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## Electronic Conduction Mechanisms in Polycrystalline Antimony Selenide

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A study on the electronic conduction mechanisms and electrically active defects in polycrystalline  $Sb_2Se_3$  is presented. It is shown that, for temperatures above 200 K the electrical transport is dominated by thermal emission of free holes, ionized from shallow acceptors, over the inter-grain potential barriers. The temperature dependence of the holes mobility, limited by the inter-grain potential barriers, is the main contributor to the observed conductivity thermal activation energy. At lower temperatures, nearest-neighbour and Mott variable range hopping transport in the bulk of the grains are the dominant conduction mechanisms. Based on this study, the important parameters of the electronic structure of the  $Sb_2Se_3$  thin-film such as free hole density and mobility, inter-grain potential barrier height, inter-grain trap density, shallow acceptor ionization energy, acceptor density, net donor density

and compensation ratio are reported.

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## 1. INTRODUCTION

Recent research in the area of thin-film photovoltaics demands high-efficiency, low toxicity, earth-abundant and low-cost alternatives solar energy absorber materials. Traditional inorganic thin-film semiconductor such as cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) have achieved record power conversion efficiency over 22%<sup>[1,2]</sup>. Recently metal-halide perovskites (e.g.,  $CH_3NH_3PbI_3$ ) has attracted enough attention because of reported certified efficiencies (22%)<sup>[2]</sup> enabled by exceptional defect tolerance and potentially low manufacturing costs. However, due to the high cost of In and Ga, the mass production of CIGS thin-film solar cells would be challenging task, whereas, the Cd-based toxicity in CdTe could hinder the further development of CdTe. On the other hand, high toxicity of Pb and low thermal stability of the absorber layer are the major drawback for the commercialization of perovskite-based solar cells.

Recently antimony selenide ( $Sb_2Se_3$ ) has emerged as a promising material for high efficiency photovoltaic devices as it possess desirable band-gap ( $\approx 1.1$ - $1.3$  eV)<sup>[3-6]</sup>, high optical absorption coefficient of above  $10^5$   $cm^{-1}$  at short wavelength, decent carrier mobility ( $10$   $cm^2V^{-1}s^{-1}$ ) and long carrier lifetime. In addition, the non-toxic properties, natural abundance and the low-cost of the Sb and Se components make this material a potential candidate to replace CdTe and CIGS for the future development of solar cells. Although the  $Sb_2Se_3$  have been studied for only few years, its efficiency rapidly increased from 1.9 % to exceeding 7%<sup>[7-19]</sup>, with latest record efficiency around 7.6%<sup>[20,21]</sup>. Moreover, Li et al.<sup>[22]</sup> reported the highest ever 9.2% efficiency of the nanorod array solar cells employing junction interface engineering. However, theoretically calculated value of the power conversion efficiency of  $Sb_2Se_3$  thin-film photovoltaics can be as high as over 30%<sup>[10]</sup>, is yet to be achieved.

$Sb_2Se_3$  thin films can be prepared using different techniques such as vapor transport deposition,<sup>[7,9,12,20,21,23]</sup> electrodeposition,<sup>[24]</sup> thermal evaporation,<sup>[10,25-29]</sup> chemical molecular beam deposition (CMBD)<sup>[30]</sup>, radio frequency (RF) magnetron sputtering,<sup>[8,15,31-33]</sup> and close spaced sublimation (CSS)<sup>[6,14,18]</sup>. The optoelectronic properties of  $Sb_2Se_3$  are being extensively studied.<sup>[10,17,24,25,28,31,34-38]</sup> with purpose for the thin-film photovoltaic applications. Electrical transport characterization is one of the most common family methods to study the electronic properties of semiconductor materials and devices. In particular, Hall effect and resistivity measurements as a function of temperature provide valuable information about conduction mechanisms and parameters such as charge-carrier density, mobility and ionization energy. Additionally, it is necessary to acquire adequate knowledge of the trap and defect properties in the  $Sb_2Se_3$  thin-film semiconductor structure which have a direct influence in the transport phenomena of the charge carrier for improving the electrical and optical characteristics in the material and thus the solar cell efficiency. Nevertheless, due to the intrinsically low electrical

conductivity ( $10^6 - 10^7 S.cm^{-1}$ ), the absence of photoluminescence due its indirect bandgap and the strong anisotropy, the fundamental features of the thin-film  $Sb_2Se_3$  such as mobility, carrier lifetime, diffusion length, defect depth, defect density and optical band tails remain largely unexplored. However, there are just a very few experimental and theoretical electrical transport and defect studies of  $Sb_2Se_3$  thin films have been reported. [28,31,32,39-41].

