Growth of In$_2$Se$_3$ Thin Films Prepared by the Pneumatic Spray Pyrolysis Method for Thin Film Solar Cells Applications

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**Abstract**—Photovoltaic (PV) technology has the potential to fulfill the world’s energy demand by replacing non-renewable fossil fuels for useful energy production. CuInSe$_2$/Cu(In,Ga)$_2$Se$_3$ (CIS/CIGS) thin film solar cell can dominate the PV market if the energy production cost is low, which is possible using inexpensive deposition methods or/and precursor materials. In this research work, we have studied In$_2$Se$_3$ thin films prepared by low-cost pneumatic spray pyrolysis (PSP), grown at three different substrate temperatures. The formation of a stable γ-In$_2$Se$_3$ phase was revealed by structural (X-ray diffraction and Raman spectroscopy), compositional, and optical studies. The crystallinity of In$_2$Se$_3$ thin films increases with an increase in substrate temperature. From scanning electron microscopy (SEM), In$_2$Se$_3$ thin films showed the surface morphology of uniform and dense particles with columnar structure. The lower values of average roughness (<10 nm) for In$_2$Se$_3$ thin films were suggesting the formation of a smooth and uniform surface. This deposited In$_2$Se$_3$ by PSP can be utilized as a precursor layer for CISE/CIGSe synthesis as well as a buffer layer in thin film solar cells.

**Keywords**—In$_2$Se$_3$, PSP, precursor layer, CIGSe thin film solar cell

I. INTRODUCTION

Solar energy, an important renewable energy source, is the most abundant, free, and non-polluting energy source where semiconductor materials are used to convert sun energy directly into electricity through the photovoltaic effect. Although wafer-based crystalline silicon solar cell has been considered as the most mature PV technology with a share of 85% in the global annual production, the fabrication cost for this solar cell is high [1]. Due to the indirect bandgap nature of silicon material, high purity as well as a high quantity of material is needed for the complete absorption of photons. Thin film solar cell technologies have the potential to reduce the cost using semiconductor material containing the characteristics of direct bandgap and a much higher absorption coefficient (>10$^4$ cm$^{-1}$) [2]. This leads that the small quantity (i.e., few micrometers of thickness) of material is sufficient to absorb sunlight. Among all, CIS/CIGSe semiconductor has been studied widely owing to its advantages on environment system, high record efficiency (23.35%), and cost considerations [3], [4]. The prospective use of In$_2$Se$_3$ thin film in PV technology has also attracted strong interest from researchers because of its widespread application area.

In$_2$Se$_3$ belongs to the III$_2$-VI$_3$ family group. It is one of the most vital compounds of indium-selenium system, which has been widely used in optoelectronic devices, diodes, solid solution electrodes, transistors, photodetectors, electro and photo memory devices, and photovoltaics. Depending on synthesis temperature and composition, there exist five different phases (i.e., α, β, γ, δ, κ) of In$_2$Se$_3$ [5]. These different phases of In$_2$Se$_3$ have different bandgap energy values, which can be used for the various roles in photovoltaics. The γ-phase of In$_2$Se$_3$ has a wider bandgap of 1.8 eV, which is exploited as a window layer in CISE/CIGSe solar cell. Besides, α and β-phases are used as an absorber layer due to their absorbing nature and lower bandgap values, 1.45 and 1.55 eV for α and β, respectively. Furthermore, β and γ phases of In$_2$Se$_3$ can also be utilized as a precursor layer for the synthesis of CISE absorber material, which exhibits rhombohedral and defect wurtzite (hexagonal) crystal structure, respectively [6].

