State of the Art on $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ Thin Film Solar Cells

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Abstract The $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ compound has received considerable attention in photovoltaic applications due to its physical properties and for containing abundant non-toxic elements. However, solar cells based on this material present low efficiencies. In this work, we review some of the physical properties reported for the semiconductors Sb_2S_3 , Sb_2Se_3 and $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$, and the main techniques of film deposition of the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ ternary material along with the reported efficiencies. Finally, a brief review of the scarce theoretical analyses of the main properties of this semiconductor (refractive index, band-gap energy, absorption coefficient and recombination) is presented. This review remarks the need of more theoretical analyses and modeling to optimize and improve the fabrication processes of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ solar cells in order to reach better conversion efficiencies.

Keywords $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ solar cells, thin-film solar cells, deposition techniques, solar cell modeling, semiconductor physical properties

Introduction

One of the main concerns in modern society is to find a renewable source of energy that can replace (at least partially) the use of fossil fuels. Among the renewable sources of energy, solar energy is perhaps the one with the greatest potential, thus a great amount of research have been focused on the development of efficient, cheaper and cleaner solar cells.

Within the variables that need to be considered in the design of solar cells, the choice of semiconductor materials is crucial. It's desirable to use a material able to absorb most of the incident photons in the solar cell, in order to generate electric power.^[1] One of such materials is silicon, which has been employed in first generation solar cells, achieving conversion efficiencies above 20%.^[2] Despite of these high efficiencies, these type of solar cells have a low indirect band-gap of around 1.12 eV, which make it a non-ideal absorbing material,^[3] requiring thick absorbent layers of approximately 500 μm ^[4] and increasing its production cost.^[5] In the so called second generation thin-film solar cells,^[6] conversion efficiencies of around 22% have been reported.^[2,7] This type of solar cells are commonly based on either toxic elements such as Cd or low abundance elements such as In and Te.^[4]

To overcome the drawbacks of solar cells based on Si, CdTe and CIGS, materials with suitable physical properties (direct band-gap transitions, high absorption coefficient, p-type conductivity) and low production cost, have been proposed.^[8] Among these materials, we can find the kesterite family, which has been described as non-toxic compounds. However, the reported conversion efficiencies are around 12%.^[2] These relatively low efficiencies can be ascribed to the formation of secondary phases, bulk defects and band-alignment among other factors.^[9] On the other hand, perovskite solar cells have achieved conversion efficiencies above 20%,^[2] but their insta-

bility with humidity and high temperature constitutes an important cons in this technology.^[6] Besides, this type of cells contain lead (for instance, methylammonium lead halide perovskites) in a soluble state,^[10,11] which is another major drawback as lead has been recognized as a health-menace widespread toxic pollutant.^[12-14]

Semiconductor materials such as Sb_2S_3 , Sb_2Se_3 and $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ have emerged as promising materials for solar cell applications because they contain abundant elements of the earth crust, have lower production cost than first generation cells, contain non-toxic elements, and don't degrade as a result of temperature and humidity.^[6,15] These type of materials have other attractive features such as a p-type conductivity, direct band-gap transitions and a relatively high absorption coefficient.^[16-18] Although the available experimental measurements of conversion efficiencies point to ~3.6%—7.6%,^[19-27] a recent theoretical modeling of solar cells based on $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ shows that higher efficiencies of up to 28% can be achieved through variation of the Se/(S+Se) compositional ratio.^[28]

Given the importance of the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ semiconductor material in the develop of more efficient solar cells, a minireview of the physical properties of the Sb_2S_3 , Sb_2Se_3 , $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ semiconductor materials is presented, along with a review of the main deposition techniques to synthesize them. In addition, a summary of a previous theoretical analysis of solar cells based on $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ semiconductor is presented, which could contribute to a further efficiency promotion.

