Contents lists available at ScienceDirect

# Solar Energy Materials and Solar Cells

# Crystal growth direction-controlled antimony selenide thin film absorbers produced using an electrochemical approach and intermediate thermal treatment

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## ARTICLE INFO

## ABSTRACT

$Sb_2Se_3$ is an emerging material among alternative light absorbers for photovoltaic applications. Unlike typical chalcogenides, $Sb_2Se_3$ is particularly appealing due to its single stable crystal phase, layered structure with loose binding of no dangling bonds. Nevertheless, a cost-effective electrochemical approach for the synthesis of $Sb_2Se_3$ compounds has not been identified, and the $Sb_2Se_3$ film with the most favorable [001] preferred orientation has only just been developed. In this study, Sb-rich precursors were prepared electrochemically at −950 mV (vs. Ag/AgCl), and homogeneous $Sb_2Se_3$ thin films were produced using a pre-thermal treatment process prior to the typical selenization process with additional Se coating. This novel procedure notably suppresses potential Sb dissolution into liquid Se due to the formation of polycrystalline Sb-related crystals. As a result, the Sb-rich precursor was successfully transformed into $Sb_2Se_3$ thin films with an enhanced perpendicular orientation of the [001] direction. Unfortunately, a high density of voids was produced in the precursor film with two distinguishable layers, and their size increased after selenization. The voids were formed through evolution of $H_2Se$ gas after the initial electrochemical reaction. The resulting photovoltaic cells demonstrated an energy conversion efficiency of 1.8% in a substrate structure consisting of $Mo/Sb_2Se_3/CdS/ZnO/ITO$.

## 1. Introduction

Traditional inorganic thin film photovoltaics, Cu(In,Ga)Se₂ (CIGS) and CdTe, have been extensively studied for several decades due to their high absorption coefficient ($> \sim 10^5$ /cm) and appropriate direct band gap [1–6]. These materials have achieved an impressive solar energy conversion efficiency of 21.5% (CdTe) and 21.7% (CIGS), but the scarcity of In and Te and the toxicity of Cd have stimulated research activity to find alternative absorbers that consist of non-toxic and earth-abundant materials [1,2]. Thus, $Cu_2(Zn,Sn)S_4$ (CZTS) thin films consisting of low-cost elements have been studied as a promising absorber [7]. However, secondary phases, such as ZnS, $Cu_2S$, and $Cu_2SnS_3$, which reduce device performance, are frequently formed since quaternary CZTS is thermodynamically stable in a narrow region of the thermodynamic phase diagram [7]. Until recently, most studies have focused on multicomponent cation chalcogenide thin film solar cells; however,

the multicomponent nature of these materials inevitably causes secondary phases and non-uniform composition distribution. On the other hand, reports of simple binary chalcogenide thin film solar cells consisting of earth-abundant elements are scarce.

A thin film of $Sb_2Se_3$ was chosen as a photovoltaic absorber in this study because of several distinctive chemical and physical characteristics that do not exist in other chalcogenides. Non-toxic and earth-abundant $Sb_2Se_3$ has received significant attention as an alternative absorber for photovoltaic applications due to p-type characteristics with high mobility ($\sim$ 42 cm²/V·s), a high absorption coefficient ($> 10^5$ cm$^{-1}$ at short wavelength), and an appropriate band-gap (1.0 − 1.2 eV) [8,9]. Based on the thermodynamic phase diagram, the Sb-Se binary material is theoretically anticipated to have only one stable chalcogenide compound phase, $Sb_2Se_3$ with an orthorhombic crystal structure [10]. This enables the solid $Sb_2Se_3$ compounds to maintain stoichiometry without producing secondary phases. On the contrary,