The deposition method for In$_2$Se$_3$ thin film can be classified into the vacuum and non-vacuum techniques based on the nature of the deposition process. Vacuum based methods including thermal evaporation, sputtering, molecular beam epitaxy, laser ablation, physical vapor deposition, electrochemical, sol-gel, chemical vapor deposition, spray pyrolysis, [12], [13], [14], [15], [16], [17] etc. have the advantage of high-quality film formation. And non-vacuum based processes such as chemical bath deposition, spin and dip coating, etc. have the advantage of high-quality film formation. The spray pyrolysis (SP) method is a simple, low-cost method that has been widely used for numerous applications [6]. This SP method consists of three main steps containing atomization, transportation, and decomposition, where small droplets of the precursor solution are sprayed onto a heated substrate [7]. Generally, the chemical reactants of the PSP process are chosen in such a way that the by-product will be volatile with deposition temperature.
In this study, we report the deposition of In$_2$Se$_3$ thin films by the PSP method at three different substrate temperatures. This work aims to prepare the γ-In$_2$Se$_3$ phase at low cost and its applicability in thin film solar cells as a precursor layer for CIGS/CIGSe absorber layer, absorber layer as well as a buffer window material. Different characterizations were carried out to investigate the suitability of In$_2$Se$_3$ thin film in a different realm.

II. EXPERIMENTAL DETAILS

A. Materials details

Precursor materials utilized for the deposition of In$_2$Se$_3$ such as soda-lime glass (SLG) substrates, extran solution, sodium hydroxide (NaOH, 98%), hydrochloric acid (HCl, 37%), ethanol, methanol, indium chloride (InCl$_3$) and N, N-dimethyl-selenourea (NH$_2$(CH$_3$)$_2$NCS), etc. were purchased from Sigma Aldrich. Industrial nitrogen (N$_2$) gas cylinder was purchased from INFRA group, Mexico. SLG substrates were subsequently cleaned with de-ionized water, extran solution, dilute NaOH solution, dilute HCl solution, methanol, and again with de-ionized water in the ultrasonic bath. Finally, Cleaned SLG substrates were dried through industrial nitrogen gas and immediately used for the deposition process.

B. Deposition procedure

The PSP films were grown on a molten tin bath because of its better heat transfer property to a solid surface. The precursor materials, including indium chloride (InCl$_3$), the concentration of 0.0015 M) and N, N-dimethyl-selenourea (NH$_2$(CH$_3$)$_2$NCS), the concentration of 0.005 M) were dissolved in the mixture containing ethanol (20 vol%) and water (80 vol%). These precursor materials can be completely soluble in 20 vol% of ethanol rather than methanol and acetone. Moreover, ethanol is not flammable which is not dangerous while spraying solution on to the hot plate. Excess amount of N, N-dimethyl-selenourea was employed in the solution to maintain high selenium content (> 60%) within the film, which allows the formation of gamma-In$_2$Se$_3$ (γ-In$_2$Se$_3$) phase. Before starting the deposition process, the parameters like the precursor solution of 500 mL, the solution flow rate of 5 ml/min, the gas flow rate of 4000 mL/min, and the substrate temperature (300-340 °C) were fixed. The In$_2$Se$_3$ film of around 1 μm of thickness was observed after 90 minutes of deposition. The following is the possible chemical reactions that occur in the PSP process (as shown in Fig. 1),

\[3\text{NH}_2(\text{CH}_3)_2\text{NCS} = \text{Se (aq)} + \text{CH}_3\text{CH}_2\text{OH (aq)} + 2\text{InCl}_3 (s) + 6\text{H}_2\text{O (aq)} \rightarrow \text{In}_2\text{Se}_3 (s) + 3\text{CO}_2 (g) + 3\text{(CH}_3\text{)}_2\text{NH (g)} + 3\text{NH}_3 (g) + \text{CH}_3\text{CH}_2\text{OH (g)} + 3\text{Cl}_2 (g) \] (1)

