



## REVIEW

### A Short Review on Raman Studies of Metal Chalcogenide Semiconductor Thin Films

S.M. HO<sup>1,\*</sup>, M.H.D. OTHMAN<sup>2</sup>, M.R. ADAM<sup>2</sup> and K. MOHANRAJ<sup>3</sup>

<sup>1</sup>INTI International University, Putra Nilai, 71800, Negeri Sembilan, Malaysia

<sup>2</sup>Advanced Membrane Technology Research Centre, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor, Malaysia

<sup>3</sup>Department of Physics, Manonmaniam Sundaranar University, Tirunelveli-627 012, India

\*Corresponding author: E-mail: [soonmin.ho@newinti.edu.my](mailto:soonmin.ho@newinti.edu.my)

Received: 1 January 2021;

Accepted: 30 April 2021;

Published online: 26 June 2021;

AJC-20386

The productions of the thin metallic chalcogenide films are of particular interest for the wide range of fabrication of the solar cells, sensors, photodiode arrays, photoconductors. Raman spectroscopy is used to measure the scattering radiation of a matter. Basically, the spectroscopic methods can be defined as the study of the interaction of electromagnetic radiation with a matter. It can be based on the phenomenon of absorption, fluorescence, emission or scattering. The observation of peaks supported the formation of amorphous or crystalline nature of the samples. In this short review, the authors had gathered some informations about the Raman studies of recently synthesized metal chalcogenide semiconductor thin films.

**Keywords:** Raman studies, Metal chalcogenide, Semiconductor, Thin films.

## INTRODUCTION

Semiconductor has been widely used in industries for various applications ranging from the energy sensing and harvesting to numerous microelectronics functionals. Conventionally, the semiconductors were mainly composed of covalent materials and characterized by the four-fold coordination of all atoms. The recent technology of the photovoltaic research has been shifted its direction over the conventional materials to the metal chalcogenide counterparts. This was mainly attributable to the considerably interest such as highly suitability as the absorber layers in the thin film solar cells [1].

The research has been conducted in developing the solar cell composing new materials such as the earth abundant source metals as the substitution to that of currently existed solar cell which mainly comprising the rare and expensive elements such as indium, tellurium and gallium. In addition, the currently available solar cell may have consisted of the toxic elements namely selenium and cadmium [2]. As opposed to the conventional semiconductor materials, metal chalcogenide is known as a highly potential alternative that can meet the need of the

development of more efficient despite the low-cost solar cells. Infacts, the exploration into these new materials might be highly beneficial since it may be satisfying the green energy demand across the globe by developing the technology that utilizing the solar power as the premiere source of energy.

The productions of the thin metallic chalcogenide films are of particular interest for the wide range of fabrication of the solar cells, sensors, photodiode arrays and photoconductors. The chalcogenization process of the metallic precursor layers will be particularly suitable for the development of the high-efficient devices. However, the understanding of the chalcogenization process is rather complex due to the formation of the intermediate constituents during the intermetallic phase transformations and the chalcogen incorporation that take place simultaneously. The separation of these two processes by annealing the precursor layers in vacuum and in chalcogen atmosphere is required. The *in-situ* real time studies on these processes has been proposed and reported in the literature [3]. The use of the Raman spectroscopy has been provided a comprehensive interpretation about the kinetic and microscopic aspects of the phase transformation of the metal chalcogenide system. The

study has also revealed the elucidation of intermetallic phase transformations and the limitation of the chalcogenide growth.

Raman spectroscopy is an instrument used to measure the scattering radiation of a matter. Basically, the spectroscopic methods can be defined as the study of the interaction of electromagnetic radiation with a matter. It can be based on the phenomenon of absorption, fluorescence, emission or scattering [4]. Raman spectroscopy mainly a scattering technique has been widely used for many applications for the purposes of quantitative and/or qualitative analyses. The qualitative analysis of this instrument can be done by measuring the frequency of the scattered radiations. Meanwhile, the quantitative analysis aiming for the measurement of the analyte concentration in the sample by quantifying the intensity of the scattered radiations of the sample [5].

The Raman spectroscopic analysis can be advantageous due to several factors. Apart from the beneficial qualitative and quantitative analyses counterparts, this technique can be used to evaluate the presence of trace amounts of elements without the extensive sample preparation with a non-destructive procedure. Despite the analysis of the reaction mechanism, Raman spectroscopy have been used and reported to determine the presence of trace element such as drugs namely barbiturates and sodium salt analogs [6]. The specific band locations were utilized to distinguish the presence of various barbiturates. Moreover, the change in the polarizability of the molecular vibration is essential in obtaining the Raman spectrum of the sample. The low Raman scattering of the water molecules thus make the water as an ideal solvent for dissolving the samples. This was eventually ensuring the simplicity of this technique [7].

Incongruent to that of other spectroscopic analyses, Raman spectroscopy is known to its simplicity approach. The Raman spectrum is recorded as an intensity *versus* wavelength shift, and significantly minimal to that of infrared (IR) spectroscopy. The normal Raman spectrum is infrequently shown the combination and difference of bands [8]. The specific and non-combined bands would eventually ensure the precision of the sample analyses. In addition, the Raman spectrometry can be used as in-field, *in-situ* or downfield which does make this analysis is portable with easy handling depending on the sample preference [9].

Apart from the advantages and beneficial outcomes of the Raman spectroscopy, this technique has also suffered from few limitations. The weak Raman scattering will lead to the low sensitivity of this technique. However, the sensitivity of the Raman spectroscopy can be enhanced using resonance Raman spectroscopy and surface enhanced Raman spectroscopy. In the resonance mode, the frequency of the incident

radiation will be matched with the electronic transition of the molecule. This will be eventually producing the more intense Raman spectrum [10]. Meanwhile, the surface enhanced mode will be modified the sample by adsorbing the sample onto the colloidal metallic surface such as gold, copper or silver which thereby improved the intensity of the Raman signals.

The study on the production of metal chalcogenide semiconductors has been widely studied and reported in the literature [11-21]. However, the review on the utilization of the Raman spectroscopy on the studies of the metal chalcogenide semiconductor is still limited. Thus, this article will discuss an overview of some important recent and selected applications of the Raman spectroscopic analysis on the metal chalcogenide semiconductors which focussed on the thin films forms.