In this work, a study of the conduction mechanism and electrically active defects in a  $Sb_2Se_3$  thin film prepared by *RF* sputtering is presented. It is shown that, at temperatures between 400 – 200 K the conductivity is dominated by thermal emission of free holes, ionized from shallow acceptors, over the inter-grain potential barriers (*GPB*). The temperature dependence of the holes mobility, limited by *GPB*, is the main contributor to the observed conductivity thermal activation energy. At low temperature nearest-neighbor hopping (*NNH*) and Mott variable range hopping (*M-VRH*), in the bulk of the grains, are the dominant conduction mechanisms. Based on this study important parameters related with the sample's electronic structure such as free hole density  $p$  and mobility  $\mu$ , *GPB* height, inter-grain trap density  $N_t$ , acceptors ionization energy  $E_{A0}$ , acceptors density  $N_A$ , net donors density  $N_D$ , and compensation ratio  $k$  are reported.

## 2. EXPERIMENTAL PROCEDURE

In this work, a  $Sb_2Se_3$  thin film sample were grown on a soda lime glass substrate (*SLG*) followed by a two-step growth process. First, a *Se*-poor *Sb – Se* thin film was sputtered from a  $Sb_2Se_3$  sputtering target (Stanford Advanced Materials) with a 99.99 % purity. Next, a rapid thermal annealing at 350 °C in  $H_2Se$  atmosphere during 15 minutes was performed to improve the stoichiometry of the sample. This methodology produces compact and *Se*-rich  $Sb_2Se_3$  films with a direct band gap energy of  $\simeq 1.0$  eV. A detailed discussion of the growth procedure, chemical and optical characterization of  $Sb_2Se_3$  thin films grown by the same procedure can be found further on. [25,31] The sample surface morphology was investigated by scanning electron microscopy (*SEM*), using a Nova Nano*SEM* 650 *SEM* system. The structural characterization was carried out by X-ray diffraction (*XRD*) measurements in Bragg Bretano configuration using a PanAnalytical X'pert *PRO MRD* system. The electrical transport properties of the sample were investigated by Hall effect and resistivity measurements as a function of temperature. A *Cr*(10 nm)/*Au*(100 nm) bilayer was thermally evaporated on the sample in order to produce good Ohmic contacts. The transport measurements were carried out in a low noise home made system. [42,43] Due to the very high resistivity and low mobility of the samples, Hall effect measurements were carried out only between 340 K and 400 K, while resistivity measurements were performed in the broad 50 – 400 K temperature range.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the surface morphology of the sample as sputtered a) and after annealing b). A clear increase in the grain size induced by the annealing can be observed. A *XRD* diffractogram of the sample is also presented in c), showing the orthorhombic *Pnma* (62)  $Sb_2Se_3$  phase.<sup>[44]</sup> No other crystal phases were detected in the sample.

The results of the Hall effect measurements are shown in Figure 2, where the Hall scattering factor has been considered unitary.<sup>[45]</sup> The sample presents a p-type conductivity with the expected rise of  $p$  with temperature. However, the hole mobility increases exponentially with temperature. This behavior is the opposite to the one expected for a monocrystalline semiconductor materials for which, at high temperature, the mobility decreases with temperature following an approximate  $T^{-3/2}$  power law.

The temperature dependence of the mobility in our sample indicates a strong effect of the *GPB* which can be expressed as:<sup>[46-48]</sup>

$$\mu_{GB}(T) = \mu_0 T^{-1/2} e^{(-\phi/k_B T)} \quad (1)$$

where  $\mu_{GB}$  is the *GPB* limited mobility,  $\mu_0$  is a constant,  $k_B$  is the Boltzmann's constant and the exponential factor describes the thermal activation of the carriers mobility flowing over the *GPB* with height  $\phi$ .