C. Characterization

The structural properties of In$_2$Se$_3$ thin films were analyzed by X-ray diffraction (XRD) and Raman spectroscopy. The surface morphology and composition analysis are studied for these films through scanning electron microscopy (SEM), atomic force microscopy (AFM), and energy dispersive X-ray spectroscopy (EDS). The optical band is derived from transmission spectra obtained from UV-vis spectroscopy. The structural properties such as crystallinity and orientation were assessed using a Bruker XRD-D2 Phaser with Cu-Kα radiation ($\lambda = 1.54\text{Å}$) with 2θ varying between 20° and 60°. The morphology and the average composition of elements of samples were studied by Tescan Vega-3 SEM equipped with an energy dispersive X-ray spectrometer at an operating voltage of 15kV. The Raman spectra and topographical analysis of deposited thin film samples were observed in NT-MDT Ntegra spectra. The optical transmittance of In$_2$Se$_3$ thin films was measured by the Jasco V-670 spectrophotometer in a wavelength range of 300-1200 nm.

III. RESULTS AND DISCUSSIONS

A. Growth rate

The nucleation and growth rate of In$_2$Se$_3$ films by PSP technique vary with the deposition parameters such as substrate temperature, the concentration of precursor materials, nozzle to substrate distance, solution and gas flow rate, etc. When droplets approach the substrate, the solvent starts to vaporize, and then diffused vapors undergo a heterogeneous reaction for the growth of film by the PSP method. Due to the presence of droplets of precursor solution at the front surface, its temperature is lower (15-20 °C) than the temperature of the back surface of the substrate [18]. From the deposited films, it is observed that the growth rate of the films falls gradually with a rise in deposition temperature. This is mainly due to the volatile nature of selenium at a higher temperature. We have studied the growth of In$_2$Se$_3$ films at various substrate temperatures in the range of 280 to 400 °C. It is seen from the samples that the poor quality (i.e., dry precipitate or powdery deposit) at low-temperature conditions (<300 °C) and a higher temperature (> 350°C). At low temperatures, there is no sufficient energy to vaporize the drops of precursor solution and the solvent vaporizes long
before reaching the substrate and chemical reaction takes place in the vapor phase resulting low-quality film deposition in higher conditions. Therefore, we have narrowed our study for the deposition of indium selenide in between substrate temperature from 300 to 340 °C with a step of 20 °C. As observed from the data, the growth rate for In$_2$Se$_3$ samples at temperatures 300, 320, and 340 °C were found around 13, 11, and 10 nanometer per minute (nm/min) respectively.

**B. XRD analysis**

In Fig. 2, XRD patterns are shown for In$_2$Se$_3$ thin films grown by the PSP method at various substrate temperatures ranging from 300 to 340 °C. From XRD results, the dominant peak (006) and minor peaks (110), (300), and (314) exhibit that the films crystallize completely in the γ-In$_2$Se$_3$ structure [19]. After matching the position of the X-ray reflections with the reported phases of In$_2$Se$_3$, the film shows a defect wurtzite structure (γ-In$_2$Se$_3$) described by the international center for diffraction data (ICDD) number 01-089-0658. X-ray diffraction data including two thetas (θ), full width half maximum (FWHM), crystallite size, strain, and dislocation density were estimated from the following equations (using the Williamson-Hall equation) [20].

\[
\beta = \frac{0.9\alpha}{D \cos \theta} + 4\varepsilon \tan \theta \tag{2}
\]

\[
D = \frac{0.9}{\beta \cos \theta} \tag{3}
\]

\[
\varepsilon = \frac{\beta \cos \theta}{4} \tag{4}
\]

\[
\delta = \frac{1}{D^2} \tag{5}
\]

It is clear from the data that the films grown at higher substrate temperature shows better crystalline quality than at lower substrate temperature.