**Binary chalcogenides:** Raman spectroscopy is one of the most powerful tools for determining the crystalline structure and quality of semiconductor thin films, since the shape and position of Raman peaks are strongly influenced by the presence of defects in the material, either in the form of structural inhomogeneity's or secondary phases [22]. It provides a fingerprint by which the molecule can be identified.

Isac *et al.* [23] and Jrad *et al.* [24] analyzed the characteristics Raman peak of CuS thin films and found that the peak in the range 474-469  $\text{cm}^{-1}$ , which belongs to hexagonal structure. It is also pointed out that the peak shift towards lower wavenumber may be attributed to the vacancies present in the CuS lattice during the film growth. The Raman spectra of CdS shows four characteristics peaks at 300, 600, 904 and 1200  $\text{cm}^{-1}$  [25], whereas the characteristic peak for CdSe was observed at 200  $\text{cm}^{-1}$  [26]. Beside this, four Raman peaks for CdTe at 84, 121, 140 and 175  $\text{cm}^{-1}$  were also observed. Among these peaks, the transverse optical phonon (TO) and longitudinal optical phonons (LO) were observed around 140 and 175  $\text{cm}^{-1}$ , respectively [27]. In case of ZnS thin films, the longitudinal optical (LO) phonons appeared at 58, 335, 347  $\text{cm}^{-1}$  and the TO phonons appeared at 264  $\text{cm}^{-1}$  [28]. While in compound ZnSe, two characteristic peaks were shown around 250 and 490  $\text{cm}^{-1}$  [29]. The  $\text{Ag}_2\text{Se}$  films showed four characteristics peaks at 232, 455, 566 and 815  $\text{cm}^{-1}$  [30]. Table-1 showed the details of the Raman peaks of binary thin films, which were prepared by using different deposition methods.

**Ternary chalcogenides:** The  $\text{CuInSe}_2$  film showed Raman characteristic peak (Al mode) around 177-174  $\text{cm}^{-1}$  and reported that the blue shift in the peak was due to the presence of defect in the nano crystalline layers [46,47]. The  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films showed two LO phonon peaks at 327-307 and 630-613  $\text{cm}^{-1}$  [48]. The Raman characteristic peak of CdZnS film was observed at 313  $\text{cm}^{-1}$  [49]. When replacing sulphur atom by selenium

TABLE-1  
RAMAN INVESTIGATION OF BINARY THIN FILMS

Thin films	Characterization and findings	Ref.
Thalium selenide	<ul style="list-style-type: none"> <li>Thallium selenide thin films have been prepared <i>via</i> thermal evaporation method</li> <li><math>\text{TlSe}_2</math> bending mode was observed at 92 <math>\text{cm}^{-1}</math></li> <li>Tl-Se symmetric stretching mode was found at 158 and 140 <math>\text{cm}^{-1}</math></li> <li>Tl-Se asymmetric stretching mode was detected at 208 and 185 <math>\text{cm}^{-1}</math></li> <li>Se-Se stretching mode was highlighted at 255 and 240 <math>\text{cm}^{-1}</math></li> <li>In terms of crystal structure, Tl-Se bond was observed in 2.66-2.73 Å</li> </ul>	[31]

