SnSe Solar Cells: Current Results and Perspectives

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Abstract This work presents current advances and perspectives on SnSe thin film solar cell technology. Nowadays, SnSe solar cells have not been able to achieve efficiency values higher than 7%. In this sense, it is necessary to study the potentiality of SnSe compound in solar cells that could help to understand further routes to promote this technology. It is demonstrated that efficiencies about 25% are expected under the ideal conditions of a low density of defects at SnSe bulk, the SnSe/buffer interface and the use of a buffer layer with a high band-gap, so that most photons get absorbed in the SnSe material with a good lattice matching to the SnSe and the negligible contribution of resistances. The comparison of our results with the one experimentally reported demonstrates that J_sc values constitute the first main issue to be solved in this technology.

Keywords SnSe solar cells, theoretical calculations, radiative limit, limiting factors

The current thin film solar cell technology is dominated by absorber compounds such as CdTe and CuInGaSe₂. However, the toxicity of Cd together with the low abundance of In, Ga, and Te in the Earth’s crust has raised the need to study new compounds to replace them. Recently, compounds such as kesterites and perovskites have been widely studied and proposed for replacing previous technologies in solar cell fabrication due to their adequate physical properties for solar cell processing. However, the formation of defects, secondary phases, and poor band-alignment have been identified as main drawbacks concerning the Kesteritces technology, resulting in efficiency values lower than 12.6%. On the other hand, despite high efficiencies that have been achieved in perovskite solar cells, the toxicity of Pb and the instability of the compound remain as the main concerns to be further studied. Therefore, other materials based on abundant and low toxic elements, fulfilling the basic properties for solar cell applications are being studied.

The SnSe semiconductor is among the new compounds that have been currently studied for solar cell applications. This compound consists of elements with a relative abundance in the Earth’s crust and low toxicity. It also shows p-type conductivity, direct band-gap transitions with an absorption coefficient higher than 10⁴ cm⁻¹, and a band-gap near 1.0 eV. It also presents an orthorhombic structure (spatial group Pnma), with lattice constant values of a = 11.52 Å, b = 4.16 Å, and c = 4.42 Å. The p-type conductivity of SnSe is mainly a result of Sn vacancies (VSn), therefore, there is no need for doping this compound with extra elements. Another important feature is that unlike kesterite compounds, better control of the phase is expected as a result of the two constituent elements, while in the case of kesterite materials consisting of at least four elements, secondary phases are prone to be formed.

The SnSe compound has been deposited by many physical and chemical deposition techniques. The main physical deposition methods for SnSe material are the two-stage process and evaporation, whereas chemical bath deposition, electrodeposition, and spray pyrolysis stand for chemical routes. Each technique has its own advantages and disadvantages. Physical techniques such as the described above relatively depend on few parameters and allow to finely control crystallinity as well as morphological and electrical properties. On the other hand, chemical routes depend on a greater number of parameters, and the effect they have on film growth and properties is less predictable than in physical routes. However, in general, low-cost deposition techniques are used for SnSe deposition, which can result in reduced values of cost per watt peak.

The first report on the fabrication of SnSe solar cells was presented in 1990 by Singh et al., where authors deposited SnO₂:F (FTO) onto a glass substrate by spray pyrolysis and later cleaned it chemically and ultrasonically, followed by the sequential deposition of Se and SnSe by thermal evaporation and finally a layer of Ag was deposited on SnSe, as the contact. The maximum efficiency reported was 2.3% with an open-circuit voltage, short-circuit current density and fill factor (FF) values of 0.41 V, 9.2 mA/cm² and 0.49, respectively. I-V characteristics were mainly attributed to the variation of the Se layer thickness. FTO/Se/SnSe heterojunctions with thinner Se layers showed a better efficiency, greater fill factor as well as a greater open-circuit voltage. However, poor values of short-circuit current density were obtained for these thicknesses, so non-specified improvement in fabrication parameters were suggested to increase efficiency. The results on open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and efficiency (η) of processed cells are summarized in Table 1.

Matthews fabricated the first inorganic solar cell with CdS as the n-type buffer layer, following the FTO/CdS/SnSe/graphite configuration, reporting a Jsc of 0.7 mA/cm², a Voc of 140 mV.
and conversion efficiency of 0.03% under the illumination of 100 mW/cm².\textsuperscript{[8]} The author quoted that such a reduced efficiency value is likely to be related to a high density of defects, resulting in a high recombination rate at the CdS/SnSe interface.

