Effect of Post-Annealing on a Sb$_2$Se$_3$ Superstrate Device

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Abstract

Antimony selenide (Sb$_2$Se$_3$) has recently attracted researchers’ attention pertaining to its suitability as an absorber material in thin film solar cells. In this investigation, Sb$_2$Se$_3$ was deposited by conventional thermal evaporation technique to form a device in superstrate configuration. A post-deposition annealing at 300 °C for 30 minutes in a 1 mbar argon atmosphere was introduced for the device treatment. Comparative studies between the as-deposited and post-annealed were conducted to identify the factors that triggered the device improvement. An improvement in device efficiency from 0.9 % to 1.6 % was recorded via the post-annealed treatment, despite the scanning electron microscope (SEM) showing little changes in grain size improvement. Other characterizations were also conducted such as energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) as well as external quantum efficiency (EQE).

Introduction

Research interest has seen an increase on antimony selenide (Sb$_2$Se$_3$) recently pertaining to its suitability as an absorber material in thin film solar cell. One of the appealing characteristic is its band gap value that lies within the range of 1.1 eV to 1.3 eV, being in close proximity to the optimum Shockley-Queisser limit [1]. Sb$_2$Se$_3$ is a binary compound with a large absorption coefficient (> 10$^5$ cm$^{-1}$) [2], avoiding the complex control of ternary/quaternary materials. Sb$_2$Se$_3$ is also a low toxicity material. Issue of material scarcity also does not apply for Sb$_2$Se$_3$ since antimony and selenium are Earth-abundant unlike indium in CIGS solar cell, for example.

Sb$_2$Se$_3$ has been deposited using various low fabrication techniques in previous publication such as rapid thermal process, solution process and electrochemistry [3-5]. High composition control can be possible using solution process such as hydrazine, however, highly hazardous material are used [6]. In this work, Sb$_2$Se$_3$ was deposited by thermal evaporation, selected due to the fact that Sb$_2$Se$_3$ has a low melting point (608 °C) and high vapour pressure (1200 Pa at 550 °C) [7].

One consideration for improvement in this investigation is by subjecting the device for post-annealing treatment. Post-annealing has shown to be beneficial from several publication to increase the performance of solar cell. Increase in crystallinity is one of the factor observed by Arindan et al. [8] whereas other notable device improvements were attribute to the reduction in non-radiative recombination [9]. However, post-annealing might also cause detrimental inter-diffusion between the interaced layers which was observed by Sousa et al. [10] through their XPS measurement, causing buried junction to be created. All of the reported post-annealing treatment were done at atmospheric pressure as well as in vacuum treated chambers. This report compile the results of superstrate Sb$_2$Se$_3$ device annealed under argon atmosphere at 1 mbar pressure.

Experimental

Fabrication of Sb$_2$Se$_3$ Devices

The substrate used in this experiment is a pre-coated soda lime glass with fluorine doped tin oxide (FTO) from Zhuhai Kaivo. It was sequentially cleaned in ultrasonic bath using detergent, isopropanol (IPA) and de-ionized water (DI water) respectively. A 60 nm thick cadmium sulphide (CdS) was deposited subsequently by chemical bath deposition. Next, a 500 nm thick Sb$_2$Se$_3$ layer was thermally evaporated at a deposition rate of 15 nm/s, from high purity source material (99.999 %) supplied by Testbourne Ltd. The substrate was set to rotate at 10 rpm with a target to source distance fixed at 30 cm. Before the deposition process start, the chamber pressure was allowed to set at 10$^{-6}$ mbar and substrate temperature to reach a stabilised 300 °C. To complete the superstrate structure, a 100 nm gold (Au) thickness was sputtered as the back contact, creating a complete device with an area of 0.25 cm$^2$. For post-deposition annealing treatment, the samples were subjected to an annealing temperature of 300
°C for 30 minutes in a 1 mbar static argon atmosphere.

