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

Thalía Jiménez,$^{a,b}$ C. I. León-Pimentel,$^b$ Diego Seuret-Jiménez,$^a$ and Maykel Courel$^c$

$^a$ Centro de Investigación en Ingeniería y Ciencias Aplicadas (CICAp), Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos, 62209, México
$^b$ Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México (UNAM), Apdo. Postal 48-3, Cuernavaca, Morelos 62251, México
$^c$ Departamento de Ciencias Naturales y Exactas, Centro Universitario de los Valles (CUNivales), Universidad de Guadalajara, Carretera Guadalajara-Amecá Km. 45.5, C.P. 46600, Amecá, Jalisco, México

Email: jimenezthalia57@gmail.com (T. J.)

Abstract The Sb$_2$(S$_{1-x}$, 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$_2$S$_3$, Sb$_2$Se$_3$, and Sb$_2$(S$_{1-x}$, Se$_x$)$_3$, and the main techniques of film deposition of the Sb$_2$(S$_{1-x}$, 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 Sb$_2$(S$_{1-x}$, Se$_x$)$_3$ solar cells in order to reach better conversion efficiencies.

Keywords Sb$_2$(S$_{1-x}$, 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\%.\(^2\)\(^3\) 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 absorbtion 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%.\(^2\)\(^8\) These relatively low efficiencies can be ascribed to the formation of secondary phases, bulk defects and band-alignment among other factors.\(^8\) On the other hand, perovskite solar cells have achieved conversion efficiencies above 20%,\(^2\) but their instability 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.\(^12,13\)

Semiconductor materials such as Sb$_2$Sn$_2$, Sb$_2$Se$_3$, and Sb$_2$(S$_{1-x}$, 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.\(^14,15\) These type of materials have other attractive features such as a p-type conductivity, direct band-gap transitions and a relatively high absorption coefficient.\(^16,17\) Although the available experimental measurements of conversion efficiencies point to ~3.6%—7.6%,\(^18,19\) a recent theoretical modeling of solar cells based on Sb$_2$(S$_{1-x}$, Se$_x$)$_3$ shows that higher efficiencies of up to 28% can be achieved through variation of the Se/(S+Se) compositional ratio.\(^20\)

Given the importance of the Sb$_2$(S$_{1-x}$, Se$_x$)$_3$ semiconductor material in the development of more efficient solar cells, a minireview of the physical properties of the Sb$_2$S$_3$, Sb$_2$Se$_3$, Sb$_2$(S$_{1-x}$, 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 Sb$_2$(S$_{1-x}$, Se$_x$)$_3$ semiconductor is presented, which could contribute to a further efficiency promotion.

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

The Sb$_2$S$_3$ and Sb$_2$Se$_3$ 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 Sb$_2$(S$_{1-x}$, Se$_x$)$_3$ ternary compound.\(^6,19,23,29,30\) An important fea-
Minireview

nature 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 $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{Se}_3$ 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).\(^{19}\) Even though these band-gap values aren’t in the Shockley-Queisser limit,\(^{25}\) 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 $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{Se}_3$ semiconductor compounds |
|--------------------------------------------------|-------|-------|-------|
| Semiconductor\(^{[19,30]}\) | $a$/nm | $b$/nm | $c$/nm |
| $\text{Sb}_2\text{S}_3$ | 1.12 | 1.13 | 0.38 |
| $\text{Sb}_2\text{Se}_3$ | 1.16 | 1.18 | 0.40 |

Some of the measured properties of the $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{Se}_3$ 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 $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{Se}_3$ semiconductors and their applications to solar cells |
|--------------------------------------------------|-------|-------|-------|
| Properties | $\text{Sb}_2\text{S}_3$ | $\text{Sb}_2\text{Se}_3$ | Ref. |
| Series resistance (Ω·cm\(^2\)) | 50.9 | 21.1 | [22] |
| Shunt resistance (Ω·cm\(^2\)) | 103.9 | 54.0 | [22] |
| Absorber minority carrier lifetime/µs | 6.77 | 67 | [33, 34] |
| Absorber minority carrier mobility (cm\(^2\)/Vs) | 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:\(^{[16]}\)

$$n = \left(\frac{2n_2 - n_1}{n_2 + n_1} + \frac{n_2^2 + 1}{2}\right) + \left(\frac{2n_2 - n_1}{n_2 + n_1} + \frac{n_2^2 + 1}{2}\right)^2 - n_2^{1/2}$$

where $n_1$ and $n_2$ 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 Se 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:

$$t = \frac{\lambda_1\lambda_2}{2(\lambda_1n_2 - \lambda_2n_1)}$$

where $n_1$ and $n_2$ are the refractive indices of two adjacent maxima (or minima) in $\lambda_1$ and $\lambda_2$. 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 $10^3$ cm\(^{-1}\) below the energy of the photon $\sim 1.5$ 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 $\text{Sb}_2(\text{Se}_{1-x}\text{S}_x)_3$ (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 $c(\text{Sb}_2\text{S}_3)$, $c(\text{Sb}_2\text{Se}_3)$ 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 $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ Thin Films and Solar Cells