In polycrystalline thin films the inter-grain boundary is a complex structure, usually consisting of a few atomic layers of disordered atoms, which represents a transitional region between the different orientations of neighbouring crystallites.<sup>[49]</sup> The large number of defects, due to incomplete atomic bonding in the inter-grain boundary, results in the formation of trapping states that capture carriers and thereby immobilize them. Figure 2c) shows the potential energy barrier at the boundary between two grains,  $\phi$ , which impedes the motion of carriers from one crystallite to another, thereby reducing their mobility. In polycrystalline thin films the *GPB* height can be calculated as:<sup>[47]</sup>

$$\phi = \frac{e^2 N_t^2}{8\epsilon_r \epsilon_0 p} \quad (2)$$

where  $e$  is the electron charge,  $\epsilon_r$  is the relative dielectric constant of  $Sb_2Se_3$ ,  $\epsilon_0$  is the vacuum permittivity and  $N_t$  is the inter-grain trap density.

By fitting the Hall mobility data with Eq. (1) values of  $\phi = 391$  meV and  $\mu_0 = 1.1 \times 10^6 \sqrt{K} \text{cm}^2/\text{Vs}$  were obtained. Now, considering the average experimental value of  $p = 5.0 \times 10^{15} \text{ cm}^{-3}$ , and the average value of  $\epsilon_r = 14.8$  a trap density of  $N_t = 3.4 \times 10^{11} \text{ cm}^{-2}$  is found.<sup>[50]</sup> This value is much lower

than the corresponding values for polycrystalline Si ( $3 \times 10^{12} \text{ cm}^{-2}$ ) and *CZTS* ( $1.7 \times 10^{12} \text{ cm}^{-2}$ ). [48,49]

In recent studies, the conductivity of *Sb<sub>2</sub>Se<sub>3</sub>* polycrystalline thin films at high temperatures ( $T > 250 \text{ K}$ ) has been associated with intrinsic excitation,<sup>[31,38,51]</sup> i.e. the thermal excitation of electrons directly from the valence band to the conduction band. This interpretation is based on the fact that the conductivity thermal activation energy is very similar to half of the band gap value of the material ( $\simeq 0.5 \text{ eV}$ ). In our case, the thermal activation energy of the conductivity is equal to 485 meV (see inset in Fig. 3), very close to the half of the sample band gap energy. However, as already shown, in our sample large part (391 meV) of the conductivity thermal activation energy is due to the temperature dependence of the holes mobility. Therefore, we should discard the hypothesis of intrinsic excitation and consider that the high temperature conduction in our *Sb<sub>2</sub>Se<sub>3</sub>* sample is due to the thermal emission of free holes, ionized from shallow acceptors, over the *GPB*.

Figure 3 shows the temperature dependence of the electrical resistivity ( $\rho(T)$ ). The changes in the slope of the resistivity curve at approximately 200 K and 110 K indicate that another two different conduction mechanisms are present at this temperature range. Two types of electrical conduction mechanisms are commonly observed in polycrystalline semiconductors.<sup>[42,43,46–48]</sup> At high temperatures, the conduction can be described by the thermal emission of carriers over the *GPB*.<sup>[46–48]</sup> On the other hand, at low temperatures, the conductivity is explained in terms of hopping conduction associated with defects in the bandgap of the material. As will be shown in the following, in our case for  $T > 200 \text{ K}$  ( $1000/T > 5 \text{ K}^{-1}$ ) conduction mechanism is dominated by free charge carriers and below that temperature *NNH* and *M-VRH* conduction mechanisms plays a significant role.<sup>[47,48]</sup> At high temperature and in the diffusive regime, the temperature dependence of the resistivity can be expressed as:<sup>[46]</sup>

$$\rho_{GB}(T) = [e\mu_{GB}(T)p(T)]^{-1} \quad (3)$$

Considering the sample a nondegenerate semiconductor, as suggested by the strong temperature dependence of the resistivity data and the moderate free hole density at high temperatures, the free hole density in the bulk of the grains can be written as:<sup>[46]</sup>

$$p(T) = \frac{1}{2} (\phi_A + N_D) \left( \sqrt{1 + \frac{4\phi_A(N_A - N_D)}{(\phi_A + N_D)^2}} - 1 \right) \quad (4)$$

$$\phi_A = \frac{g_{A1}}{g_{A0}} N_v^{Eff} e^{\alpha_{A0}/k_B} T^{3/2} e^{-E_{A0}/k_B T} \quad (5)$$

where  $N_D$  is the net density of compensating donors,  $N_A$  is the density of acceptors,  $g_{A0}$  and  $g_{A1}$  are the degeneracy factors of the fundamental and first excited acceptor levels respectively,  $N_v^{eff}$  is the effective valence band density of states,  $E_A(T) = E_{A0} - \alpha_{A0}T$  is the temperature dependence of the thermal ionization energy of the shallow acceptors, and  $\alpha_{A0}$  is the constant decreasing temperature rate of the acceptors ionization energy as temperature increases.