As <sub>2</sub> Se <sub>3</sub>	<ul style="list-style-type: none"> <li>As<sub>2</sub>Se<sub>3</sub> thin films have been prepared <i>via</i> thermal evaporation</li> <li>The asymmetric (amorphous phase) was observed peak at 224 cm<sup>-1</sup></li> <li>Se-Se vibration was observed at 480 cm<sup>-1</sup></li> <li>The In-doped As<sub>2</sub>Se<sub>3</sub> films peak at 221 cm<sup>-1</sup></li> <li>The films prepared with indium content of 2 % showed peaks at 216-219 cm<sup>-1</sup> and 240-242 cm<sup>-1</sup>.</li> </ul>	[32]
Sb <sub>2</sub> Se <sub>3</sub>	<ul style="list-style-type: none"> <li>The Sb<sub>2</sub>Se<sub>3</sub> thin films have been prepared <i>via</i> RF magnetron sputtering</li> <li>Sb-Se stretching mode was observed at 188 cm<sup>-1</sup></li> <li>Sb-Sb bond was found at 150 cm<sup>-1</sup></li> <li>Vibration mode Se-Se bond was detected at 120, 210 cm<sup>-1</sup></li> <li>Raman spectra indicated selenium rich in samples, peaks appeared at 70, 102, 129, 252 cm<sup>-1</sup>.</li> </ul>	[33]
WS <sub>2</sub> film	<ul style="list-style-type: none"> <li>WS<sub>2</sub> films have been prepared <i>via</i> pulsed laser deposition</li> <li>Vibration mode at 175 cm<sup>-1</sup> represented</li> <li>WS<sub>2</sub> phase at 419 cm<sup>-1</sup></li> </ul>	[34]
SnS <sub>2</sub>	<ul style="list-style-type: none"> <li>SnS<sub>2</sub> films have been prepared <i>via</i> chemical bath deposition method</li> <li>Citric acid was used as complexing agent</li> <li>The films prepared at various concentrations of citric acid (0.375, 0.5 and 0.625 ml/L) showed peak at 315 cm<sup>-1</sup></li> <li>Hexagonal SnS<sub>2</sub> phase could be seen in Raman spectra.</li> </ul>	[35]
SnS	<ul style="list-style-type: none"> <li>SnS films have been prepared <i>via</i> RF sputtering</li> <li>Peak at 307 cm<sup>-1</sup> (Sn<sub>2</sub>S<sub>3</sub>) could be seen when the pressure values are 40 and 50 mTorr</li> <li>The peaks at 93 and 224 cm<sup>-1</sup> could be seen when the pressure values are 6 and 10 mTorr.</li> </ul>	[36]
FeS <sub>2</sub>	<ul style="list-style-type: none"> <li>FeS<sub>2</sub> films have been prepared <i>via</i> evaporation technique</li> <li>Pyrite phase was observed at 343, 379, and 430 cm<sup>-1</sup></li> <li>Marcasite phase was seen at 323, and 386 cm<sup>-1</sup></li> <li>The ratio of pyrite to marcasite was 49:51 (temperature =250 °C), and 99: 1 (temperature=420 °C)</li> </ul>	[37]
InS	<ul style="list-style-type: none"> <li>The InS films have been prepared <i>via</i> chemical bath deposition method</li> <li>Amorphous phase could be detected at 200-500 cm<sup>-1</sup></li> <li>In<sub>2</sub>S<sub>3</sub> was observed at 200-400 cm<sup>-1</sup></li> <li>Sulphur (S-S mode) was found at 460 cm<sup>-1</sup></li> </ul>	[38]
In <sub>2</sub> S <sub>3</sub>	<ul style="list-style-type: none"> <li>In<sub>2</sub>S<sub>3</sub> films have been prepared <i>via</i> chemical bath deposition technique</li> <li>The films prepared at 60, 70, 80 °C showed 3 peaks (115, 135, 180 cm<sup>-1</sup>)</li> <li>The films prepared at 60 °C showed In<sub>2</sub>O<sub>3</sub> phase</li> <li>The intensity of peaks improved in annealed films.</li> </ul>	[39]
As <sub>2</sub> S <sub>3</sub>	<ul style="list-style-type: none"> <li>As<sub>2</sub>S<sub>3</sub> films have been prepared <i>via</i> thermal evaporation</li> <li>The films prepared using laser light showed 3 peaks at 336, 230, and 485 cm<sup>-1</sup></li> <li>Pyramidal phase was observed at 335-340 cm<sup>-1</sup> (As-S bond stretching vibration)</li> <li>As-As homopolar bond vibration was seen at 180 and 230 cm<sup>-1</sup></li> <li>S-S vibration of AsS<sub>4</sub> was observed at 485 cm<sup>-1</sup></li> </ul>	[40]
CdTe	<ul style="list-style-type: none"> <li>CdTe films have been prepared <i>via</i> thermal evaporation</li> <li>Transverse mode was observed at 142 cm<sup>-1</sup></li> <li>Longitudinal mode was found at 170.5 cm<sup>-1</sup></li> <li>Phonon of tellurium was detected at 120 cm<sup>-1</sup></li> </ul>	[41]
ZnS films	<ul style="list-style-type: none"> <li>ZnS films have been prepared <i>via</i> physical vapour deposition</li> <li>The as-deposited films and annealed films showed peaks at 773 and 1078 cm<sup>-1</sup></li> <li>Lattice constant value for the as-deposited (5.3 Å) film and annealed films (5.66 Å) was reported.</li> <li>Annealed films showed better results because of crystallite size and strain.</li> </ul>	[42]
Bi <sub>2</sub> Te <sub>3</sub>	<ul style="list-style-type: none"> <li>Bi<sub>2</sub>Te<sub>3</sub> films have been synthesized <i>via</i> electro deposition technique</li> <li>Vibration mode of BiTe was observed at 77 cm<sup>-1</sup></li> <li>Vibration mode of trigonal was observed at 65 and 131 cm<sup>-1</sup></li> <li>Vibration mode in the basal plane was seen at 102 cm<sup>-1</sup></li> </ul>	[43]
CdS	<ul style="list-style-type: none"> <li>CdS films have been synthesized <i>via</i> chemical bath deposition</li> <li>Longitudinal optical phonons were detected at 299, 600 and 900 cm<sup>-1</sup></li> </ul>	[44]
CdS	<ul style="list-style-type: none"> <li>CdS films have been prepared <i>via</i> chemical bath deposition</li> <li>Longitudinal optical phonon modes were detected at 296 and 593 cm<sup>-1</sup> for the films prepared under various pH values</li> <li>Raman intensity increased with decreasing the pH value (pH 11 to 9).</li> </ul>	[45]

atom (CdZnSe), the peak shifted to lower wavenumber about 230 cm<sup>-1</sup>. In the Cd<sub>1-x</sub>Zn<sub>x</sub>Te thin films, the TO and LO phonons were observed around 140.30 and 159.65 cm<sup>-1</sup>, respectively [50]. The Cu<sub>2</sub>SnS<sub>3</sub> thin films showed three characteristic peaks at 342, 327 and 287 cm<sup>-1</sup>, whereas Cu<sub>3</sub>SnS<sub>4</sub> thin films indicated

a characteristic peak at 318 cm<sup>-1</sup> [51]. Ag<sub>2</sub>Se<sub>0.2</sub>Te<sub>0.8</sub> film shows a single prominent peak at 154 cm<sup>-1</sup> [52]. Raman spectra of as-deposited Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin films indicated a broad peak around 151.75 cm<sup>-1</sup>, which may be due to the amorphous (Te-Te stretching). Peak at 110 cm<sup>-1</sup> may be corresponding to vibration of

hetero polar bond in the tetrahedral  $\text{GeTe}_4$  and/or pyramidal  $\text{SbTe}_3$ . Similarly, peak appears at  $160\text{ cm}^{-1}$  due to a Sb-Sb vibration in  $(\text{Te}_2)\text{Sb-Sb}(\text{Te}_2)$ , in which there is a Sb-Sb bond connected with four tellurium (Te) atoms and in other units such as  $(\text{TeSb})\text{Sb-Sb}(\text{Te}_2)$  and  $(\text{Sb}_2)\text{Sb-Sb}(\text{SbTe}_2)$  [53]. Table-2 reported the Raman studies of ternary thin films, which were produced *via* different deposition techniques.