Physical Properties of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ Thin Films

The Sb_2S_3 and Sb_2Se_3 compounds are isomorphous and have the same orthorhombic crystalline structure (Figure 1 and Table 1). A S atom can be replaced by a Se atom to build up the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ ternary compound.^[6,19,23,29,30] An important fea-

ture of the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ compound is the tunable band-gap that can be varied through the Se/(S+Se) compositional ratio. The reported band-gap values for Sb_2S_3 and Sb_2Se_3 are around 1.7 and 1.1 eV, respectively,^[18,24] thus a band-gap that lies between these two values can be obtained for the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ compound (Figure 2).^[22] Even though these band-gap values aren't in the Shockley-Queisser limit,^[31] it's expected that the band-gap of the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ compound gets near to an optimal band-gap, reaching a conversion efficiency about 32%.^[6,23,32]

Figure 1 Orthorhombic crystal structure of $\text{Sb}_2\text{S}(\text{Se})_3$ compound. The yellow spheres represent S(Se) atoms while purple ones represent Sb atoms.

Figure 2 Band structure scheme for the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ based solar cells. The energy levels are referred to the vacuum level.^[22]

Table 1 Lattice parameters of the Sb_2S_3 and Sb_2Se_3 semiconductor compounds

Semiconductor ^[19,30]	a/nm	b/nm	c/nm
Sb_2S_3	1.12	1.13	0.38
Sb_2Se_3	1.16	1.18	0.40

Some of the measured properties of the Sb_2S_3 and Sb_2Se_3 compound that are of interest and commonly employed for the modeling of solar cells are shown in Table 2.

Table 2 Some physical properties measured for Sb_2S_3 and Sb_2Se_3 semiconductors and their applications to solar cells

Properties	Sb_2S_3	Sb_2Se_3	Ref.
Series resistances/ $(\Omega \cdot \text{cm}^2)$	50.9	21.1	[22]
Shunt resistance/ $(\Omega \cdot \text{cm}^2)$	103.9	54.0	[22]
Absorber minority carrier lifetime/ns	6.77	67	[33, 34]
Absorber minority carrier mobility/ $(\text{cm}^2/\text{V} \cdot \text{s})$	10.0	16.9	[17, 34]
Absorber acceptor concentration/ (cm^{-3})	10^{12}	10^{15}	[6, 35]
Absorber electron effective mass	$1.035 m_e$	—	[36]
Absorber hole effective mass	$1.843 m_e$	—	[36]
Relative dielectric permittivity	8.85	18.0	[17, 34]
Refractive index	3.4	4.4	[16]

Optical properties of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ thin films

The refractive index can be calculated through the following relationship:^[16]

$$n = \left[\left(2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \right) + \left(\left(2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \right)^2 - n_2^2 \right)^{1/2} \right]^{1/2}$$

where T_M and T_m are the maximum and minimum transmittance, and n is the refractive index of the substrate. In that paper, the author observed that the refractive index decreases with the increase of S concentration and the wavelength. On the other side, the author mentioned that the values of the refractive index could be of great help in the determination of the film thicknesses through the relation as follows:

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$

where n_1 and n_2 are the refractive indices of two adjacent maxima (or minima) in λ_1 and λ_2 . Finally, once the values of the refractive indices and the thicknesses of the films were determined, the author was able to calculate the absorption coefficient (not reproduced here). It shows that the absorption coefficient decreases with the increase of Se and presents two absorption regions. In one region, the absorption coefficient increases slightly till 10^4 cm^{-1} below the energy of the photon $\sim 1.5 \text{ eV}$. In another region, it increases until reaching a constant value of around 10^5 cm^{-1} above 1.9 eV .

