Raman Investigations of Metal Chalcogenide Thin Films  
(A Short Review)

HO SOONMIN

Centre for Green Chemistry and Applied Chemistry, INTI International University,  
Putra Nilai, 71800, Negeri Sembilan, Malaysia.
*Corresponding author E-mail: soonmin.ho@newinti.edu.my

http://dx.doi.org/10.13005/ojc/35Specialissue101

(Received: December 26, 2018; Accepted: February 01, 2019)

ABSTRACT

Preparation and characterization of thin films have been reported by many researchers. Because of thin films could be used in wide applications including optoelectronic, solar cells, laser devices and gas sensor. There are several tools have been employed to characterize the obtained materials such as structural, morphological, compositional, optical and electrical of samples. For example, X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, UV-Visible spectrophotometer, transmission microscopy and Fourier Transform Infrared spectroscopy as reported in literature review. In this work, Raman spectroscopy will be used to investigate the obtained films. Briefly discuss the advantages and disadvantages of this tool will be described also.

Keywords: Raman spectroscopy, Thin films, Band gap, Solar cells, Semiconductor.

INTRODUCTION

The binary, ternary, quaternary and pentenary compounds have received great attention owning to their unique properties. These films are used in a wide variety of applications such as solar cell, sensors, photodiode arrays, photoconductors and optoelectronic devices. The chalcogen is the elements (oxygen, sulfur, selenium and tellurium) in Group 16 of the periodic table. The band gap energy was estimated to be in the range of 1-3 eV. Currently, the solar cell market is dominated by silicon solar cell due to being abundant, non-toxic and showing remarkably higher power conversion efficiency. However, these solar cells are more expensive that other types of cells. Thin film solar cell has always been cheaper but less efficient. This solar cell is favorable due to its minimum material usage. The two major thin film technologies such as cadmium telluride and copper indium gallium diselenide successfully contributed about 10% of the global production market share. The major drawback is a highly toxic material such as tellurium, cadmium, and selenium.
In this work, thin films were investigated using Raman spectroscopy. The purity of sample and the phase identification were also examined.

**Literature survey**

Raman spectroscopy provides useful information on molecular interactions, crystallinity, crystal phase and chemical structure. Raman is based upon the interaction of light with the chemical bonds within a material. Raman spectra exhibit the intensity of the scattered photons versus the frequency difference to the incident photons. Typically, the peaks fall within a range of 500 to 2000 cm\(^{-1}\) and only appear if vibrational modes are sensitive to the laser wavelength used.

Raman spectroscopy is chemical analysis technique and is employed to measure the scattering radiation of a matter (Fig. 1). Generally, when light is scattered by matter, almost all of the scattering is an elastic process and does not give useful information (commonly known as Rayleigh Scatter). However, a very small percentage of scattering is an inelastic process (known as Raman effect). Raman spectroscopy is both qualitative (measuring the frequency of the scattered radiations) and quantitative (measurement of the analyte concentration in the sample by quantifying the intensity of the scattered radiations). The obtained Raman spectra give a unique data to identify a material and distinguish it from others. Table 1 shows the advantages and limitations of Raman spectroscopy technique.

![Fig. 1. Raman is a light scattering technique.](image)

Several efforts have been made by researchers to synthesize semiconductor thin films such as sulfur, selenium and tellurium-based nanostructured films. Typical deposition technique is shown in Table 2. In this study, the utilization of Raman spectroscopy for the characterization of thin films was discussed.

