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Growth of Sb_2Se_3 thin films by selenization of RF sputtered binary precursors

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ABSTRACT

In this work we present a method to grow Sb_2Se_3 thin films with a potential use as absorber layers in solar cell structures. The films were grown on several substrates: soda-lime glass, Mo coated soda-lime glass and Si. The Sb-Se precursor's films were deposited by RF magnetron sputtering and then selenized under a H_2Se gas flow. Different selenization temperatures were tested and analysed. Compositional and morphological analyses were performed by Energy Dispersive Spectroscopy and Scanning Electron Microscopy, respectively. Phase identification and structural characterization were done by X-ray Diffraction and Raman scattering spectroscopy showing that Sb_2Se_3 is the dominant phase with an orthorhombic crystalline structure. Traces of rhombohedral and amorphous Se secondary phases were also observed supported by their Se-rich compositions. Visible-NIR reflectance measurements allowed to extract a direct bandgap with a value close to 1.06 eV. Photoluminescence spectroscopy shows an emission with a broad band at 0.85 eV for samples selenized at lower temperatures and an intense peak at 0.75 eV for the sample selenized at higher temperatures. Electrical characterization shows low free hole concentrations and mobilities. At low temperatures, the nearest neighbour hopping is the dominant mechanism for the electronic transport for the analysed samples. Both electrical and optical properties are influenced by the type of defects present on samples. A discussion is made on the properties that need to be improved in order that these films can be integrated into thin film solar cells.

1. Introduction

It is well known that one way of creating an environmentally friendly energy production momentum, which allows mitigating the effects of climate change, is closely linked to the commercial relevance of renewable energy production systems. Photovoltaic (PV) technology can play an important role in this field. Currently dominated by Si-based technology, it has some drawbacks that prevent a greater market presence. High energy payback time, low industrial production rate, and high values of initial investment for a production facilities, among others, are constrains to a higher PV share in the energy production systems in most countries. Due to monolithic integration, lower energy processes and lower material demand, thin film technology presents good arguments to overcome Si technology. CIGS and CdTe based PV cells are currently the most powerful representatives of thin film technology on the market. However, the solar cells based on these materials present problems related to the scarcity and toxicity of some elements that compose them. Alternative materials are currently been studied, such like $Cu_2 ZnSn(S,Se)_4$, to be applied as absorber layer in the solar cell structure. But due to its intrinsic complex pentanary structure and restricted growth conditions some difficulties have been encountered. These facts have prevented the production of devices with efficiencies compatible with their commercialization.

Antimony selenide, Sb_2Se_3, is a semiconductor material that belongs to the $A_m^V B_n^{VI}$ group, crystallising in an orthorhombic configuration of the *Pnma* (62) space group [1]. The first research was published in the 50 s, where Sb_2Se_3, belonging to the same space group of the antimony

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Table 1
Comparison of the literature data on the Sb_2Se_3 cell dimensions.

Lattices param.	Ref. [1]	Ref. [2]	Ref. [3]
a (nm)	1.168	1.171	1.17938
b (nm)	1.158	1.162	1.16478
c (nm)	0.398	0.396	0.39858

sulfide, Sb_2S_3, is investigated and structural parameters of Sb_2Se_3 were estimated [2]. Later, this data was confirmed by other research groups [3,4], as shown in Table 1. As a current standard, the crystal lattice parameters for Sb_2Se_3 are taken to be $a = 1.16330$ nm, $b = 1.1700$ nm and $c = 0.39850$ nm.

Over the years, as the interest in Sb_2Se_3 became stronger, researchers devoted to the synthesis of this compound have doubled in the recent decade. Studies revealed that this material has excellent electrochemical, opto- and thermo-electric properties. Sb_2Se_3 exhibits a direct bandgap between 1.04 and 1.3 eV and optical absorption coefficient higher than 10^5 cm^{-1} in the visible region [5], carrier mobility ≈ 10 $cm^2V^{-1}s^{-1}$ for minority carriers and, based on the transient absorption spectroscopy, a carrier lifetime ≈ 60 ns [6]. In addition, it has been discovered that Sb_2Se_3 shows an extremely large magnetoresistance [7]. Based on the electrochemical properties, this material has been suggested as an anode material for lithium-ion batteries [8] and hydrogen storage materials [9]. Optoelectronic properties of the material have found applications in optical recording material [10,11], in thermoelectric devices [12], solar cells and photoelectrochemical cells [13]. At the moment, the best power conversion efficiency value for a Sb_2Se_3 based thin film solar cell with a substrate/FTO/ZnO/Sb_2Se_3/Au structure configuration is 5.93% [14]. However, theoretically calculated gaps with the ideal Shockley-Queisser value predicted that the efficiency of a solar cells based on Sb_2Se_3 can surpass 30% [15]. In addition to efficiency of solar cells, the critical parameter for development of such devices is its production cost. Here, Sb_2Se_3 also satisfies necessary criteria as antimony and selenium are widespread and rather cheap elements.