Characterisation Technique

The crystal orientations were examined by X-ray diffractometer (XRD) using a Siemens D5000 diffractometer with Cu-Kα (λ = 0.154 nm). Surface microstructure and cross-section analysis were conducted using a MIRA3 scanning electron microscopy (SEM) from Tescan. Coupled with the SEM is an energy dispersive spectroscopy (EDS) detector to analyse the atomic composition between the as-deposited and post-annealed samples. For external quantum efficiency measurement (EQE), a PVE300 system was used from Bentham. Current density vs voltage (J-V) characteristics were measured with a Keithley 2400 source-meter coupled with an Abet technologies sun 2000 solar simulator to collect the device output at AM1.5G. The solar simulator was calibrated beforehand using a Kipp & Zonen silicon pyrometer with a sensitivity of 71 µV/W·m².

Results and Discussion

The crystal phase of the deposited Sb₂Se₃ was determined by X-ray diffraction. Fig. 1 shows the XRD pattern for the Sb₂Se₃ for as-deposited and post-annealed devices, where the crystal orientations labelled correspond to the pdf card number from joint committee on powder diffraction standards (JCPDS) no. 015-0861 and no other diffraction peaks of other impurity was observed. The orientations of concern are the (020) and (221) peaks as labelled in Fig. 1. Both peaks were present in the as-deposited (AD) sample. Upon annealing treatment, the (020) peak diminished, which can be related to the horizontally stacked nano-ribbon. The presence and dominance of this (221) peak is reported to be beneficial for high efficiency Sb₂Se₃ devices, due to the vertical alignment of the Sb₂Se₃ nano-ribbons growing vertically to the substrate, with benign grain boundaries [11]. Unlike the horizontally stacked (020) crystals, where the carriers need to “hop” between the weaker Van der Waals force [12], the (221) crystal orientation favours the charge carrier transport throughout the film due to the strong covalent bond that holds the Sb₂Se₃ molecules, and likely beneficial to reduce carrier recombination at grain boundaries. The texture coefficient was calculated from Eq. 1 [13] where C_{hkl} is the calculated texture coefficient, I_{hkl} is the measured peak intensity, I_{Rkl} is the reference peak intensity and n is the total number of peaks considered in the calculation.

\[ C_{hkl} = \frac{I_{hkl}}{\sum I_{Rkl}} \]  \hspace{1cm} (1)

Calculation of the preferred orientation using Eq. 2 reveals the value obtained for AD and PA samples are 1.19 and 1.50, respectively. This shows that both of the samples are randomly oriented, but the PA sample has an increased preferred orientation.

\[ C_{hkl} = \sqrt{\sum \frac{1}{n} (C_{hkl} - 1)^2} \]  \hspace{1cm} (2)

Fig. 2 (a-b) compares the surface morphology of as-deposited vs post-annealed Sb₂Se₃ film, respectively. The as-deposited sample shows a compact Sb₂Se₃ grain structure with little void present, and this characteristic is retained for the annealed sample. The as-deposited SEM image shows that the film has an average grain size of 140 nm, while the post-annealed film shows an increase to 170 nm, indicating an enhancement in grain size with post-annealing treatment, due to re-crystallization. Cross-sectional analysis (not shown here) for as-deposited (AD) and post-annealed (PA) samples confirms the thickness of Sb₂Se₃ to average 501.5 nm and 503.4 nm respectively.

In order to confirm the film composition deposited in this project, the samples were subjected to energy dispersive spectroscopy (EDS) analysis. To avoid picking up EDS signal from other layer on the device such as CdS and FTO, acceleration voltage as low as 10 keV were used. All of the EDS peaks (Fig. 3) can be attributed to Sb₂Se₃ and no other peak from other layers was observed (except for carbon and oxygen peak being an artefact signal and can be ignored). As can be seen from Table 1,
both AD and PA samples suffer from selenium deficiency where the atomic percentage of Se for the samples is 5% – 6% lower than the expected value, making the Sb:Se ratio at 0.75 and 0.77 respectively, which is more than the theoretical ratio of 2:3 at 0.66.

