

6.6% efficient antimony selenide solar cells using grain structure control and an organic contact layer

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ABSTRACT

We report a high efficiency antimony selenide (Sb₂Se₃) photovoltaic device structure using a new multi-step close space sublimation deposition process incorporating a Sb₂Se₃ seed layer; key to achieving higher efficiency devices via close space sublimation. Utilizing a glass|FTO|TiO₂|Sb₂Se₃|PCDTBT|Au structure, a peak efficiency of 6.6% was achieved, which is comparable to the current record devices for this material. Crucially, this device avoids toxic lead in the hole transport material, and cadmium in the window layer. Moreover, the addition of the PCDTBT back contact both maintains peak efficiency of 6.6%, and improves the uniformity of performance, increasing the average efficiency from 4.3% to 6.1%.

1. Introduction

Antimony selenide (Sb₂Se₃) is emerging as one of the most exciting new photovoltaic (PV) absorber materials, combining abundant, low toxicity constituents with rapidly improving efficiencies [1,2]. A near-direct bandgap of ~1.2 eV and a high absorption coefficient over much of the visible spectrum [2] means that it has the potential to outperform absorbers such as CdTe [3,4]. Its crystal structure comprises 1D (Sb₄Se₆)_n ribbons [5,6] and thus the grains are terminated by van der Waals interactions rather than dangling covalent bonds, offering grain boundaries which are potentially benign [1,7,8]. This is evidenced by a large directional variability in hole mobilities [9]. Ribbons oriented perpendicular to the substrate should therefore offer improved charge transport and reduced recombination [9].

The first reported power conversion efficiency (PCE) of a functional Sb₂Se₃ PV device was 3.2% by Choi *et al.* in 2014, doubling to 6.5% for a CdS|Sb₂Se₃|PbS quantum dot device, the current record, by 2017 [10,11]. However, whilst further device efficiency improvements are of course required, it is also of importance to produce non-toxic device structures, in order not to undermine the use of a non-toxic absorber layer. As an example, CdS is a highly toxic source of cadmium [12], and thus should be avoided if possible. Sb₂Se₃ is commonly reported to have a low carrier concentration [1,13], hence recent literature reports using a PIN device structure, partnering the quasi-intrinsic absorber with n-type electron and p-type hole extraction layers to enhance charge extraction [10]. Recent work by our group was the first to demonstrate

the efficacy of close space sublimation (CSS) as a deposition route for Sb₂Se₃ for photovoltaics [3]. CSS is highly promising for Sb₂Se₃ as it yields large grains with preferred orientation, and importantly the ability to control the grain structure.

In this work we report on improved Sb₂Se₃ cell performance to world leading levels via a two-stage CSS deposition to generate a compact “seed” layer prior to the deposition of large Sb₂Se₃ grains. Furthermore, a significant improvement in uniformity was achieved by including a hole transport material (HTM). A TiO₂ layer was employed as the electron extraction layer while poly[N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) was selected as the optional HTM due to the position of its ionization potential and electron affinity at 5.4 and 3.6 eV respectively [14]. Photo-oxidation is known to generate sub-bandgap states close in energy to the valence band of Sb₂Se₃ and therefore allow efficient hole extraction [15,16]. The LUMO is also high enough to block the transfer of minority carriers (electrons) from the Sb₂Se₃ to Au and thereby reduce recombination at the back-contact (Fig. S1) [14].

2. Materials and methods

FTO-coated glass substrates (TEC10, NSG Ltd.) were spin coated with 0.15 M and 0.3 M titanium isopropoxide in ethanol at 3000 rpm for 30 s, and dried after each deposition at 120°C under N₂. The substrates were then annealed in air at 550°C for 30 min and cooled rapidly to create compact titania layers [17]. The Sb₂Se₃ layers were grown via

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CSS in a novel two step process. First a compact seed layer was grown for 5 mins at 0.05 mbar, with a source temperature of 350°C, followed by annealing for 10 mins in 260 mbar N₂. Secondly, a 30 min growth step was carried out at a source temperature of 450°C and pressure of 13 mbar to produce a more compact and orientated grain structure, similar to previous work on CdTe [18]. The substrate was then cooled rapidly with N₂. Where included, PCDTBT was spin-cast in air at 6000 rpm for 60 s from a 4 mg/mL solution in chloroform. Cells were completed by thermally evaporating 100 nm of gold through a shadow mask to define 0.1 cm² contacts and JV measurements were recorded under AM1.5 conditions using a TS Space Systems AAA100 solar simulator calibrated with a photodiode. 48 devices of each type were fabricated. SEM images were taken using a JEOL 7001 FEGSEM, X-Ray Diffraction (XRD) was carried out using a Rigaku Smartlab and AFM measurements were carried out using a Veeco diInnova AFM in tapping mode. UV/Vis spectra were recorded using a Shimadzu Solid Spec 3700 UV-Vis spectrophotometer and an integrating sphere.