<table>
<thead>
<tr>
<th>Table 1: Advantage and disadvantage of Raman spectroscopic technique</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantage</strong></td>
</tr>
<tr>
<td>Evaluation of trace element contents without the extensive analysis</td>
</tr>
<tr>
<td>Water is the best solvent to dissolve sample.</td>
</tr>
<tr>
<td>Raman spectroscopy detected organic or inorganic materials</td>
</tr>
<tr>
<td>It is simplicity method</td>
</tr>
<tr>
<td>It can be used for in-field, in-situ or down-field in the range 4000-50 cm(^{-1})</td>
</tr>
<tr>
<td>Raman spectroscopy allows quick identification of materials</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2: Raman spectroscopic investigation of thin films prepared under various deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thin films</strong></td>
</tr>
<tr>
<td>Thallium selenide</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
In terms of crystal structure, Tl-Se bond was observed in 2.66-2.73 Å. Arsenic triselenide (As$_2$Se$_3$) peak at 224 cm$^{-1}$ corresponded to asymmetric (for amorphous phase) weak peak at 480 cm$^{-1}$ represented Se-Se vibration. The peak at 221 cm$^{-1}$ could be seen in In-doped As$_2$Se$_3$ films. There are two peaks at 216-219 cm$^{-1}$ and 240-242 cm$^{-1}$ for the films prepared with indium content of 2%. Antimony peak at 188 cm$^{-1}$: Sb-Se stretching mode. Triselenide peak at 150 cm$^{-1}$: Sb-Sb bond. Peak at 181 cm$^{-1}$ attributed to WS$_2$ phase. Tungsten peak at 175 cm$^{-1}$ represented vibration mode disulfide. Peak at 419 cm$^{-1}$ attributed to WS$_2$ phase. SnS$_2$ films peak at 224 cm$^{-1}$: Sb-Se stretching mode. Thermal evaporation. SnS peak at 307 cm$^{-1}$ for the films prepared using 40 and 50 mTorr, indicating that the formation of SnS$_2$. Researchers confirm the phase purity of sample. Chemical bath deposition. SnS$_2$ films peak at 460 cm$^{-1}$ attributed to the S-S mode of sulphur. Chemical bath deposition. SnS peak at 307 cm$^{-1}$ for the films prepared using 40 and 50 mTorr, indicating that the formation of SnS$_2$. Researchers confirm the phase purity of sample. Chemical bath deposition. In$_2$S$_3$ peak at 180 cm$^{-1}$ attributed to As-As homopolar bond vibration. Peak at 485 cm$^{-1}$ corresponded to S-S vibration of AsS$_4$. CdTe both the transverse (142 cm$^{-1}$) and longitudinal (170.5 cm$^{-1}$) mode could be found. Peak at 120 cm$^{-1}$ attributed to phonon of tellurium. ZnS films two peaks at 773 and 1078 cm$^{-1}$ were detected in annealed and as-deposited films. The lattice constant value for both as-deposited (5.3 Å) and annealed films (5.66 Å) was determined. Bi$_2$Te$_3$ peak at 77 cm$^{-1}$ attributed to vibration mode of BiTe. CdS three peaks (299, 600 and 900 cm$^{-1}$) were found and could be observed as longitudinal optical phonons.
CdS
• There are 2 peaks could be identified (296 and 593 cm\(^{-1}\)), for the films prepared under various pH values.
• The intensity of the Raman peak decreases with increasing the pH value from pH 9 to 11.

Ternary thin films
Ag-Ge-Se
• The films showed GeSe\(_2\)/2 corner sharing tetrahedral at 192-201 cm\(^{-1}\), vibration of Se atom at 210-218 cm\(^{-1}\), Se-Se bond at 255-270 cm\(^{-1}\) and Ge-Ge mode at 178 cm\(^{-1}\) and could be detected when x=1, and x=0, 0.3, respectively. Vapor transport deposition [66]

Ge-Sb-Se
• Four main modes such as symmetric stretching mode of GeSe\(_2\)/2 tetrahedral (200, 215 cm\(^{-1}\)), stretching mode of Ge-Ge bond (170 cm\(^{-1}\)), Se-Se stretching mode (235-245 cm\(^{-1}\)) and Se-Se bond vibration (265 cm\(^{-1}\)) are observed in these films RF magnetron sputtering [67]

Ge\(_{x}\)Sb\(_{3-x}\)Te\(_{3}\)
• They observe some peaks such as 80 (GeTe4 tetrahedral), 125 (GeTe4-nGen(n=1,2)), 153 (presence of Sb2Te3) and 300 cm\(^{-1}\) (presence of Ge-Ge) in spectra Thermal evaporation evaporation [68]

Ge\(_{x}\)As\(_{3-x}\)Se\(_{3}\)
• The films exhibited symmetric vibrational stretching GeSe\(_2\)/2 at 198 cm\(^{-1}\), vibration mode of AsSe\(_2\)/2 at 230 cm\(^{-1}\), vibration mode of selenium at 260 cm\(^{-1}\) and vibration mode of GeSe\(_2\)/2 tetrahedral at 215 cm\(^{-1}\)

As\(_{x}\)Sb\(_{4-x}\)Te\(_{10}\)
• Three major modes such as asymmetric stretching As-Te-Se mode (127 cm\(^{-1}\)), As-Se vibration mode (228 cm\(^{-1}\)) and Te-Te vibrational mode (472 cm\(^{-1}\)) are observed in these films