![SEM surface microstructure for Sb$_2$Se$_3$ film](image)

**Fig. 2** SEM surface microstructure for Sb$_2$Se$_3$ film a) as-deposited sample b) post-annealed sample.

One of the concerns in depositing Sb$_2$Se$_3$ thin film is the selenium deficiency in the deposited film because of the decomposition of Sb$_2$Se$_3$ into gas phase of Se$_2$, Sb$_4$ and SbSe. This decomposition is not only observed for thermal evaporation technique, but also has been reported when Sb$_2$Se$_3$ was deposited by electron beam and electrodeposition method as quoted in Table 1 [14–16]. The decomposition of Sb$_2$Se$_3$ during thermal evaporation was reasoned to be due to the difference in vapour pressure between Se and Sb, as initially explained by V. Piacente et al. [17] and Liu X et al. [18]. The selenium deficient Sb$_2$Se$_3$ is an n-type donor which not only reduces the p-type characteristics, but also may introduce deep recombination centre in the device [19].

To identify the effect of post-annealing treatment onto electrical performance of the superstrate device, J-V characteristics are shown in Fig. 4, while the extracted device parameters are shown in Table 2.

From Table 2, an overall increase in all of the device output is observed, however, significant improvement can be seen for both the open circuit voltage ($V_{oc}$) and the short-circuit current density ($J_{sc}$). A 58 mV increase in $V_{oc}$ and a 5.19 mA/cm$^2$ increase in $J_{sc}$ were

![J-V characteristics for the as-deposited and post annealed sample](image)

**Fig. 3** EDS spectra for the as-deposited device. All of the shown peaks were attributed to Sb$_2$Se$_3$ except for Carbon and oxygen peaks which are the artefacts and can be ignored.

**Table 1.** Compilation of atomic percentage between Sb and Se at various deposition technique.

<table>
<thead>
<tr>
<th>Sample/Reference</th>
<th>Dep. Type</th>
<th>Sb (At%)</th>
<th>Se (At%)</th>
<th>Sb:Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>Thermal evaporation</td>
<td>42.90</td>
<td>57.10</td>
<td>0.75</td>
</tr>
<tr>
<td>Post-annealed</td>
<td></td>
<td>43.40</td>
<td>56.60</td>
<td>0.77</td>
</tr>
<tr>
<td>Y.H. Kwon et al. [14]</td>
<td>Electrochemical</td>
<td>43.40</td>
<td>56.60</td>
<td>0.77</td>
</tr>
<tr>
<td>K.J. Tiwari et al. [15]</td>
<td>Electron beam</td>
<td>42.14</td>
<td>57.86</td>
<td>0.73</td>
</tr>
<tr>
<td>R. Tang et al. [16]</td>
<td>Magnetron sputtering</td>
<td>44.93</td>
<td>55.07</td>
<td>0.82</td>
</tr>
<tr>
<td>Ideal Sb$_2$Se$_3$</td>
<td></td>
<td>40.00</td>
<td>60.00</td>
<td>0.67</td>
</tr>
</tbody>
</table>

**Table 2.** Electrical output for as-deposited and post-annealed sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>233</td>
<td>12.01</td>
<td>31.96</td>
<td>0.90</td>
</tr>
<tr>
<td>Post-Annealed</td>
<td>291</td>
<td>17.20</td>
<td>32.80</td>
<td>1.64</td>
</tr>
</tbody>
</table>
observed, leading to a conversion efficiency improvement from 0.9 % to 1.6 %. A possible explanation for the increase in Jsc could be attributed to the change in crystal orientation as discussed in section 3.

The increase in Jsc was also confirmed from EQE (not shown here), where an improvement in the blue region was recorded. The spectral response for the AD sample peaked at around 60 % at around 820nm, while the PA sample showed higher spectral response, peaking at 70 % in the wavelength range from 400 nm to 900 nm. The energy band gap (Eg) from the EQE spectra was determined by plotting [hν × ln(1-EQE)]² against hν, giving a value of 1.19 eV for both AD and PA samples, which is in agreement with previously reported Sb₂Se₃ band gap values.

Conclusion

A superstrate Sb₂Se₃/CdS device has been successfully deposited by thermal evaporation and chemical bath techniques, respectively. Once exposed to a post-annealing treatment, the device conversion efficiency improved by 0.74 %, as a result of a 25 % and 43 % increase in Voc and Jsc, respectively. The post-annealed device has a high proportion of (221) crystal orientation with little to no influence of horizontally stacked (020) orientated crystals. With a slight increase in the grain size for the post annealed sample, it is likely that recrystallization has taken place which may have contributed to the improvement of the device performance. Further investigation will be needed to confirm the causes for these increase in electrical output.

References