the most commonly available binary chalcogenides can be synthesized with various solid phases in the crystallization stage. Examples of such materials include Cu-S, Fe-S, and Sn-Se binaries, which have $Cu_2S$ and CuS, $FeS_2$ and FeS, and $SnSe_2$ and SnSe, respectively, depending on the composition, temperature, and partial pressure in the reaction chamber. Hence, the presence of the relevant secondary phases and non-stoichiometric phases are distinctly possible even in binary compounds and significantly affect solar cell performance by shunting current paths or providing recombination centers. In multicomponent chalcogenides with several metal cations, these secondary phases have crystal structures compatible with CIGS and CZTS, which can form many heterointerfaces and induce the severe degradation of cell performance. Thus, the presence of only one possible stable crystal phase is a very attractive characteristic in photovoltaic applications, but this kind of binary chalcogenide is rare.

Interestingly, the orthorhombic structure of $Sb_2Se_3$ tends to form strong covalent bonds along the anisotropic [001] direction (JCPDS, 15–0861) and is parallel-stacked with one-dimensional ribbon-like structures weakly bonded by van der Waals forces [9]. Unlike traditional absorber materials exhibiting a three-dimensional crystal structure, the $Sb_2Se_3$ is free of dangling bonds between loosely bonded layers and has low potential differences (< 10 mV) at grain boundaries due to a lack of dangling bonds, resulting in minimal recombination loss [11,12]. In particular, carrier transport via the covalently bonded [001] direction is more favorable than hopping conduction through the [120] direction, which is bonded by van der Waals forces. Accordingly, the [001] preferred orientation of the $Sb_2Se_3$ film normal to the substrate is critical for the transport of carriers in photovoltaic applications, since carriers can travel in parallel with the electrical potential direction, as shown in Fig. S1. In addition, $Sb_2Se_3$ materials are the only feasible phase in the Sb-Se binary system, making possible the use of various approaches to synthesize large and uniform thin films [8,13]. Low melting temperature (590 °C) is also appropriate for applications in flexible devices (typical process temperature, 300–350 °C). Therefore, several methods have been employed to synthesize $Sb_2Se_3$ thin films, such as thermal evaporation, electrodeposition, spin-coating, spray pyrolysis, and reactive pulse laser deposition [11,13–16]. To date, a certified energy conversion efficiency of 5.6% was reported by Y. Zhou et al. in $Sb_2Se_3$ thin film solar cells using thermal evaporation [11]. Among several available methods, electrodeposition has been categorized as a low-cost process because of its low capital investment for initial set-up and minimal waste generation. In addition, this process can be applied on a large-scale and can be prepared on a nanostructured substrate. T.T. Ngo et al. addressed the electrodeposition approach in alkaline solution and reported an energy conversion efficiency of 2.1% in the inorganic/organic sensitized solar cells ($FTO/TiO_2/Sb_2Se_3/CuSCN/Au$) [13]. However, the typical electrochemical process required more than 1 h in order to produce a 1 µm thickness due to the low reductive rate [17]. Furthermore, even though the orientation of the grains was strongly related to the carrier transport, there are no methods which control the [001] growth direction of the $Sb_2Se_3$ in the electrodeposition and most studies have mainly surveyed superstrate structure.

In this paper, electrodeposition was employed to synthesize binary $Sb_2Se_3$ thin films with large size grains. The Sb-rich precursors were electrochemically prepared, and Sb dissolution was suppressed by a pre-thermal treatment prior to additional Se deposition. In the sample with pre-treatment, the $Sb_2Se_3$ thin film could be deposited with an enhanced growth orientation along the [001] direction. Additionally, the photovoltaic performance was demonstrated by preparing and characterizing a $Mo/Sb_2Se_3/CdS/ZnO/ITO$ heterojunction device with a substrate structure. Based on the microstructural characterizations, a growth procedure detailing the structural evolution from precursors to thin film was proposed.