Another reported result was the lattice parameters of the ternary $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ (Table 1). The measurements of X-ray diffraction show that Vegard's law is given by:

$$c(x) = \frac{x}{3}c(\text{Sb}_2\text{S}_3) + \frac{3-x}{3}c(\text{Sb}_2\text{Se}_3)$$

where $c(\text{Sb}_2\text{Se}_3)$, $c(\text{Sb}_2\text{S}_3)$ and $c(x)$ are the respective c -axis lattice constants of the orthorhombic structures. It gives good approximations of the lattice parameters in agreement with the results of X-ray measurements of Deng Z. *et al.*^[30] and Deng H. *et al.*^[19]

Synthesis Techniques of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ Thin Films and Solar Cells

The synthesis of Sb_2S_3 and Sb_2Se_3 compounds for solar cell devices has been reported employing mainly the following techniques: chemical bath deposition (CBD),^[37-43] thermal and rapid thermal evaporation,^[34,35,44-49] spin coating,^[50,51] vapor transport deposition,^[21,52,53] and magnetron sputtering deposition.^[53,54] Though these compounds own their own interesting properties, $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ compound has a greater potential to solar cells application as previously mentioned. Therefore, great efforts have been done to synthesize the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ absorbing material and optimize the efficiency of the resulting device in recent years. Then, we will review the main reports of the synthesis of the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ compound and its application to solar cell devices.

One of the first reports on the synthesis of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ thin films was made by El-Sayad.^[16] In this work, thin films were deposited by means of thermal evaporation. Thin films of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ with $x = 0, 1, 2$ and 3 were successfully formed (confirmed with energy dispersion analysis). In their measurements, they found that the band-gap increases nearly quadratically with the increase of sulfur content in the film with respect to the Se concentration, following the relationship $E_g(x) = 0.02x^2 + 0.137x + 1.292$ eV.

As far as we know, the first report to produce $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ material in large scale was presented by Deng *et al.*^[30] They synthesized for the first time $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ nanotubes using a colloidal synthetic technique. Similar to the findings of El-Sayad,^[16] they found a quadratic relationship between the band-gap of the compound and its sulfur to selenium compositional ratio, showing that changing the S concentration in the compound $\text{Sb}_2\text{Se}_{3-x}\text{S}_x$ leads to an increase in the band-gap from 1.18 eV (the Sb_2Se_3 case) to 1.63 eV (the Sb_2S_3 case), this change followed the $E_g(x) = 0.0344x^2 + 0.0481x + 1.18$ eV equation. Furthermore, they reported the lattice constants of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ and showed that they vary linearly as a function of the sulfur concentration.

Another approach for fabrication of $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ based solar cells is the sequential deposition of semiconductor layers of Sb_2S_3 and Sb_2Se_3 in a step-wise manner. Choi *et al.*^[25] proposed a method to obtain efficient graded $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ absorber material through the sequential deposition of a Sb_2Se_3 layer (using spin coating method), which was followed by the deposition of a Sb_2S_3 layer (through CBD) onto the surface of a mesoporous TiO_2 . The best device produced by this group could reach a conversion efficiency of 6.6%, which is the maximum efficiency reported so far. Though a higher efficiency of 7.5% was reported by the same group under 50% solar irradiation, this was achieved under 100% solar irradiation. We show a brief summary of the efficiencies that have been reported for various devices in Figure 3.

Yang and coworkers^[18] were devoted to obtaining polycrystalline $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ films for photovoltaic applications. With this purpose, they fabricated the films with the aid of Sb-Se-S-hydrazine solutions that were spin coated onto a TiO_2 substrate. They were able to form and characterize films with compositions of $x = 0.14, 0.33, 0.51, 0.70, 0.85, 0.96$ and 0.99 . When varying the Se concentration in the $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ films in the range $0 \leq x \leq 1$, there is a quadratic dependence on the band-gap that follows the relation $E_g(x) = 0.118x^2 - 0.662x + 1.621$ eV. This indicates that the non-linear dependency can be ascribed to the variation in the lattice parameters that can change the band structure or due to the different electronegativity of the atoms of the compound.

Figure 3 Efficiencies of the solar cells mentioned in main text. Values taken from Refs. [19, 22-27, 56-58]. ^a The authors don't mention the exact composition of the devices.