**Quaternary chalcogenides:** For quaternary compounds, X-ray diffraction (XRD) is not alone consider for phase identification, in such cases Raman spectrum is one of the efficient

tool for the phase identification. In  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) thin films. The existence of CZTS film was confirmed by the most intense peak around  $335\text{ cm}^{-1}$  and two shoulders at  $386$  and  $291\text{ cm}^{-1}$  [65]. However, quaternary compounds have some additional peaks, which may be considered as secondary or impurity phases such as  $\text{ZnS}$ ,  $\text{SnS}_2$  and  $\text{Cu}_{2-x}\text{S}$ , shown at  $351$ ,  $274$ ,  $315$  and  $479\text{ cm}^{-1}$  [66]. Further, sulphur atom is replaced by selenium atom, that exhibits four characteristic Raman peaks at  $170$ ,  $192$ ,  $230$ , and  $243\text{ cm}^{-1}$  and three secondary phases, such as  $\text{Cu}_x\text{Se}$  ( $261\text{ cm}^{-1}$ ),  $\text{Cu}_2\text{SnSe}_3$  ( $180\text{ cm}^{-1}$ ) or  $\text{ZnSe}$  ( $253\text{ cm}^{-1}$ ) [67,68]. In case

TABLE-2  
RAMAN INVESTIGATION OF TERNARY THIN FILMS

Thin films	Characterization and findings	Ref.
Ag-Ge-Se	<ul style="list-style-type: none"> <li>Ag-Ge-Se thin films have been prepared by using pulsed laser deposition</li> <li><math>\text{GeSe}_{4/2}</math> corner sharing tetrahedral: at <math>192\text{-}201\text{ cm}^{-1}</math></li> <li>Vibration of Se atoms: at <math>210\text{-}218\text{ cm}^{-1}</math></li> <li>Se-Se bonds: at <math>255\text{-}270\text{ cm}^{-1}</math></li> <li>Ge-Ge mode: at <math>178\text{ cm}^{-1}</math></li> </ul>	[54]
Ge-Sb-Se	<ul style="list-style-type: none"> <li>Ge-Sb-Se thin films have been synthesized by using RF magnetron sputtering</li> <li>Symmetric stretching mode of <math>\text{GeSe}_{4/2}</math> tetrahedral: at <math>200</math>, <math>215\text{ cm}^{-1}</math></li> <li>Stretching mode of Ge-Ge bond: at <math>170\text{ cm}^{-1}</math></li> <li>Se-Se stretching mode: at <math>235\text{-}245\text{ cm}^{-1}</math></li> <li>Se-Se bond vibration: at <math>265\text{ cm}^{-1}</math></li> </ul>	[55]
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	<ul style="list-style-type: none"> <li><math>\text{Ge}_2\text{Sb}_2\text{Te}_5</math> thin films have been produced by using thermal evaporation</li> <li><math>\text{GeTe}_4</math> tetrahedral: at <math>80\text{ cm}^{-1}</math></li> <li><math>\text{GeTe}_{4-n}\text{Ge}_n</math> (<math>n=1,2</math>): at <math>125\text{ cm}^{-1}</math></li> <li><math>\text{Sb}_2\text{Te}_3</math>: at <math>153\text{ cm}^{-1}</math></li> <li>Ge-Ge: at <math>300\text{ cm}^{-1}</math></li> </ul>	[56]
$\text{Ge}_x\text{As}_{35-x}\text{Se}_{65}$	<ul style="list-style-type: none"> <li><math>\text{Ge}_x\text{As}_{35-x}\text{Se}_{65}</math> thin films have been synthesized by using thermal evaporation</li> <li>Symmetric vibrational stretching <math>\text{GeSe}_{4/2}</math>: at <math>198\text{ cm}^{-1}</math></li> <li>Vibration mode of <math>\text{AsSe}_{3/2}</math>: at <math>230\text{ cm}^{-1}</math></li> <li>Vibration mode of selenium: at <math>260\text{ cm}^{-1}</math></li> <li>Vibration mode of <math>\text{GeSe}_{4/2}</math> tetrahedral: at <math>215\text{ cm}^{-1}</math></li> </ul>	[57]
$\text{As}_{50}\text{Se}_{40}\text{Te}_{10}$	<ul style="list-style-type: none"> <li><math>\text{As}_{50}\text{Se}_{40}\text{Te}_{10}</math> thin films have been prepared by using thermal evaporation</li> <li>Asymmetric stretching As-Te-Se mode: at <math>127\text{ cm}^{-1}</math></li> <li>Te-Te vibrational mode: at <math>472\text{ cm}^{-1}</math></li> <li>As-Se vibration mode: at <math>228\text{ cm}^{-1}</math></li> </ul>	[58]
$\text{Cu}_2\text{SnS}_3$	<ul style="list-style-type: none"> <li><math>\text{Cu}_2\text{SnS}_3</math> thin films have been produced by using evaporation method</li> <li>Vibration mode (monoclinic): at <math>292</math>, <math>353\text{ cm}^{-1}</math></li> </ul>	[59]
$\text{CuSbSe}_2$	<ul style="list-style-type: none"> <li><math>\text{CuSbSe}_2</math> thin films have been synthesized by using E-beam evaporation deposition</li> <li><math>\text{Sb}_2\text{Se}_3</math>: at <math>188</math>, <math>250</math>, <math>372</math>, <math>450\text{ cm}^{-1}</math></li> <li><math>\text{Cu}_3\text{SbSe}_3</math>: at <math>185\text{ cm}^{-1}</math></li> <li><math>\text{CuSbSe}_2</math>: at <math>82</math>, <math>117</math>, <math>144\text{ cm}^{-1}</math></li> </ul>	[60]
$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	<ul style="list-style-type: none"> <li><math>\text{Cu}_{12}\text{Sb}_4\text{S}_{13}</math> thin films have been synthesized by using e-beam evaporation</li> <li><math>\text{Cu}_{12}\text{Sb}_4\text{S}_{13}</math>: at <math>351\text{ cm}^{-1}</math></li> <li>Sb-S bond stretching: at <math>354\text{ cm}^{-1}</math></li> <li>Sb-S bond bending mode: at <math>315\text{ cm}^{-1}</math></li> <li><math>\text{Cu}_3\text{SbS}_4</math>: at <math>330\text{ cm}^{-1}</math></li> <li>CuS as secondary phase: at <math>468\text{ cm}^{-1}</math></li> </ul>	[61]
$\text{Cu}_2\text{SnS}_3$	<ul style="list-style-type: none"> <li><math>\text{Cu}_2\text{SnS}_3</math> thin films have been prepared by using radio frequency magnetron sputtering</li> <li>Monoclinic phase: at <math>290</math> and <math>350\text{ cm}^{-1}</math></li> <li>Tetragonal phase: at <math>325\text{ cm}^{-1}</math></li> <li><math>\text{Cu}_2\text{Sn}_3\text{S}_7</math> phase: at <math>223</math> and <math>371\text{ cm}^{-1}</math></li> </ul>	[62]
$\text{Cu}_2\text{SnS}_3$	<ul style="list-style-type: none"> <li><math>\text{Cu}_2\text{SnS}_3</math> thin films have been synthesized by using spray pyrolysis</li> <li>Orthorhombic <math>\text{Cu}_3\text{SnS}_4</math> phase (as-deposited): at <math>295\text{ cm}^{-1}</math></li> <li>Monoclinic <math>\text{Cu}_2\text{SnS}_3</math> (as-deposited films): at <math>289\text{ cm}^{-1}</math></li> <li>Tetragonal <math>\text{Cu}_2\text{SnS}_3</math> in anneal films (vibrational mode): at <math>326\text{ cm}^{-1}</math></li> </ul>	[63]
$\text{Cu}_2\text{SnSe}_3$	<ul style="list-style-type: none"> <li><math>\text{Cu}_2\text{SnSe}_3</math> thin films have been produced by using electro deposition method</li> <li>C-H stretching vibration of <math>\text{CH}_2</math> for the films produced using <math>0.5\text{ M}</math> of sodium citrate: at <math>2926\text{ cm}^{-1}</math></li> <li>This peak could not be detected when <math>0.1\text{ M}</math> of sodium citrate was used.</li> </ul>	[64]



