV and 0.89 eV, respectively;
- PL measurements show a peak at 0.89 eV for the Cu_3SbS_4 sample.