



# Mechanisms and modification of nonlinear shunt leakage in $\text{Sb}_2\text{Se}_3$ thin film solar cells



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## ABSTRACT

Antimony selenide ( $\text{Sb}_2\text{Se}_3$ ) based thin film solar cells have recently drawn a growing research interest due to their increasing power conversion efficiency, proper bandgap, high absorption coefficient, and earth abundant nature. Herein, the  $\text{Sb}_2\text{Se}_3$  thin films were prepared by close spaced sublimation (CSS) for efficient  $\text{Sb}_2\text{Se}_3$  solar cells. The origin and the mechanisms of shunt current were analyzed. Non-ohmic space-charge limited current (SCLC) was identified to be an important contribution to the nonlinear shunt current in  $\text{Sb}_2\text{Se}_3$  thin film solar cells. To tackle this issue, a high-resistance  $\text{SnO}_2$  buffer was introduced at the front contact. With the insertion of a  $\text{SnO}_2$  buffer, the micro-shunt paths were modified and a significant efficiency improvement to 5.18% was obtained.

## 1. Introduction

Antimony selenide ( $\text{Sb}_2\text{Se}_3$ ) is a promising photovoltaic material with a variety of attractive features, such as proper band gap (1–1.2 eV), high absorption coefficient, intrinsically benign grain boundaries, low toxicity, earth-abundant elements and high theoretical conversion efficiency up to 31% [1,2].  $\text{Sb}_2\text{Se}_3$  based thin-film solar cells have demonstrated increased power conversion efficiency (~ 6.5%) in recent years [2–4]. However, due to the relatively short history and rather small scientific community devoted to the  $\text{Sb}_2\text{Se}_3$  solar cell research, many fundamental problems, both material and device, are remained to be investigated. From the point of view of material,  $\text{Sb}_2\text{Se}_3$  has a one-dimensional (1D) crystal structure. The film growth and microstructure are very sensitive to preparation process and experimental conditions. To improve the solar cell performance further, the most challenging work is to obtain high quality  $\text{Sb}_2\text{Se}_3$  film [4]. So far, various approaches including vacuum evaporation, sputtering, spin-coating, electrodeposition, spray pyrolysis, and chemical bath deposition have been explored to fabricate the  $\text{Sb}_2\text{Se}_3$  thin films [4–10]. Tang et al. had developed a fast  $\text{Sb}_2\text{Se}_3$  film deposition based on rapid thermal evaporation (RTE) technique, which demonstrated a simple and successful method to get high quality p- $\text{Sb}_2\text{Se}_3$  layer that can be finished in tens of seconds [2,4]. From the point of view of device, the CdS/ $\text{Sb}_2\text{Se}_3$  thin film solar cell is typically made in the superstrate configuration with Glass/TCO/CdS/ $\text{Sb}_2\text{Se}_3$ /Metal structure [3,4].

Thickness of the  $\text{Sb}_2\text{Se}_3$  layer influences the performance of the devices. Taking into account the factors such as the optical absorption coefficients, the junction depletion width and the minority carrier (electron) diffusion length, the optimal thickness of the  $\text{Sb}_2\text{Se}_3$  absorber layer was found to be about 500 nm [11]. This is a rather small thickness and is one reason for the limited efficiency of the devices reported. In  $\text{Sb}_2\text{Se}_3$  solar cells, the CdS layer works as a n-type window layer, which absorbs photons with energy greater than its bandgap of 2.42 eV [12]. In order to reduce the light absorption in the CdS window layer, the thickness of CdS layer should be decreased to as thin as several ten nanometers. However, when the CdS layer is too thin, the pinholes or discontinuity would inevitably happen so that  $\text{Sb}_2\text{Se}_3$  directly contacts the front electrode, leading to electric micro-shunt paths and low quality p-n junction diode [12,13]. In addition, due to the fabrication procedure of superstrate structure, the interdiffusion/reaction occurred at the CdS/ $\text{Sb}_2\text{Se}_3$  interface during the subsequent deposition of  $\text{Sb}_2\text{Se}_3$  would lead to part of the CdS consumed up [14]. Actually, the discontinuity in CdS or the interdiffusion at junction interface induced shunt leakages have been reported in both superstrate CdTe thin film solar cells and substrate  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  thin film solar cells [15,16]. Shunt leakage is a key issue affecting solar cell performance especially for large area thin film solar cells. Shunt currents are detrimental to the cell/module output parameters, especially fill factor (FF) and open-circuit voltage ( $V_{oc}$ ) [13]. Understanding the origin of shunt current and minimizing shunt current loss are essential to enhance solar cell efficiency further.