Among Sb_2Se_3 thin-film growth technology, the most common are thermal evaporation [16–20], spin coating [21], chemical bath deposition [22], ionic layer adsorption and reaction methods [23], spray pyrolysis [24], reactive pulsed laser deposition [8], electrodeposition [25,26], DC magnetron sputtering [29], resistance-heated floating zone furnace [7], just to mention the most used ones.

In this work, we use a method of growing Sb_2Se_3 thin films based on the deposition of Sb-Se precursors by RF-magnetron sputtering followed by an selenization step in a H_2Se gas atmosphere. The films are prepared on different substrates: soda lime glass (SLG), SLG/Mo and Si. We report the effect of the selenization temperatures on the properties of the films. The crystalline structure of the films has been studied by X-ray diffraction and Raman scattering spectroscopy. The characterization of the morphology is done by scanning electron microscopy. Spectrophotometry measurements allowed the study of the optical behaviour of the samples and the determination of the bandgap energies of the compounds. The optoelectronic properties of the samples are also investigated using photoluminescence spectroscopy, Hall effect and electrical resistivity measurements.

2. Experimental methods

2.1. Preparation of the films

The growth method is based on two steps. The first one refers to the deposition of the binary precursor layer, Sb_xSe_y, by RF magnetron sputtering. The chalcogen incorporation, Se, the composition adjustment and, the selenization process, which allows the crystalline phase formation, are performed in the second stage. In this work we used three types of substrates: 3×3 cm^2 soda lime glass (SLG), 2.5×2.5 cm^2 Mo coated SLG and 2.5×2.5 cm^2 p-Si (100) without removal of the native oxide. The Mo layer thickness is near 350 nm [27]. The samples preparation process begins with the substrate cleaning, with successive ultrasound baths of acetone/alcohol/deionised water. This process ends with the substrate being dried with a N_2 flow. Next, the precursor layers were deposited directly on the different substrates using an Ar atmosphere at an operating pressure of 5×10^{-3} mbar. The Sb_2Se_3 target purity was 99.99%. To avoid target excessive thermal stress or cracking, a low energy density of 0.86 Wcm^2 was used. The precursor film thicknesses of 900 nm was confirmed by contact profilometry described in next section. For the second stage, a rapid thermal furnace system was used. The samples were placed in a susceptor box and submitted to the selenization process depicted in Fig. 1. After a quick initial step at 150 °C, the temperature is raised at a rate of 1 °C/s until the maximum temperature is reached. In this work we tested three different maximum temperatures, 300, 350 and 400 °C. This last step has a duration of 900 s. During ramping and fixed-temperature steps a constant H_2Se gas flow at 200 sccm is used as the Se supplier. After this step the H_2Se gas flow is closed and the furnace is subjected to a rapid cooling. During this step the furnace chamber is filled with a mixture of N_2 and H_2.

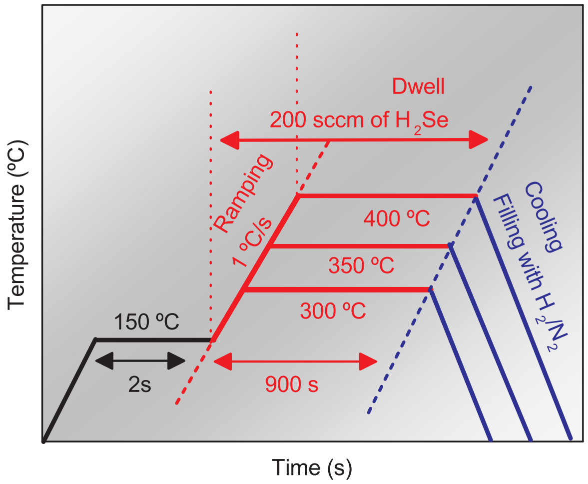

Fig. 1. Temperature profiles for the selenization process with three different tested maximum temperatures (300, 350 and 400 °C). The H_2Se gas flux was 200 sccm during the heating ramp and the fixed-temperature step.

2.2. Sample characterization

The composition of the films was analysed by EDS using a Rontec EDS system coupled to a High-resolution NovaNanoSEM 650 SEM system. The accelerating voltage used for the EDS measurements was 30 kV. The same system was used to surface SEM imaging, but with a acceleration voltage of 10 kV. XRD was done in Bragg-Brentano θ-2 θ configuration with a PanAnalytical X Pert PRO MRD system with a CuK_α line of 1.5406 Å with the following generator settings: current intensity 40 mA and voltage 45 kV. To measure the precursors' roughnesses and thicknesses a KLA TENCOR P-16 + contact profilometer was used. Raman scattering experiments were carried out at room temperature (RT) using a Jobin-Yvon LabRaman HR800 spectrometer equipped with a multi- 126 channel Peltier cooled (-70° C) CCD detector, in the backscattering geometry, and using the 632.8 nm excitation line of a HeNe laser. The sample surface was focused with an objective of 50x (N.A = 0.50; WD = 10.6 mm), and the incident power was varied from 70 to 790 μ W. The visible-NIR reflectance spectra were recorded at RT, using a dual-beam spectrometer Lambda 950, (Perkin-Elmer) with a 150 mm diameter Spectralon integrating sphere. The photoluminiscence (PL) was measured with the help of a Bruker Vertex 80v Fourier transform infrared spectrometer equipped with an