**Table I. Structural parameters for In$_2$Se$_3$ thin films**

<table>
<thead>
<tr>
<th>Samples</th>
<th>In$_2$Se$_3$ 300 °C</th>
<th>In$_2$Se$_3$ 320 °C</th>
<th>In$_2$Se$_3$ 340 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>FWHM (β) (×10$^{-5}$ Rad)</td>
<td>Crystallite Size (D) (nm)</td>
<td>Strain (ε) (×10$^{-3}$ Rad)</td>
</tr>
<tr>
<td>In$_2$Se$_3$ 340</td>
<td>27.530</td>
<td>42.13</td>
<td>0.883</td>
</tr>
<tr>
<td>In$_2$Se$_3$ 320</td>
<td>27.527</td>
<td>46.89</td>
<td>0.794</td>
</tr>
<tr>
<td>In$_2$Se$_3$ 300</td>
<td>27.525</td>
<td>50.85</td>
<td>0.732</td>
</tr>
</tbody>
</table>

**C. Raman spectroscopy**

Fig. 3 displays the Raman spectroscopy of In$_2$Se$_3$ samples deposited at various substrate temperatures, which helps to identify the phase of In$_2$Se$_3$ through the presence of distinct vibrational modes. From these results, the characteristics peak at 150 cm$^{-1}$ of samples is related to the γ-In$_2$Se$_3$ phase and polycrystalline films. The extra minor phonon frequencies located at 203 and 227 cm$^{-1}$ are also compatible with the γ-In$_2$Se$_3$ phase [21]. The peak at 203 cm$^{-1}$ is related to the β-In$_2$Se$_3$ phase too [22]. The FWHM value of the predominant peak at 150 cm$^{-1}$ for In$_2$Se$_3$ thin films grown at 300, 320, and 340 °C, are 12.92 cm$^{-1}$, 12.60 cm$^{-1}$, and 13.11 cm$^{-1}$ respectively.

**D. SEM and EDS analysis**

SEM was employed to study morphology and the grain size of different In$_2$Se$_3$ thin films. The SEM images for In$_2$Se$_3$ thin films grown at different substrate temperatures (300, 320, 340 °C) are shown in Figure 4. It is seen from the SEM images that the grains are composed of columnar structure lying in different directions. The grain size of films, are composed of both smaller (<100 nm) and larger (>100 nm) grains, was
calculated by EVA software (is the software attached with Tescan Vega-3 SEM, which helps to calculate grain size directly from the SEM image of the film). The rise in mobility and migration (i.e., coalescence of neighboring grains) of grains cause to increase the grain size of films. The number of grain boundaries, which impact the performance of the solar cell devices by recombing generated charge carriers, decreases when the grains of films have bigger in size. From the EDS spectrum (inserted in SEM images), the observed peaks ensured the presence of indium and selenium elements in the film. Fig. 5 demonstrates the elemental compositions (i.e., In and Se) of In$_2$Se$_3$ films estimated by EDS where data were acquired from 10 different random points of the samples. In$_2$Se$_3$ phases depend mainly on the selenium content within the film (i.e. the γ-phase contains ≥ 60 at% of selenium and β-phase comprises selenium deficient (< 60 at%)) [23]. In an excess selenium condition, an atomic arrangement of constituents in the films is similar to γ-phase rather than other phases.

Fig. 4. SEM images (inserted with EDS spectrum) of In$_2$Se$_3$ thin films prepared at three different substrate temperatures, a) 300, b) 320, and c) 340 °C

Fig. 5. Schematic diagram of EDS compositional details of In$_2$Se$_3$ thin films

E. AFM studies

Figure 6 shows the 2D AFM images for In$_2$Se$_3$ thin films deposited at three different substrate temperatures, with a surface area of 2×2 µm$^2$. This topographical study helps to investigate the surface texture, average grain size as well as the average surface roughness of films. From AFM images, it is seen that the grains are composed of closely packed sphere-like structures, which is distributed uniformly on the surface of films. The formation of the regular shape of grains infers that the kinetic energy is adequate to coalesce the grains [24]. Table 2 presents the values of parameters such as average grain size, average roughness, root mean square (RMS) roughness, skewness, and kurtosis. The average roughness is measured by the vertical spacing of the real surface from its ideal form, which is found to be less than 10 nm for deposited samples indicating the smooth surface of the film. The positive values of skewness generalize that the height distribution is near to symmetrical. And kurtosis values (greater than 3) suggest that the difference between the number of the peaks and valleys is a positive value (i.e. +1 because the peak must follow by a valley).
TABLE II. TOPOGRAPHICAL PARAMETERS FOR In$_2$Se$_3$ THIN FILMS CALCULATED FROM AFM