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Herein, we employ close spaced sublimation (CSS) deposition to grow  $\text{Sb}_2\text{Se}_3$  thin films. CSS is a rapid and industrially scalable deposition technique which was widely used in many kinds of inorganic film deposition for photovoltaic application, like binary compound CdTe [17]. This work demonstrated that CSS is highly suitable for fabrication of  $\text{Sb}_2\text{Se}_3$  thin film solar cells. Focusing on the relatively large and nonlinear shunt current discovered in this study, we tried to make clear the physical origin of shunt leakage in  $\text{Sb}_2\text{Se}_3$  solar cells and to find solutions to improve the device performance. On the basis of the experiments and theoretical models, the device characteristics were analyzed and the non-ohmic space-charge limited current (SCLC) was identified to be responsible for the nonlinear shunt current in  $\text{Sb}_2\text{Se}_3$  solar cells. The shunt paths were found mainly caused by the local discontinuity or pinholes in the CdS window layer. With the insertion of a high-resistance tin oxide layer as front contact buffer, the micro-shunt paths were effectively modified. The presence of  $\text{SnO}_2$  buffer significantly reduced the shunt current and improved the junction quality, resulting in the cell efficiency increasing from 3.73% to 5.18%.

## 2. Experimental

The  $\text{Sb}_2\text{Se}_3$  solar cells fabricated in this study had superstrate structures of glass/FTO/CdS/ $\text{Sb}_2\text{Se}_3$ /Au or glass/FTO/ $\text{SnO}_2$ /CdS/ $\text{Sb}_2\text{Se}_3$ /Au. CdS window layers with a thickness of  $\sim 60$  nm were prepared on glass/FTO or glass/FTO/ $\text{SnO}_2$  substrates by chemical bath deposition (CBD) technique from a solution composed of de-ionized water, cadmium acetate, ammonium acetate, and thiourea. The  $\text{Sb}_2\text{Se}_3$  absorber layers, which had a thickness of  $\sim 550$  nm, were deposited by the CSS technique in a home-made film-deposition system, as sketched in Fig. 1(a). The source material is commercial  $\text{Sb}_2\text{Se}_3$  powder with

99.999% purity. The source temperature was  $520^\circ\text{C}$  and the substrate temperature was  $320^\circ\text{C}$ . The detailed CdS and  $\text{Sb}_2\text{Se}_3$  fabrication processes can be found in our previous work [10,15]. The highly resistive  $\text{SnO}_2$  buffer layer between FTO and CdS was deposited by the RF magnetron sputtering technique at a substrate temperature of  $200^\circ\text{C}$ . A 99.99%  $\text{SnO}_2$  target (diameter 3 in.) was sputtered in a reactive gas mixture of  $\text{O}_2$  and Ar with an  $\text{O}_2/\text{Ar}$  pressure ratio of 1/20. The working pressure was 0.5 Pa and the RF power was 60 W. The  $\text{SnO}_2$  layer thickness was controlled by varying the sputtering time. The Au back contact was prepared by thermal evaporation in a vacuum chamber. The size of individual  $\text{Sb}_2\text{Se}_3$  solar cell was  $4 \times 4 \text{ mm}^2$  defined by Au contacts.

The film morphologies were characterized by using a field emission scanning electron microscope (SEM, FEI Apreo LoVac) and conductive atomic force microscopy (C-AFM, Veeco Multimode V). X-Ray Diffraction (XRD) measurements were performed by an X-ray diffractometer (Bruker D8 Advance). The solar cell current density–voltage (J–V) curves of  $\text{Sb}_2\text{Se}_3$  solar cells were recorded using a Keithley 2400 source measurement unit and a Newport solar simulator (Oriental-SOI3A) with an AM1.5 G spectrum. The light intensity was adjusted to  $100 \text{ mW/cm}^2$  using a standard Si solar cell (91150 V). The external quantum efficiency (EQE) spectra were measured with a spectral response system (Enlitech QE-R).