However, as temperature decreases most of the free holes are recaptured by the acceptors strongly reducing the conduction in the valence band. Furthermore, due to compensation,  $k = N_D/N_A$ , hole hopping between empty acceptors states in the impurity band turns into the main conduction mechanism. The conduction, in this case, is performed through  $NNH$  of charge carriers with low activation energy:<sup>[42,47,48]</sup>

$$\sigma_{NNH}(T) = \sigma_1 T^{-1} e^{-\frac{E_{NNH}}{k_B T}} \quad (6)$$

where  $\sigma_1$  is a constant and  $E_{NNH}$  is the activation energy for  $NNH$  hopping.

At even lower temperatures hopping between nearest neighbor sites is not favored due to significant energy difference of the levels.<sup>[52]</sup> Then, carriers prefer to jump to a more energetically similar and also a remote site. Therefore, in disordered or compensated materials the conduction mechanism changes from  $NNH$  to  $M - VRH$ .  $M - VRH$  considers a constant density of states  $N_0$  near the Fermi level. In this model the resistivity is given by:<sup>[52]</sup>

$$\sigma_{VRH}(T) = \sigma_0 T^{1/2} e^{(T_M/T)^{1/4}} \quad (7)$$

where  $\sigma_0$  is a constant, and the Mott characteristic temperature  $T_M$  measures the degree of disorder in the sample.

Due to the reduced measured temperature range Eq. (4) can not be used to fit the experimental Hall data, shown in figure 2a). However, since the slope of the resistivity Arrhenius plot (inset of Fig. 3) is constant in the 400 – 200 K temperature range  $\phi$  should be also constant and Eq. (1) could be considered valid over this temperature range. In this case all three conduction, mechanisms should be considered:

$$\rho(T) = [e\mu_{GB}(T)p(T) + \sigma_{NNH}(T) + \sigma_{VRH}(T)]^{-1} \quad (8)$$

The outcome of the fitting of the resistivity data with Eq.(8) is shown by a solid red line in Figure 3, with  $E_{A0} = (124 \pm 3)$  meV,  $\sigma_{NNH} = (230 \pm 1) \times 10^{-8} \Omega^{-1} \text{ cm}^{-1} \text{ K}$ ,  $N_D = (8.3 \pm 0.8) \times 10^{16} \text{ cm}^{-3}$ ,  $N_A = (4.7 \pm 0.2) \times 10^{17} \text{ cm}^{-3}$  ( $k = 0.21$ ).



These results show that our synthesis method produces samples with optimum doping levels for photovoltaic applications ( $N_A \sim 10^{17} \text{ cm}^{-3}$ ). The obtained ionization energy of the shallow acceptors is comparable with the values reported in the literature from a more simple analysis of the temperature dependence of resistivity measurements, is  $\sim 110 \text{ meV}$ .<sup>[51]</sup> Theoretical calculations<sup>[39–41]</sup> have also shown that under Se-rich conditions selenium antisites acceptors ( $Se_{Sb}$ ) presents the lower formation energy and ionization energy of  $120 \text{ meV}$ , in excellent agreement with our findings. Such point defect is responsible for the p-type conductivity of  $Sb_2Se_3$  and generates a free hole density in the range of  $10^{15} \text{ cm}^{-3}$  at room temperature<sup>[40]</sup>, also in agreement with our results. Other point defects are too deep or do not contribute to the free carrier concentration. By taking these considerations, we assign that the shallow acceptor level with  $E_{A0} = (124 \pm 3) \text{ meV}$  is compatible with  $Se_{Sb}$  point defects.