Peréz-Martínez *et al.*^[26] reported a simple four step procedure based on chemical bath deposition and thermal evaporation to prepare transparent conductive oxide solar cells (FTO)/CdS/ $\text{Sb}_2\text{S}_x\text{Se}_{3-x}$ /C-Ag. They were able to make thin films with different sulfide-selenide compositions and reported that the best conversion efficiency of 3.6% is achieved when the S to Se ratios are nearly 1 ($\text{Sb}_2\text{S}_{1.5}\text{Se}_{1.5}$). Furthermore, they argue that their procedure of preparing these solar cells is made widely accessible. Recently, an effort to synthesize carbon electrode based FTO/CdS/ $\text{Sb}_2(\text{S},\text{Se})_3$ /carbon devices through the CBD and post-selenization method has been made by Wang *et al.*^[56] The maximum obtained efficiencies are relatively low (2.64%).

Yang *et al.* made crystalline $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ semiconductor absorbing material by rapid thermal evaporation (RTE).^[23] In the process of preparation, they add simply a sulfur powder *in situ* and fabricate superstrate solar cells (ITO/CdS/ $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ /Au). The maximum conversion efficiency obtained was 5.79% with a compositional of 0.20 for sulfur and 0.8 for selenium in the absorbing layer. More recently, Ishaq *et al.*^[57] employing RTE with a single source of mixed powders of Sb_2S_3 and Sb_2Se_3 , and double buffer layer (ZnO/CdS), were able to synthesize $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ solar cells. The champion device ($\text{Sb}_2(\text{S}_{0.32}\text{Se}_{0.68})_3$) showed a maximum efficiency of 5.73%. Following the proposal of employing a double buffer layer, Wang *et al.*^[58] fabricated $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ solar cells by a hydro-thermal and post-selenization method. They obtained ITO/ TiO_2 /CdS/ $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ devices with a maximum efficiency of 5.77%.

The preparation of planar heterojunction solar cells based on selenium-graded $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ was reported by Zahng *et al.*^[22] They obtained selenium-graded films by a technique, in which a solution of Se is spin-coated over a Sb_2S_3 film. The solution is then evaporated by low temperature annealing, and finally the S is diffused on the film by thermal annealing. They obtained $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ films with a higher concentration of Se near the surface. Their performance tests show that films with more S had a high voltage output, while the spectral response can reach longer wavelengths with more Se concentration, allowing them to reach a conversion efficiency of 5.71%. Figure 4 shows this behavior through the J-V characteristics and the incident photon-to-current conversion efficiency (IPCE), for its best appreciation.

Figure 4 (a) J-V characteristic of the Sb₂(S_{1-x}, Se_x)₃, Sb₂S₃ and Sb₂Se₃ devices; (b) IPCE of the Sb₂(S_{1-x}, Se_x)₃, Sb₂S₃ and Sb₂Se₃ devices. Figure taken from Ref. [20]

Jaramillo-Quintero *et al.*^[27] evaluated the effect that the buffer layers c-CdS and c-TiO₂ and the combination cd-TiO₂/c-CdS has in multilayer thin film solar cells with the absorber material Sb₂(S_xSe_{1-x})₃. The latter was deposited on the buffer layers through thermal vacuum evaporation. They showed that a maximum conversion efficiency of around 5.47% can be reached with a FTO/c-TiO₂/c-CdS/Sb₂(S_{0.47}Se_{0.53})₃/C/Ag structure in the solar cell, probing that using the right buffer layer, or its combination with CdS, causes the electron recombination processes to decrease.

Another proposal for the fabrication of sulfide-selenite solar cells, is the use of naturally abundant minerals. That is the case of Nair *et al.*^[24] who made thin-film solar cells through thermal evaporation of Stibnite mineral (Sb₂S₃) added with Sb₂Se₃ powder. The more efficient solar cells in this study were the ones with a composition of Sb₂S_{0.5}Se_{2.5} showing a power conversion efficiency of 4.24%.