## 3. Results and discussion

### 3.1. Properties of $\text{Sb}_2\text{Se}_3$ thin film and solar cell performances

The quality of the  $\text{Sb}_2\text{Se}_3$  absorber layer is crucial to the performance of  $\text{Sb}_2\text{Se}_3$  solar cells. Fig. 1(b) shows the surface morphology of a

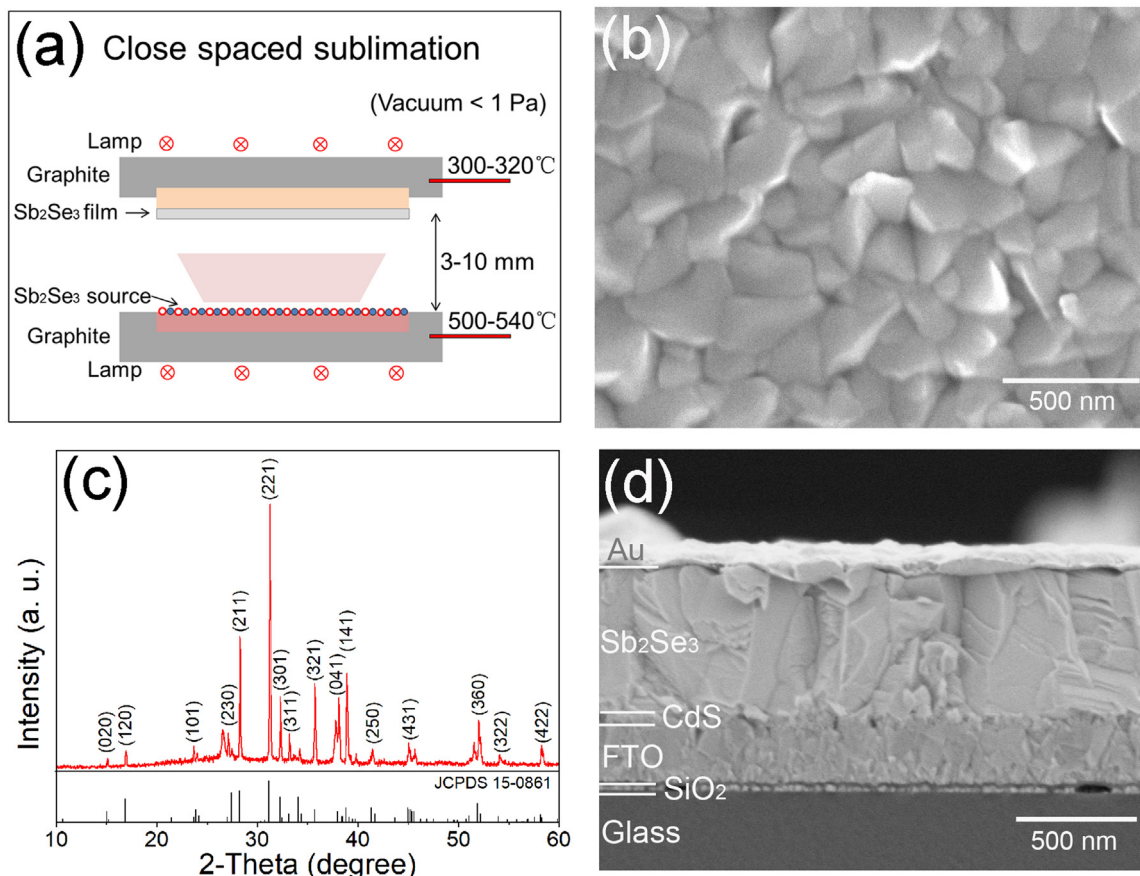


Fig. 1. (a) The schematic diagram of CSS equipment for  $\text{Sb}_2\text{Se}_3$  film deposition; (b) SEM surface morphology and (c) XRD pattern of  $\text{Sb}_2\text{Se}_3$  film with a thickness of  $\sim 550$  nm; (d) cross-sectional SEM image of a  $\text{Sb}_2\text{Se}_3$  thin film solar cell with a structure of glass/FTO/CdS/ $\text{Sb}_2\text{Se}_3$ /Au.

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