Cu\(_3\)SnS\(_3\)
• The Raman peaks exhibit strong (vibration mode in monoclinic) and weak peak (Cu\(_3\)Sn\(_3\) phase).
• They observe several peaks such as 188, 250, 372, 450 cm\(^{-1}\) (Sb\(_2\)Se\(_2\)), 185 cm\(^{-1}\) (Cu\(_3\)SbSe\(_2\)), and 82, 117, 144 cm\(^{-1}\) (presence of CuSbSe\(_2\) in spectra)

Cu\(_3\)Sb\(_2\)S\(_3\)
• There are many peaks such as 351 cm\(^{-1}\) (Cu\(_3\)Sb\(_2\)S\(_3\)), 354 cm\(^{-1}\) (Sb-S bond stretching), 315 cm\(^{-1}\) (Sb-S bond bending mode), 330 cm\(^{-1}\) (CuSbSe\(_2\)), 468 cm\(^{-1}\) (CuS) could be confirmed. E-beam evaporation thermal evaporation [70]

Cu\(_3\)SnS\(_3\)
• There are several peaks could be identified such as 290 and 350 cm\(^{-1}\) (monoclinic), 325 cm\(^{-1}\) (tetragonal phase), 223 and 371 cm\(^{-1}\) (Cu\(_3\)Sn\(_3\)S\(_3\))

Cu\(_2\)SnS\(_3\)
• The films indicated orthorhombic Cu\(_2\)SnS\(_3\) phase at 295 cm\(^{-1}\), monoclinic Cu\(_2\)SnS\(_3\) at 289 cm\(^{-1}\) and vibration mode of tetragonal Cu\(_2\)SnS\(_3\) in anneal films at 326 cm\(^{-1}\)

Cu\(_2\)SnSe\(_3\)
• Peak at 2926 cm\(^{-1}\) was observed (attributed to C-H stretching vibration of CH\(_3\)) for the films prepared using 0.5 M of sodium citrate. Radio frequency magnetron sputtering [74]

• However, this peak could not be detected when using higher concentration (0.1 M).

Quaternary thin films
Cu\(_3\)ZnSnS\(_4\)
• The films showed a prominent kesterite phase (331-336 cm\(^{-1}\)), indicating microwave treatment enhanced nucleation and grow process.
• The films prepared could be detected for the films prepared at room temperature and within the first 15 minutes.
• The films prepared under 30 min of sulfurization show peak at 330 cm\(^{-1}\)
• The films synthesized under 80 and 180 min of sulfurization show higher intensities if compared to other conditions.
• There are no other impurities (ZnS, SnS\(_2\), and CuS) indicating high purity of sample. Sol gel method [77]

Cu\(_3\)FeSnS\(_4\)
• Two main modes such as sulfur pure anion around the copper metal (285 cm\(^{-1}\)) and asymmetry vibration mode of sulphur around the tin atom could be confirmed. Spray pyrolysis [79]

Cu\(_{x}\)Ga\(_{1-x}\)In\(_{2}\)S\(_3\)
• The presence of Cu\(_x\)Ga\(_{1-x}\) (290 cm\(^{-1}\)) and Cu\(_x\)In\(_{1-x}\)Se\(_3\) (175 cm\(^{-1}\)) could be detected when x=1, and x=0, 0.3, respectively. Close spaced vapor transport technique [80]

Cu\(_2\)ZnSnS\(_4\)
• Kesterite phase (332, 285, 356 and 368 cm\(^{-1}\)), copper tin sulphide (303 cm\(^{-1}\)) and copper sulphide (468 cm\(^{-1}\)) were observed in Raman spectra. Spray pyrolysis [81]

Culn(S,Se)\(_2\)
• There are many peaks at 473 cm\(^{-1}\) (Cu2-xS), 390-475 cm\(^{-1}\) (sulfur rich Culn(S,Se)\(_2\)), 228 cm\(^{-1}\) (Culn2Se\(_3\)) and 150-400 cm\(^{-1}\) (amorphous In\(_2\)S\(_3\)) could be confirmed. Chemical bath deposition [82]
**CONCLUSION**

Raman spectroscopy is a powerful technique for characterization of thin films. Here, the author reviews the Raman spectra of nanostructured films. Also, the author indicates how to use it to determine structure and composition of samples. The purity of the compound and phase formation can be verified by this technique.

**REFERENCES**

27. Saxena, R.S.; Aparna, S. **Superlattices Microstruct.**, 2019, 126, 139-149.
34. Saga, T. NPG Asia Mater., 2010, 2, 96-102.