TABLE-3  
RAMAN INVESTIGATION OF QUATERNARY THIN FILMS

Thin films	Characterization and findings	Ref.
Cu <sub>2</sub> ZnSnS <sub>4</sub>	<ul style="list-style-type: none"> <li>Sol gel method was used to produce Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films</li> <li>Kesterite phase: at 331-336 cm<sup>-1</sup></li> </ul>	[74]
Cu <sub>2</sub> ZnSnS <sub>4</sub>	<ul style="list-style-type: none"> <li>Sol gel technique was employed to prepare Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films</li> <li>There is no peak could be observed at room temperature and the first 15 min of sulfurization process</li> <li>The films prepared under 30 min of sulfurization: at 330 cm<sup>-1</sup></li> <li>The films prepared at 60 and 180 min of sulfurization: higher intensity in Raman peaks</li> </ul>	[75]
Cu <sub>2</sub> FeSnS <sub>4</sub>	<ul style="list-style-type: none"> <li>Spray pyrolysis was used to synthesize the Cu<sub>2</sub>FeSnS<sub>4</sub> thin films</li> <li>Asymmetry vibration mode of sulphur around the tin: at 319 cm<sup>-1</sup></li> <li>Sulfur pure anion around the copper: at 285 cm<sup>-1</sup></li> </ul>	[76]
CuGa <sub>x</sub> In <sub>1-x</sub> Se <sub>2</sub>	<ul style="list-style-type: none"> <li>Close spaced vapour transport technique was employed to produce the CuGa<sub>x</sub>In<sub>1-x</sub>Se<sub>2</sub> thin films</li> <li>Cu(In,Ga)Se<sub>2</sub> phase was observed with x = 0 and 0.3: at 175 cm<sup>-1</sup></li> <li>Cu<sub>2</sub>Se structure when x = 1: at 290 cm<sup>-1</sup></li> </ul>	[77]
Cu <sub>2</sub> ZnSnS <sub>4</sub>	<ul style="list-style-type: none"> <li>Spray pyrolysis was employed to prepare Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films</li> <li>Kesterite phase: at 332, 285, 356 and 368 cm<sup>-1</sup></li> <li>Copper tin sulphide: at 303 cm<sup>-1</sup></li> <li>Copper sulphide: at 468 cm<sup>-1</sup></li> <li>Vibration of anion: at 331 cm<sup>-1</sup></li> </ul>	[78]
CuIn(S,Se) <sub>2</sub>	<ul style="list-style-type: none"> <li>Chemical bath deposition was used to synthesize the CuIn(S,Se)<sub>2</sub> thin films</li> <li>Amorphous In<sub>2</sub>S<sub>3</sub>: at 150-400 cm<sup>-1</sup></li> <li>Cu<sub>2-x</sub>S phase: at 473 cm<sup>-1</sup></li> <li>Sulfur rich Cu<sub>2-x</sub>(S,Se): at 390-475 cm<sup>-1</sup></li> <li>CuIn<sub>3</sub>Se<sub>5</sub> phase: at 228 cm<sup>-1</sup></li> </ul>	[79]

of Cu<sub>2</sub>Mn-SnS<sub>4</sub> thin film, five characteristic Raman peaks appeared at 156, 247, 286, 347 and 363 cm<sup>-1</sup> [69]. Cu<sub>2</sub>FeSnS<sub>4</sub> thin films showed prominent Raman peak shifted at 318 cm<sup>-1</sup> [70]. In Cu<sub>2</sub>CdSnS<sub>4</sub> thin films, three peaks exhibited at 284, 304, 333 cm<sup>-1</sup>, while in Cu<sub>2</sub>CdSnSe<sub>4</sub> films, these three peaks were shifted towards lower wavenumber at 170, 191 and 231 cm<sup>-1</sup> [71,72]. From Raman analysis, the most metal chalcogenide semiconductor thin films indicated Raman peaks around 600-50 cm<sup>-1</sup> and Raman peak shifted towards lower wavenumber when the sulfur atom is replaced by Se-atom. Cu<sub>2</sub>ZnSi(S,Se)<sub>4</sub> single crystals showed the three dominant Raman peaks at 278, 291 and 394 cm<sup>-1</sup> for Cu<sub>2</sub>ZnSiS<sub>4</sub> compound and at 170, 179 and 222 cm<sup>-1</sup> for Cu<sub>2</sub>ZnSiSe<sub>4</sub> compound [73]. The major Raman peaks of the reported quaternary thin films are summarized in Table-3.

### Conclusion

Preparation and characterization of several metal chalcogenide semiconductor thin films have been reported by many researchers. Raman spectroscopy has been used by many researchers to characterize the structure and composition of sample. Thus, a short review on the Raman studies on the various types of metal chalcogenide semiconductor thin films were carried out. The observation of peaks supported the formation of amorphous or crystalline of samples.

### ACKNOWLEDGEMENTS

One of the authors (SMH) is grateful to INTI International University for the financial support.

### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

### REFERENCES

- M. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon and R. Noufi, *Prog. Photovolt. Res. Appl.*, **7**, 311 (1999); [https://doi.org/10.1002/\(SICI\)1099-159X\(199907/08\)7:4<311::AID-PIP274>3.0.CO;2-G](https://doi.org/10.1002/(SICI)1099-159X(199907/08)7:4<311::AID-PIP274>3.0.CO;2-G)
- J. Trajic, M. Romcevic, M. Petrovic, M. Gilic, P. Balaz, A. Zorkovska and N. Romcevic, *Opt. Mater.*, **75**, 314 (2018); <https://doi.org/10.1016/j.optmat.2017.10.043>
- E. Rudigier, J. Djordjevic, C. von Klopmann, B. Barcones, A. Pérez-Rodríguez and R. Scheer, *J. Phys. Chem. Solids*, **66**, 1954 (2005); <https://doi.org/10.1016/j.jpcs.2005.09.096>
- D.A. Skoog, S. Crouch, and J. Holler, *Principles of Instrument Analysis*, Thomson Brooks/Cole: Belmont, USA (2007).
- H.H. Willard, L.L. Merritt Jr., J.A. Dean and F.A. Settle Jr., *Instrumental Methods of Analysis*, United States, Eds. 7 (1988).
- J. Willis, R. Cook and R. Jankow, *Anal. Chem.*, **44**, 1228 (1972); <https://doi.org/10.1021/ac60315a032>
- E. Smith and G. Dent, *Modern Raman Spectroscopy: A Practical Approach*, John Wiley & Sons: New Jersey, Eds. 2 (2019).
- G.S. Bumbrah and R.M. Sharma, *Egypt. J. Forensic Sci.*, **6**, 209 (1998); <https://doi.org/10.1021/ja975671k>
- J. Chalmers, H. Edwards and M. Hargreaves, *Infrared and Raman Spectroscopy in Forensic Science*, John Wiley & Sons: New Jersey (2012).
- J. Lombardi and R. Birke, *J. Phys. Chem. C*, **112**, 5605 (2008); <https://doi.org/10.1021/jp800167v>
- A. Kassim, S.M. Ho, L. Siang and S. Nagalingam, *Sultan Qaboos Univ. J. Sci.*, **16**, 24 (2011); <https://doi.org/10.24200/squj.vol16iss0pp24-33>
- S.M. Ho, *Int. J. Chem. Sci.*, **14**, 143 (2016).
- N. Saravanan, W. Tan, S.M. Ho and K. Anuar, *Pak. J. Sci. Ind. Res.*, **54**, 1 (2011).
- S.M. Ho, *Am. Chem. Sci. J.*, **14**, 1 (2016).
- R. Kumar and S. Chawla, *Asian J. Chem.*, **31**, 1805 (2019); <https://doi.org/10.14233/ajchem.2019.22054>
- K. Noraini, A. Kassim, S.M. Ho and H. Abdul, *Dig. J. Nanomater. Biostruct.*, **5**, 975 (2010).
- K. Devi, G. Selvan, M. Karunakaran and K. Kasirajan, *Asian J. Chem.*, **31**, 901 (2019); <https://doi.org/10.14233/ajchem.2019.21834>