Other works have been published on the application of SnSe thin film in solar cells. Shinde et al. fabricated solar cells with different configurations. For ITO/CdS (100 nm)/SnSe (800 nm)/polysulfide/Pt/FTO configuration, where SnSe was grown by electrodeposition, an efficiency of 1.4% was reported.\textsuperscript{[8]} This value was higher than the one obtained for a solar cell with ITO/CdS (100 nm)/SnSe (800 nm)/Au (100 nm) configuration of 0.8% under 100 mW/cm². According to Shinde et al., the photovoltaic performance is influenced by the conductivity, compactness, and uniformity of the film as well as the quality of the contact between layers. Polysulfide electrolytes present in the liquid junction significantly increased the efficiency since the conductivity was improved and consequently, the recombination losses were reduced. Better performance with respect to previous works was achieved by improving the quality of the junction to prevent leakage current and recombination at the grain boundaries, which increased fill factor (FF) and open circuit voltage (Voc) values. However, it was suggested to optimize parameters such as layer thickness, annealing temperature, and device structure to improve the characteristics of SnSe-based devices. On the other hand, Makori et al. reported the fabrication of solar cells with glass substrate/Ag/CdO:SnSnSe (148 nm)/Ag structure, where SnSe was deposited by thermal evaporation, resulting in a short-circuit current, open-circuit voltage, fill factor and efficiency values of 0.993 mA, 273 mV, 0.69 and 0.59%, respectively.\textsuperscript{[10]} Although the physical phenomena behind such characteristics were not described, the authors suggested three possible routes to increase the conversion efficiency in SnSe solar cells including optimizing the deposition temperature of the SnSe films, designing multi-layered solar cells using SnSe, and varying the ohmic contact materials.

So far, one of the highest SnSe solar cell efficiencies reported in the literature was presented by Abd El-Rahman et al., where Si is used as the n-type semiconductor buffer layer.\textsuperscript{[11]} Under an illumination source of 50 mW/cm², values of efficiency, open-circuit voltage, short-circuit current density, and fill factor of 6.44%, 425 mV, 17.23 mA/cm², and 0.44 were measured, respectively. Few suggestions were made concerning the paths than can be followed to improve the characteristics of the cell. According to the authors, corrections to light reflection and transmission could be carried out as an effort to achieve better characteristics.

Table 1 The results on Voc, Jsc, FF, and η of SnSe solar cells processed under the glass substrate/FTO/Se/SnSe/Ag configuration.\textsuperscript{[6]}

| Number of cells | Voc/V | Jsc/(mA/cm²) | FF | η/% |
|-----------------|-------|--------------|----|-----|
| FTTS-3          | 0.41  | 9.2          | 0.49| 2.3 |
| FTTS-9          | 0.39  | 10.8         | 0.43| 2.2 |
| FTTS-12         | 0.33  | 12.4         | 0.37| 1.9 |

Table 1: The results on Voc, Jsc, FF, and η of SnSe solar cells processed under the glass substrate/FTO/Se/SnSe/Ag configuration.\textsuperscript{[6]} The impact of SnSe thickness on open-circuit voltage, short-circuit current density, and efficiency is illustrated in Figure 1. It is observed that maximum open-circuit voltage values in the range of 624—702 mV are expected under the radiative limit. Taking the experimental results into account, it is pointed out that Voc is almost reduced by 300 mV, which is a result of the role that the formation of defects is playing, increasing carrier recombination and thereby reducing Voc of experimental solar cells. An interesting result is that SnSe solar cells can provide maximum Jsc value of 47.6 mA/cm² for SnSe thicknesses higher than 2 μm. This implies losses of almost 30 mA/cm² in experimental cells. In the theoretical calculations, fill factor values in the range of 0.83—0.85 are found (not shown), while experimental values lower than 0.5 have been reported elsewhere. In addition, maximum efficiency of 25.6% is expected for a SnSe thickness of 1 μm as illustrated in Figure 1. This value has not been reached experimentally due to the reduced Voc, Jsc, and FF reported. In this sense, this value stands for the goal of the scientific community.

From the comparison between results summarized in Ref. [6] for different SnSe solar cells and the theoretically expected values illustrated in Figure 1, it can be concluded that the first limiting factor concerning this technology is the reduced Jsc.

Some of the factors that produce Jsc losses are reflection, very short minority carrier lifetimes, and diffusion lengths, and a high density of defects that might contribute to the poor carrier collection. In particular, the influence of defects and the presence of non-ideal band-alignment and non-ideal contacts can inhibit carrier transport. If a high defect density is formed, carriers would recombine, thereby reducing Voc and resulting in poor carrier diffusion length and mobility values. In addition, the presence of an ideal spike-like alignment with a relatively low band offset and ideal contacts are also mandatory to guarantee the correct carrier collection. In this sense, further
Conflicts of Interest

The authors declare no conflict of interest.

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