## 2. Experimental

For the present electrochemical deposition, a chemical bath containing 0.055 M $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$ (antimony potassium tartrate), 0.045 M $H_2SeO_3$ (selenous acid), and 1 M $NH_4Cl$ (ammonium chloride) was used as the electrolyte for the Sb-Se precursors. The pH of the solution was approximately 1.8. In this experiment, a conventional three-electrode system was employed by Versastat 3 potentiostat system (AMETEK), where Ag/AgCl and Pt foils were used as the reference and counter electrodes, respectively. Soda-lime glass (SLG) substrates coated with an 800 nm Mo layer were used as the working electrode, as shown in Fig. S2. Before electrodeposition, the substrates were sequentially rinsed using acetone, ethanol, and deionized water, each for a 10 min duration, in an ultrasonic bath. In order to remove the native molybdenum oxide layer, substrates were dipped in 25 vol% ammonia solution for 5 min, followed by rinsing in deionized water shortly before dipping in an electrolyte [3]. Versastat 3 potentiostat system can control and measure the voltage of electrodes in the three-electrode system, and thus help us monitor the voltage applied to working electrode for chemically uniform deposition during electrodeposition process. To determine the applied potential range for the appropriate precursor film, linear sweep voltammetry (LSV) was carried out over a range from 100 mV to −1300 mV, and the precursors were electrodeposited at a potential range from −300 mV to −1300 mV. Versastat 3 potentiostat system can also measure the current through the working electrode and the accumulated total amount of charge per unit surface (coulomb/$cm^2$) can be in-situ measured. Thus, the thickness of the deposited film is determined by calculating the relationship between current density and the amount of charge consumed during electrodeposition. In this work, the electrodeposition was processed by applying a constant potential to working electrode until the total charges reached 1C/$cm^2$. The precursors, which had a uniform film structure and Sb-rich composition deposited at −950 mV, were selected to fabricate the $Sb_2Se_3$ absorber layer.

An additional Se layer (~ 5 µm) was coated on the electrodeposited Sb-Se precursors by a thermal evaporation system to provide uniform and sufficient Se sources during selenization. Prior to an additional Se coating, the Sb-rich precursors were thermally preheated at 300 °C for 1 h in a $N_2$ atmosphere (500 Torr) by a rapid thermal annealing system (RTA) to reinforce the crystallinity of the precursors, preventing the dissolution of Sb into liquid Se [8]. The annealing process for the selenization was also performed with a thick Se layer at 300 °C for 1 h in a $N_2$ atmosphere (500 Torr). After the selenization, an additional heat treatment was performed at 250 °C in a vacuum to eliminate excess elemental Se on the surface, resulting high purity $Sb_2Se_3$ crystal.

In order to manufacture a $Sb_2Se_3$ solar cell, a CdS (~ 50 nm) buffer layer was deposited on the $Sb_2Se_3$ thin films by a conventional chemical bath deposition (CBD) process. The bath solution, which consisted of 0.0015 M $CdSO_4$ (cadmium sulfate), 1.5 M $NH_4OH$ (ammonium hydroxide), and 0.0075 M thiourea, was prepared, and deposition was performed at 60 °C [18]. Radio-frequency sputtering was employed to deposit the i-ZnO (60 nm)/ITO (200 nm) window layers. Next, ZnO (3 in., 99.9999% of purity) and ITO (3 in., 99.9999% of purity) targets were sputtered with a mixture of high-purity argon and oxygen at 150 °C. The Ni/Al metal electrodes were deposited by e-beam evaporation. The prepared sample size was 2.5 × 2.5 $cm^2$ and was divided into ~16 cells with a cell size of 0.072 $cm^2$ by scribing each metal electrode.

The structural characteristics of the electrodeposited precursors and absorber layers were evaluated by field-emission scanning electron microscopy (SEM, JEOL-JSM6700F) and X-ray diffraction (XRD, Bruker AXES D8 Discover) with Cu Kα (λ = 1.54 Å). A microstructural analysis was carried out by transmission electron microscopy (TEM, JEOL JEM-2100F). In addition, the chemical composition of the precursors was analyzed by energy dispersive X-ray spectroscopy (EDS, Oxford Instruments, X-Max).