18. H. Soonmin, S. Mandati, R. Chandran, A. Mallik, M.A.S. Bhuiyan and K. Deepa, *Orient. J. Chem.*, **35**, 1 (2019); <https://doi.org/10.13005/ojc/35Specialissue101>
19. P. Kumar, Samiksha, Shalini and R. Gill, *Asian J. Chem.*, **30**, 2737 (2018); <https://doi.org/10.14233/ajchem.2018.21574>
20. M.B. Tahir, M. Malik, S.M. Ho, A. Ahmed, T. Nawaz and S. Muhammad, *Int. J. Environ. Anal. Chem.*, (2020); <https://doi.org/10.1080/03067319.2019.1700970>
21. S. Tulenin, A. Pozdin, K. Karpov, D. Novotorkina and M. Rogovoy, *Asian J. Chem.*, **30**, 1655 (2018); <https://doi.org/10.14233/ajchem.2018.21307>
22. M. Dimitrievska, A. Fairbrother, X. Fontane, T. Jawhari, V. Izquierdo-Roca, E. Saucedo and A. Perez-Rodriguez, *Appl. Phys. Lett.*, **104**, 021901 (2014); <https://doi.org/10.1063/1.4861593>
23. L. Isac, A. Duta, I. Kriza, M. Enesca and M. Nanu, *J. Phys. Conf. Ser.*, **61**, 477 (2007); <https://doi.org/10.1088/1742-6596/61/1/096>
24. A. Jrad, W. Naffouti, C. Nefzi, T. Ben Nasr, S. Ammar and N. Turki-Kamoun, *J. Mater. Sci. Mater. Electron.*, **27**, 10684 (2016); <https://doi.org/10.1007/s10854-016-5168-z>
25. N.A. Abdul-Manaf, A.R. Weerasinghe, O.K. Echendu and I.M. Dharmadasa, *J. Mater. Sci.: Mater. Electron.*, **26**, 2418 (2015); <https://doi.org/10.1007/s10854-015-2700-5>
26. S. Ham, S. Jeon, U. Lee, K. Paeng and N. Myung, *Bull. Korean Chem. Soc.*, **29**, 939 (2008); <https://doi.org/10.5012/bkcs.2008.29.5.939>
27. S. Ray and K. Mallick, *Int. J. Chem. Eng. Appl.*, **4**, 183 (2013); <https://doi.org/10.7763/IJCEA.2013.V4.290>
28. A. Das, A. Buzarbaruah and S. Bardaloi, *J. Mod. Phys.*, **4**, 1022 (2013); <https://doi.org/10.4236/jmp.2013.47137>
29. M. Prabhu, K. Kamalakkannan, N. Soundararajan and K. Ramachandran, *J. Mater. Sci. Mater. Electron.*, **26**, 3963 (2015); <https://doi.org/10.1007/s10854-015-2931-5>
30. M. Pandiaraman and N. Soundararajan, *J. Theor. Appl. Phys.*, **6**, 7 (2012); <https://doi.org/10.1186/2251-7235-6-7>
31. A.E. Ozel, D. Deger, S. Celik, S. Yakut, B. Karabak, S. Akyüz and K. Ulutas, *Physica B*, **527**, 72 (2017); <https://doi.org/10.1016/j.physb.2017.10.043>
32. Y. Azhniuk, V. Dzhagan, D. Solonenko, I. Grytysyshe, V. Lopushansky, V. Loya, A. Gomonnai and D.R.T. Zahn, *Appl. Surf. Sci.*, **471**, 943 (2019); <https://doi.org/10.1016/j.apsusc.2018.12.097>
33. A. Shongalova, M.R. Correia, J.P. Teixeira, J.P. Leitão, J.C. González, S. Ranjbar, S. Garud, B. Vermang, J.M.V. Cunha, P.M.P. Salomé and P.A. Fernandes, *Sol. Energy Mater. Sol. Cells*, **187**, 219 (2018); <https://doi.org/10.1016/j.solmat.2018.08.003>
34. K. Tian, K. Baskaran and A. Tiwari, *Thin Solid Films*, **668**, 69 (2018); <https://doi.org/10.1016/j.tsf.2018.10.015>
35. J. Li, Y.C. Zhang and M. Zhang, *Mater. Sci. Forum*, **663-665**, 104 (2010); <https://doi.org/10.4028/www.scientific.net/MSF.663-665.104>
36. V.K. Arepalli, Y. Shin and J. Kim, *Superlatt. Microstruct.*, **122**, 253 (2018); <https://doi.org/10.1016/j.spmi.2018.08.001>
37. A. Walimbe, A. Wertheim, A. Ravi, C. Kopas, A. Saxena, R.K. Singh, S.W. Lehner, J. Domenico, J. Makar, R.W. Carpenter, P.R. Buseck and N. Newman, *Thin Solid Films*, **669**, 49 (2019); <https://doi.org/10.1016/j.tsf.2018.10.022>
38. A. Asenjo, C. Guillen, A. Chaparro, E. Saucedo and V. Bermudez, *J. Phys. Chem. Solids*, (2010); <https://doi.org/10.1016/j.jpccs.2010.09.011>
39. E. Rodriguez, F. Flores, A. Cervantes, E. Campos and S. Mayen, *Chalcogenide Lett.*, **13**, 389 (2016).
40. Y. Azhniuk, D. Solonenko, V. Loya, I. Grytysyshe, V. Lopushansky, A.V. Gomonnai and D.R.T. Zahn, *Appl. Surf. Sci.*, **467-468**, 119 (2019); <https://doi.org/10.1016/j.apsusc.2018.10.157>
41. J. Mitric, N. Paunovic, M. Mitric, B. Vasic, U. Ralevic, J. Trajic, M. Romcevic, W.D. Dobrowolski, I.S. Yahia and N. Romcevic, *Physica E*, **104**, 64 (2018); <https://doi.org/10.1016/j.physe.2018.07.021>
42. R. Keshav and G. Mahesha, *Mater. Res. Bull.*, **105**, 360 (2018); <https://doi.org/10.1016/j.materresbull.2018.05.018>
43. J. Thorat, V. Mohite, A. Bagade, T. Shinde, J. Fulari, Y. Rajpure and S. Shinde, *Mater. Sci. Semicond. Process.*, **79**, 119 (2018); <https://doi.org/10.1016/j.mssp.2018.02.002>
44. I.O. Oladeji, L. Chow, J.R. Liu, W.K. Chu, A.N. Bustamante, C. Fredricksen and A.F. Schulte, *Thin Solid Films*, **359**, 154 (2000); [https://doi.org/10.1016/S0040-6090\(99\)00747-6](https://doi.org/10.1016/S0040-6090(99)00747-6)
45. E. Kariper Guneri, F. Gode and C. Gumus, *Chalcogenide Lett.*, **9**, 27 (2012).
46. J.I. Montes, A. Morales, R. Bernal, and A. Pulzara, *Chalcogenide Lett.*, **13**, 381 (2016).
47. V. Izquierdo-Roca, E. Saucedo, C.M. Ruiz, X. Fontané, L. Calvo-Barrio, J. Álvarez-García, P.-P. Grand, J.S. Jaime-Ferrer, A. Pérez-Rodríguez, J.R. Morante and V. Bermudez, *Phys. Status Solidi., A Appl. Mater. Sci.*, **206**, 1001 (2009); <https://doi.org/10.1002/pssa.200881239>
48. M. Zakria, T. Khan, A. Nasir and A. Mahmood, *Mater. Sci. Pol.*, **33**, 677 (2015); <https://doi.org/10.1515/mssp-2015-0096>
49. S. Ham, S. Cho, U. Lee, S. Jeon, J. Shin, N. Myung and K. Paeng, *J. Korean Electrochem. Soc.*, **10**, 262 (2007); <https://doi.org/10.5229/JKES.2007.10.4.262>
50. M. Sridharan, M. Mekaladevi, S. Narayandass, D. Mangalaraj and H. Lee, *J. Optoelectron. Adv. Mater.*, **7**, 1479 (2005).
51. V.V. Brus, I.S. Babichuk, I.G. Orletsykyi, P.D. Maryanchuk, V.O. Yuhymchuk, V.M. Dzhagan, I.B. Yanchuk, M.M. Solovan and I.V. Babichuk, *Appl. Opt.*, **55**, B158 (2016); <https://doi.org/10.1364/AO.55.00B158>
52. C. Vijayan, M. Pandiaraman, N. Soundararajan, R. Chandramohan and S. Ramaswamy, *Surf. Eng.*, **321**, 267 (2016); <https://doi.org/10.1179/1743294414Y.0000000353>
53. L. Bo, S. Zhi-Tang, Z. Ting, F. Song-Lin and C. Bomy, *Chin. Phys.*, **13**, 1947 (2004); <https://doi.org/10.1088/1009-1963/13/11/033>
54. M. Erazu, J. Rocca, M. Fontana, A. Urena, B. Arcondo and A. Pradel, *J. Alloys Compd.*, **495**, 642 (2010); <https://doi.org/10.1016/j.jallcom.2009.10.251>
55. E. Baudet, C. Cardinaud, A. Girard, E. Rinnert, K. Michel, B. Bureau and V. Nazabal, *J. Non-Cryst. Solids*, **444**, 64 (2016); <https://doi.org/10.1016/j.jnoncrysol.2016.04.017>
56. S. Kozuyukhin, M. Veres, H.P. Nguyen, A. Ingram and V. Kudoyarova, *Phys. Proc.*, **44**, 82 (2013); <https://doi.org/10.1016/j.phpro.2013.04.011>
57. P. Khan, B. Arinjoy, J. Abin, S. Vasant, D. Uday and K. Adarsh, *Thin Solid Films*, **621**, 76 (2017); <https://doi.org/10.1016/j.tsf.2016.11.037>
58. M. Behara, P. Naik, R. Panda and R. Naik, *Opt. Mater.*, **66**, 616 (2017); <https://doi.org/10.1016/j.optmat.2017.03.015>
59. Y. Kim and I. Choi, *Thin Solid Films*, **669**, 351 (2019); <https://doi.org/10.1016/j.tsf.2018.11.023>
60. K.J. Tiwari, V. Vinod, A. Subrahmanyam and P. Malar, *Appl. Surf. Sci.*, **418**, 216 (2017); <https://doi.org/10.1016/j.apsusc.2017.01.279>
61. D.S.P. Kumar, M. Ren, T. Osipowicz, R.C. Mallik and P. Malar, *Sol. Energy*, **174**, 422 (2018); <https://doi.org/10.1016/j.solener.2018.08.080>
62. Y. Dong, X. Lu, P. Shen, Y. Chen, F. Yue, P. Xiang, L. Sun, P. Yang and J. Ch, *Mater. Sci. Semicond. Process.*, **84**, 124 (2018); <https://doi.org/10.1016/j.mssp.2018.05.012>
63. P. Biren, P. Ranjan, M. Indrajit and A. Ray, *Vacuum*, **158**, 263 (2018); <https://doi.org/10.1016/j.vacuum.2018.10.015>
64. R. Juskėnas, Z. Mockus, R. Giraitis, A. Selskis, S. Kanapeckaitė, G. Stalnionis, A. Drabavičius, P. Kalinauskas and G. Niaura, *J. Alloys Compd.*, **767**, 345 (2018); <https://doi.org/10.1016/j.jallcom.2018.06.276>
65. M.P. Suryawanshi, S.W. Shin, U.V. Ghorpade, K.V. Gurav, G.L. Agawane, C.W. Hong, J.H. Yun, P.S. Patil, J.H. Kim and A.V. Moholkar, *Sol. Energy*, **110**, 221 (2014); <https://doi.org/10.1016/j.solener.2014.09.008>
66. S.S. Mali, B.M. Patil, C.A. Betty, P.N. Bhosale, Y.W. Oh, S.R. Jadkar, R.S. Devan, Y.-R. Ma and P.S. Patil, *Electrochim. Acta*, **66**, 216 (2012); <https://doi.org/10.1016/j.electacta.2012.01.079>