The synthesis of $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{Se}_{2}\text{S}_3$ compounds for solar cell devices has been reported employing mainly the following techniques: chemical bath deposition (CBD),[21,22-25] thermal and rapid thermal evaporation,[26,27] spin coating,[28,29] vapor transport deposition,[30,31] and magnetron sputtering deposition.[32,33] Though these compounds own their own interesting properties, $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ compound has a greater potential to solar cells application as previously mentioned. Therefore, great efforts have been done to synthesize the $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ 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 $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ compound and its application to solar cell devices.

One of the first reports on the synthesis of $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ thin films was made by El-Sayed.[34] In this work, thin films were deposited by means of thermal evaporation. Thin films of $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ 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 $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ material in large scale was presented by Deng et al.[35] They synthesized for the first time $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ nanotubes using a colloidal synthetic technique. Similar to the findings of El-Sayed,[34] 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 $\text{Sb}_2\text{S}_3\text{S}_x$ leads to an increase in the band-gap from 1.18 eV (the $\text{Sb}_2\text{Se}_3$ case) to 1.63 eV (the $\text{Sb}_2\text{S}_3$ case), this change followed the $E_g(x) = 0.0344x^2 + 0.0481x + 1.16$ eV equation. Furthermore, they reported the lattice constants of $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ and showed that they vary linearly as a function of the sulfur concentration.

Another approach for fabrication of $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ based solar cells is the sequential deposition of semiconductor layers of $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{Se}_{3}\text{S}_x$ in a step-wise manner. Choi et al.[36] proposed a method to obtain efficient graded $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ absorber material through the sequential deposition of a $\text{Sb}_2\text{Se}_3$ layer (using spin coating method), which was followed by the deposition of a $\text{Sb}_2\text{S}_3$ 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[37] were devoted to obtaining polycrystalline $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ 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 $\text{Sb}_2(\text{S}_{1.\text{x}}, \text{Se}_{\text{x}})_3$ films in the range $0 \leq x \leq 1$, there is a quadratical dependence on the band-gap that follows the relation $E_g(x) = 0.118x^2 - 0.662x + 1.521$ eV. This indicates that the non-linear dependence 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](www.genchemistry.org)
There are shallow defects in the absorber and it decreases the support from the n—p junction. However, a maximum efficiency of 29% is achieved considering a thickness greater than 1.5 μm and with an optimal compositional ratio about 0.4 under the radiative limit (Figure 5a).

Figure 4  (a) J-V characteristic of the Sb₂(Sₓ₋₁, Seₓ)₃, Sb₂S₃ and Sb₂Se₃ devices; (b) IPCE of the Sb₂(Sₓ₋₁, Seₓ)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(SₓSeₓ)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(Sₓ₋₁,Seₓ)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-selenide solar cells, is the use of naturally abundant materials. That is the case of Nair et al.,[28] 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 Sb₂S₃:Sb₂Se₃ showing a power conversion efficiency of 4.24%.

Deng et al.[19] were able to deposit a film of Sb₂(Sₓ₋₁,Seₓ)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(Sₓ₋₁,Seₓ)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(Sₓ₋₁,Seₓ)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(Sₓ₋₁, Seₓ)₃ Semiconductor Materials

The compound Sb₂(Sₓ₋₁, Seₓ)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 absorbber/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(Sₓ₋₁,Seₓ)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(Sₓ₋₁,Seₓ)₃ with thicknesses of 0.3—3 μm, depending on the incorporation of selenium. However, a maximum efficiency of 29% is achieved considering a thickness greater than 1.5 μm and with an optimal compositional ratio about 0.4 under the radiative limit (Figure 5a).

Figure 5  Efficiency of Sb₂(Sₓ₋₁,Seₓ)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.[29] 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 10⁻¹³ 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(Sₓ₋₁,Seₓ)₃.

This work represents the first approach to tackle the theoretical modeling of Sb₂(Sₓ₋₁,Seₓ)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 being done by our group.

Conclusions

In this work, a mini-review of the main physical properties of the semiconductor Sb₂(Sₓ₋₁,Seₓ)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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