3. Results and discussion

3.1. Sb₂Se₃ seed layer

Fig. 1a shows a top-down SEM image of the initial low-temperature seed layer. The seed layer is compact, yielding a high density of nucleation points for the second stage of growth, similar to work on CdTe [19]. The seed layer also serves to prevent shorting pathways between large CSS grains of the final film and increase the shunt resistance. Optical transmission measurements show a bandgap of ~1.3 eV and very high absorption (Fig. 1b) for this seed layer. The thickness of this seed layer was found to be 66 ± 8 nm using cross sectional AFM (Fig. 1c). The XRD pattern (Fig. 1d) shows preferred crystal structure orientation, confirmed by the lack of a significant (120) peak around 17°, but a strong (211) peak at 28.4°. This indicates that the 1D ribbons are mostly tilted on the substrate, which although not ideal for carrier transport is preferred to ribbons parallel to the substrate (120) [1,7,10]. The largest peak in the XRD pattern comes from the FTO glass [20], as both the titania and seed layers are very thin compared to the X-ray penetration depth. Single stage CSS-deposited Sb₂Se₃ films typically

have pinholes leading to a lower fill factor [3]. The combination of these properties mean that the seed layer is thus a key feature for achieving higher efficiency Sb₂Se₃ devices via CSS, and has improved the device performance by over 1% absolute compared to similar control devices without this seed layer, as explained in Section 3.3. The seed layer in isolation as a sole absorber material did not produce a working device due to a very thin absorber thickness creating a high number of shunting pathways.

3.2. Complete Sb₂Se₃ layer

Fig. 2a shows an SEM image of the complete Sb₂Se₃ layer after both stages of CSS growth. This two-stage approach generates large columnar Sb₂Se₃ grains of $\approx 2 \mu\text{m}$ diameter. These grains are packed tighter, more uniformly orientated and thereby minimize pinholes within the Sb₂Se₃ film compared to a film without the seed layer (Fig. S2). The device cross-sectional SEM image (Fig. 2c) shows that the Sb₂Se₃ grain height ($\approx 1.5 \mu\text{m}$) is sufficient to span the full thickness of the device and connect the TiO₂ and the PCDTBT layers without lateral grain boundaries that could impede charge transport. EDX analysis confirmed the composition as being stoichiometric Sb₂Se₃ within experimental error (Fig. S3) while optical transmission measurements show a bandgap of ~1.2 eV and high absorption (Fig. 2b), similar to previously reported values [1,2,8,21]. A difference in band gap and absorption coefficient is observed between the seed and final layers, indicating that the seed layer is likely consumed during the second growth stage. As the seed layer has a continuous slab like morphology which is very morphologically distinct to the full Sb₂Se₃ film, a large difference in absorption coefficient would be expected. Anisotropic optical absorption properties with ribbon orientation are also predicted for Sb₂Se₃ [22,23]. The Sb₂Se₃ film XRD pattern (Fig. 2c) shows a preferred crystal structure orientation, confirmed by the lack of a significant (120) peak around 17°, but strong (211) and (221) peaks at 28.4° and 31.4° respectively. This indicates the 1D ribbons are mostly predominantly inclined with respect to the substrate, which is beneficial for carrier transport [1,7,10]. It also indicates that the Sb₂Se₃ seed layer may be acting a templating layer for vertical ribbon growth, although the (211) peak is more intense in the final film compared to the

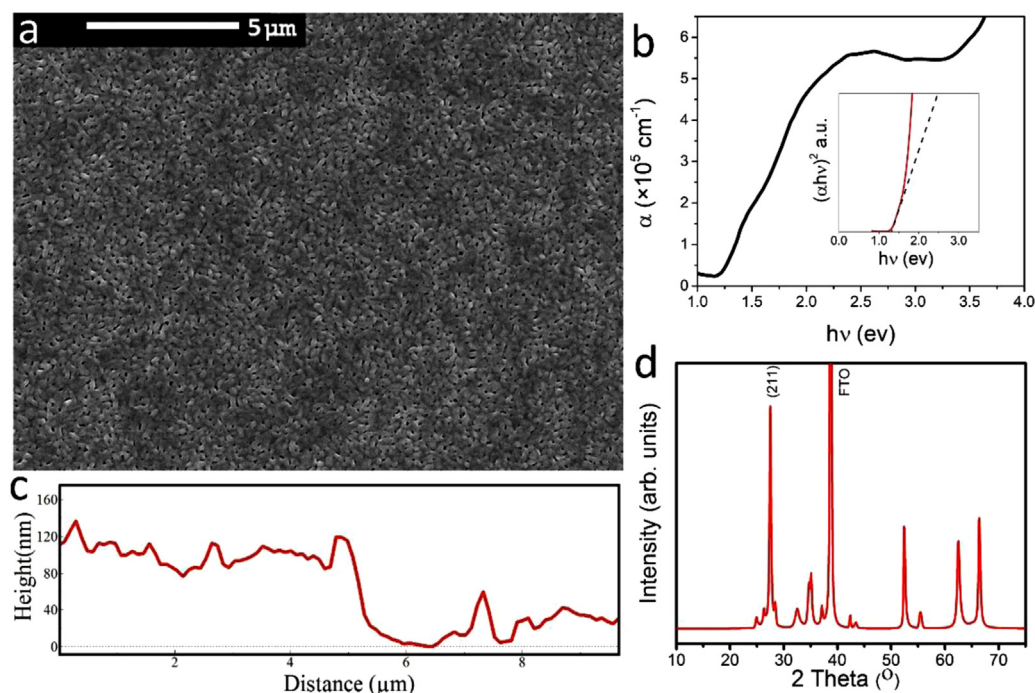


Fig. 1. Sb₂Se₃ seed layer characteristics: (a) Top-down SEM image, (b) Absorption coefficient and Tauc plot (inset), (c) AFM cross section, (d) XRD pattern.

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