67. J.-O. Jeon, K.D. Lee, L. Seul Oh, S.-W. Seo, D.-K. Lee, H. Kim, J. Jeong, M.J. Ko, B.S. Kim, H.J. Son and J.Y. Kim, *ChemSusChem*, **7**, 1073 (2014);  
<https://doi.org/10.1002/cssc.201301347>
68. M. Meng, L. Wan, P. Zou, S. Miao and J. Xu, *Appl. Surf. Sci.*, **273**, 613 (2013);  
<https://doi.org/10.1016/j.apsusc.2013.02.088>
69. J. Yu, H. Deng, J. Tao, L. Chen, H. Cao, L. Sun, P. Yang and J. Chu, *Mater. Lett.*, **191**, 186 (2017);  
<https://doi.org/10.1016/j.matlet.2016.12.067>
70. G.L. Agawane, S.W. Shin, S.A. Vanalakar, A.V. Moholkar and J.H. Kim, *Mater. Lett.*, **137**, 147 (2014);  
<https://doi.org/10.1016/j.matlet.2014.08.118>
71. H. Guan, J. Zhao, X. Wang and F. Yu, *Chalcogenide Lett.*, **10**, 367 (2013).
72. F.-J. Fan, B. Yu, Y.-X. Wang, Y.-L. Zhu, X.-J. Liu, S.-H. Yu and Z. Ren, *J. Am. Chem. Soc.*, **133**, 15910 (2011);  
<https://doi.org/10.1021/ja207159j>
73. M. Guc, S. Levchenko, V. Izquierdo-Roca, X. Fontane, M.Ya. Valakh, E. Arushanov and A. Pérez-Rodríguez, *J. Appl. Phys.*, **114**, 173507 (2013);  
<https://doi.org/10.1063/1.4828885>
74. L. Qiu, J. Xu, W. Cai, Z. Xie and Y. Yang, *Superlatt. Microstruct.*, **126**, 83 (2019);  
<https://doi.org/10.1016/j.spmi.2018.12.020>
75. O. Awadallah and Z. Cheng, *Sol. Energy Mater. Sol. Cells*, **176**, 222 (2018);  
<https://doi.org/10.1016/j.solmat.2017.11.038>
76. C. Nefzi, M. Souli, Y. Cuminal and N. Kamoun-Turki, *Superlatt. Microstruct.*, **124**, 17 (2018);  
<https://doi.org/10.1016/j.spmi.2018.09.033>
77. H. Tassoult, A. Bouloufa, M. Pawlowski and M. Igalson, *Mater. Sci. Semicond. Process.*, **88**, 167 (2018);  
<https://doi.org/10.1016/j.mssp.2018.08.001>
78. M. Sampath, K. Sankarasubramanian, J. Archana, Y. Hayakawa, K. Ramamurthi and K. Sethuraman, *Mater. Sci. Semicond. Process.*, **87**, 54 (2018);  
<https://doi.org/10.1016/j.mssp.2018.07.001>
79. S. Lugo, Y. Sánchez, M. Neuschitzer, H. Xie, C. Insignares-Cuello, V. Izquierdo-Roca, Y. Peña and E. Saucedo, *Thin Solid Films*, **582**, 74 (2015);  
<https://doi.org/10.1016/j.tsf.2014.10.039>