#### 4. CONCLUSIONS

In this work, we performed a study of the electrical conduction mechanism and electrically active defects in polycrystalline  $Sb_2Se_3$ . It is shown that, at high temperatures the electrical transport is dominated by thermal emission of free holes, ionized from shallow acceptors, over the inter-grain potential barriers. The temperature dependence of the holes mobility, limited by inter-grain potential barriers, is the main contributor to the observed conductivity thermal activation energy. Our results show that, the common interpretation in the literature of attributing the electrical conductivity thermal activation energy of  $\sim E_g/2$  to intrinsic excitation in  $Sb_2Se_3$  is not correct. It is also shown that, at low temperatures,  $NNH$  transport in the bulk of the grains is the dominant conduction mechanism. Based on this study, parameters such as free hole density and mobility, inter-grain potential barrier height, inter-grain trap density, shallow acceptor ionization energy, acceptor density, net donor density and compensation ratio are reported. These parameters, as well as the temperature dependence of the holes mobility, are of great importance for the understanding of the electronic structure of  $Sb_2Se_3$  polycrystalline thin films and the development and simulation of electronic and optoelectronic devices based on this material. Furthermore, the values found for the above mentioned parameters are appropriated for thin film solar cells. The compensation ratio, lower than the corresponding values for CIGS and CZTS, make  $Sb_2Se_3$  a very promising photovoltaic material.

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## 5. FIGURES

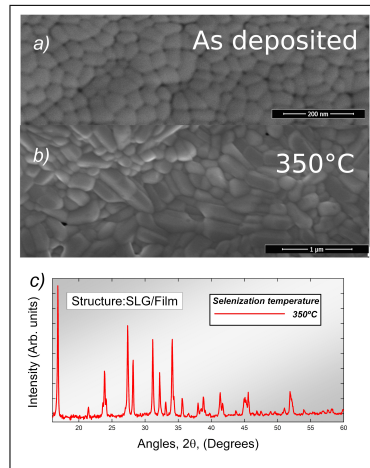


FIG. 1. SEM images of the surface of the sample as-deposited a) after selenization at 350°C b) and *XRD* diffractogram of the sample after selenization.

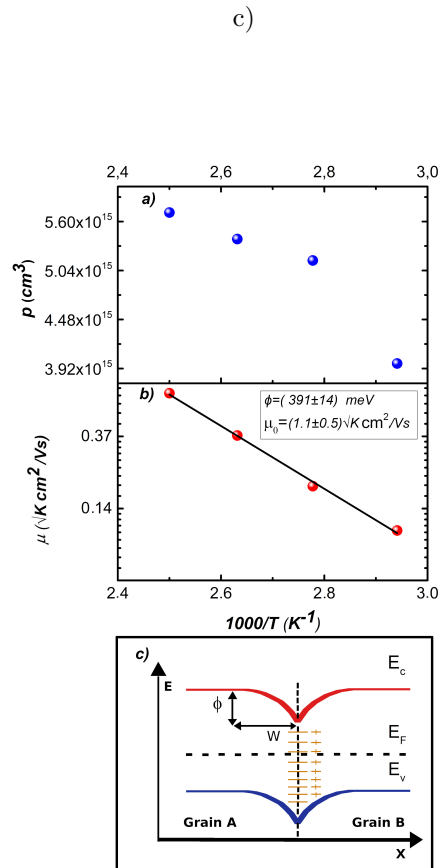


FIG. 2. Temperature dependence of the free holes concentration a), and mobility b). The solid line corresponds to the fitting of the mobility data with Eq. (1). c) Inter-grain potential barrier model used to interpret the electronic transport in the sample.

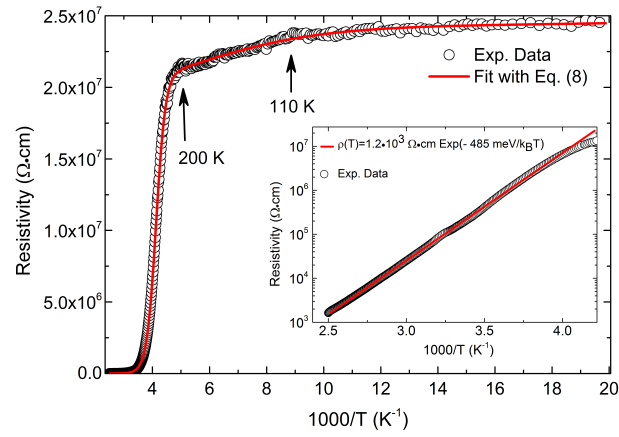


FIG. 3. Temperature dependence of the electrical resistivity. The red solid line corresponds to the fitting of the data with eq. (8). The exponential temperature dependence of the electrical resistivity in the 400 K - 200 K range is shown in the inset.