Deng *et al.*^[19] were able to deposit a film of Sb₂(Se_xS_{1-x})₃ with a continuous x composition across the xy plane of the film. They employed a close-space-dual-plane-source evaporation to this aim. In this way, they could form a series of devices at once by putting a series of Au contacts on the surface of the film. This procedure is a proposal for the study of physical properties and optimization of composition of solar cells based on Sb₂(S_{1-x}Se_x)₃ in a more efficient way. They showed that the conversion efficiencies go from 1.8% to 5.6% and it decreases to 4.95% later as the Se composition increases. The maximum achieved efficiency was 5.6% for a composition of Sb₂(Se_{0.68}S_{0.32})₃. Their study also shows that there are shallow defects with a rich Se concentration, while the defects were deep for S rich concentrations.

Theoretical Analyses of Sb₂(S_{1-x}, Se_x)₃ Semiconductor Materials

The compound Sb₂(Se_{1-x}S_x)₃ has adequate physical properties, and the conversion efficiencies reported are in the range 5%—7.5% (see above). These low values can be due to volume defects in the absorber, an inadequate absorber/buffer band alignment, reflection losses and high series resistance or low values of shunt resistance, implying a great probability of recombination in the solar cell affecting its conversion efficiency. Until now, very little effort has been put to understand from a theoretical point of view the impact of the different mechanisms of recombination in the output efficiency of the solar cell. To the best of our knowledge, no study has addressed this issue prior to our work.^[28] We have reported for the first time a theoretical study to seek for an explanation of the origin of these low efficiencies. We have modelled Sb₂(Se_{1-x}S_x)₃ under the radiative and non-radiative limit varying the compositional ratio Se/(S+Se) in a range of 0 ≤ x ≤ 1 and the thickness of the absorber. We disclosed that the conversion efficiency can reach values of around 18%—29% for solar cells of Sb₂(Se_{1-x}S_x)₃ with thicknesses of 0.3—3 μm, depending on the incorporation of sele-

num. However, a maximum efficiency of 29% is achieved considering a thickness greater than 1.5 μm and with an optimal compositional rate about 0.4 under the radiative limit (Figure 5a).

Figure 5 Efficiency of Sb₂(S_{1-x}, Se_x)₃ solar cell considering Se/(S+Se) compositional ratio as a function of (a) absorber thickness under the radiative limit, (b) minority carrier lifetime.^[28]

On the other hand, we made the analysis of the possible impact of recombination centers under the non-radiative limit employing the Shockley-Read-Hall theory.^[59] We found that the conversion efficiency decays from 28% (absorber with a minority carrier lifetime of 1 ns) to 2% for very low minority carrier lifetimes of around 10⁻¹⁰ s (Figure 5b). This indicates that there are more carrier losses due to the reduction of the band gap with a greater concentration of Se (Figure 5b), implying that especial attention has to be given to fabricate absorber layers with a greater crystalline quality in order to obtain better efficiencies in solar cells of Sb₂(Se_{1-x}S_x)₃.

This work represents the first approach to tackle the theoretical modeling of Sb₂(Se_{1-x}S_x)₃ based solar cells. However, we are aware that it is necessary to model not only the absorber material but also the whole cell and take into account how the recombination mechanisms are affected by the material that make up the solar cell. Further research in this matter is currently been done by our group.

Conclusions

In this work, a mini-review of the main physical properties of the semiconductor Sb₂(Se_{1-x}S_x)₃ is presented. A special emphasis has been made on the reports of deposition techniques to obtain films of this material. Through years, the maximum conversion efficiencies of synthesized solar cells seem to converge to a value of around 7%. However, recent solar cell theoretical modeling indicates that higher values of around 29% can be achieved with an optimal Se/S compositional ratio and optimal film thickness. Nevertheless, the theoretical modeling efforts are quite scarce, and more works are needed in order to comprehend the physical process occurring in the solar cell that hinders its performance. We hope that this work helps and foster further investigations on this matter.

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