<table>
<thead>
<tr>
<th>Samples Parameters</th>
<th>In$_2$Se$_3$ 300 °C</th>
<th>In$_2$Se$_3$ 320 °C</th>
<th>In$_2$Se$_3$ 340 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average grain size (nm)</td>
<td>122</td>
<td>112</td>
<td>114</td>
</tr>
<tr>
<td>Average roughness (nm)</td>
<td>8.38</td>
<td>5.94</td>
<td>7.95</td>
</tr>
<tr>
<td>RMS roughness (nm)</td>
<td>10.72</td>
<td>7.40</td>
<td>10.23</td>
</tr>
<tr>
<td>Skewness ($S_k$)</td>
<td>0.711</td>
<td>0.603</td>
<td>0.819</td>
</tr>
<tr>
<td>Kurtosis ($S_k$)</td>
<td>3.856</td>
<td>3.248</td>
<td>4.132</td>
</tr>
</tbody>
</table>

F. Optical studies

In photovoltaic technology, the important parameter is the bandgap of the material, which provides information about the fundamental absorption properties. Since the In$_2$Se$_3$ is a direct bandgap semiconductor, the bandgap of this material is calculated using Tauc relation [25]:

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

Where $h \nu$ is the photon energy, $\alpha$ is the absorption coefficient, $A$ is a constant, and $E_g$ is the bandgap of In$_2$Se$_3$. The optical bandgap of the material was computed by extrapolating the straight line of the plot $(\alpha h \nu)^2$ versus energy ($h \nu$) to the energy axis. The estimated bandgap for In$_2$Se$_3$ thin films grown at 300, 320, and 340 °C substrate temperatures are 2.22, 2.34, and 2.55 eV, respectively. Comparing these calculated bandgap values with the reported values for various In$_2$Se$_3$ phases [20], it is found that computed bandgap values were closer to the bandgap value for $\gamma$-phase, which indicates the formation of a stable compound. The optical transmission for two In$_2$Se$_3$ films grown at 320 and 340 °C were identical, which is around 50% at visible region (shown in Fig. 7). The slightly lower value of transmission for In$_2$Se$_3$ at 300 °C is due to its high thickness value than others.
IV. CONCLUSION

The influence of temperature on PSP-grown In$_2$Se$_3$ thin films at three different substrate temperatures has been investigated. The formation of the $\gamma$-In$_2$Se$_3$ phase (i.e., crystal structure) is noticed by XRD patterns with a preferential orientation of (006). It is also remarked that the crystalline quality of In$_2$Se$_3$ films slightly enhances with a rise in substrate temperature. The strong A$_2$ vibrational mode at 150 cm$^{-1}$ for In$_2$Se$_3$ thin films by Raman spectroscopy is also matched with the wurtzite crystal structure. The surface of In$_2$Se$_3$ thin films showed uniform and regular shape with a grain size of about 500 nm. From EDS analysis, more than 60 at% of selenium content inside the film is related to the property of the $\gamma$-In$_2$Se$_3$ phase. The growth of smooth as well as compact films were confirmed by the lower values of RMS roughness. The calculated optical bandgap values were found near to that of the $\gamma$-In$_2$Se$_3$ phase coinciding with the results obtained from XRD and Raman spectroscopy studies. Hence, the optimized condition for In$_2$Se$_3$ thin film grown by PSP was observed at a substrate temperature of 340 °C.

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