Close-Spaced Sublimation for Sb_2Se_3 Solar Cells

Laurie J. Phillips,[1]* Peter Yates,[1] Oliver S. Hutter,[1] Tom Baines,[1] Leon Bowen,[2]
Ken Durose,[1] and Jonathan D. Major[1]

1 - Stephenson Institute for Renewable Energy, University of Liverpool, L69 7ZF, UK.
2 - G. J. Russell Microscopy Facility, University of Durham, South Road, DH1 3LE, UK.
*corresponding author – laurie.phillips@liverpool.ac.uk

***Abstract* — A CSS technique for depositing large-grained, well-orientated Sb_2Se_3 thin films has been developed, and solar cells based around this material have been fabricated. Adapting a standard CdTe methodology can produce high efficiency devices in a FTO/TiO_2/Sb_2Se_3/P3HT/Au heterostructure. The influence of temperature during deposition is examined to show larger columnar grain growth at increasing source temperature. Optimising the temperature of deposition both increases the proportion of grains in the correct orientation and balances the improvements due to larger grains while limiting void formation. At optimized conditions of 475ºC, the peak performing device exhibited a maximum PCE of 4.3%.**

***Index Terms* — Antimony Selenide, Sb_2Se_3, CSS**

I. Introduction

Photovoltaics installations continue to grow around the world. However, if solar is to make a substantial contribution to the switch to sustainable energy sources, new absorber materials are needed that are abundant for terawatt-scale manufacture. Silicon-based technologies dominate the market, as the promise of thin-film photovoltaics is yet to be fully realized. Copper indium gallium di-selenide (CIGS) and cadmium telluride (CdTe) have the most widely accepted thin-film technologies, with efficiencies exceeding 20%. However, the scarcity of indium and tellurium, and the toxicity of cadmium are limiting factors, difficult to overcome for more widespread adoption. The recent emergence of lead-halide-based perovskite absorbers, while rapidly achieving similarly high efficiencies, have stability issues and contain highly toxic, and restricted, lead. The relatively lower toxicity of antinomy selenide (Sb_2Se_3), coupled with its low-cost and higher abundance, means it is a material that shows considerable promise as an alternative.[1],[2] A single phase V-VI chalcogenide, Sb_2Se_3 has a near-ideal band-gap of 1.1-1.3 eV, and high absorption coefficient. It is composed of $(Sb_4Se_6)_n$ 1D ribbon structures that theoretical work has suggested should lead to grain-boundaries that are relatively benign, due to edges terminating without dangling bonds, and therefore should exhibit reduced recombination.[3] It has been proposed that the $6s^2$ electronic configuration of lead is an important factor in the success of the lead-halide perovskites. Other nS^2 materials, such as Sb are likely to offer similar benefits, which is another reason for the increasing interest in Sb_2Se_3.[4] Solar cells using this material have been demonstrated by several methods including spin-coating, chemical bath deposition, and evaporation with the best PCE currently at 5.9%.[5]-[7] However, closed-spaced sublimation (CSS), a technique related to evaporation and widely used for the fabrication of CdTe, has yet to be investigated. It is a technique whereby material is sublimed from a source onto a substrate separated by a small gap, typically a few millimeters. It is capable of producing films with large grains and high deposition rates, and can be scaled up for industrial manufacturing easily due to modest vacuum and temperature requirements, and high material usage.

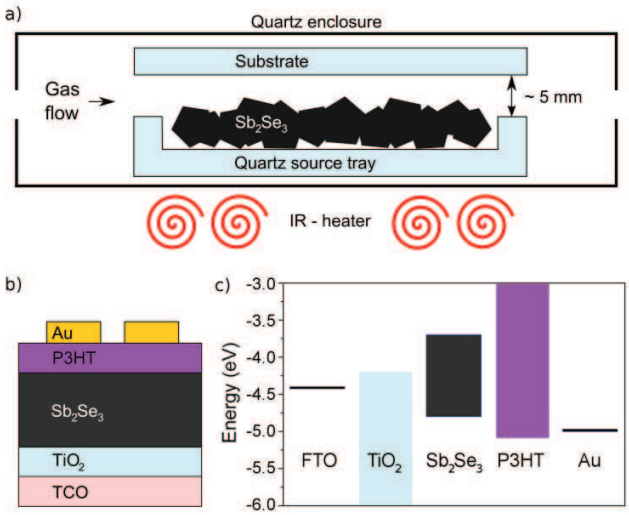

Fig. 1. a) Schematic of the CSS experimental setup b) Cell layer heterostructure c) Energy level diagram of the cell.

In this work, we investigate Sb_2Se_3 thin films deposited at source temperatures from 400 to 500ºC using the CSS method, and solar cells made with layers deposited under the same conditions. We show that Sb_2Se_3 material, deposited by CSS, can be made to form exceptionally large grains by adjusting the temperature of deposition. XRD measurements suggest that grain orientation can be altered by changing the deposition conditions, and optical transmission measurements show a 0.04 eV shift in the bandgap. A power conversion efficiency of 4.3% has been achieved by using a Sb_2Se_3 film deposited at the optimum temperature of 475ºC under AM 1.5 illumination.

II. Experimental

Thin-films of Sb_2Se_3 were grown on glass and within cell structures to examine both the material in isolation and its performance in a photovoltaic device. The glass surface was cleaned using sequential ultrasonic baths of DI-water, acetone, and IPA, followed by a 15 minutes UV-Ozone treatment. The Sb_2Se_3 layer was deposited using an entirely quartz-based CSS chamber as shown in figure 1a. The layers were deposited at four source temperatures from 400 to 500ºC in 10 mTorr nitrogen for 15 minutes (source material 99.999% Sb_2Se_3 from Alfa Aesar). Cells were grown on FTO coated 2.2 mm glass substrates (TEC7, Sigma Aldrich). The TCO was cleaned in the same way as the glass and a TiO_2 blocking layer was then coated onto the substrates via spin-coating in two sequential steps using 0.15M and 0.30M titanium isopropoxide solutions in ethanol. The solutions were made up under heavy stirring, filtered with a 0.45 um PTFE filter and spin-coated at 3000 rpm for 30s in a nitrogen filled glove-box. Each sub-layer was dried at 120ºC for 10 minutes before removing the substrates from the glovebox and sintering the complete layer at 550ºC for 30 minutes in air. Thin-films of the Sb_2Se_3 absorber were deposited at the different temperatures in identical conditions to the layers on glass. A thin layer of un-doped P3HT (Mw=34,100 Ossila) was then spin-coated on the back from a 10 mg/ml solution in chlorobenzene at 3000 rpm for 30s. Finally, the cells were completed by depositing 50 nm gold back-contacts through 10 mm^2 apertures in a shadow-mask to create an 8×8 pixel array. The complete cell structure and expected energy level diagram of the resultant heterostructure are shown in figures 1b and 1c, respectively.

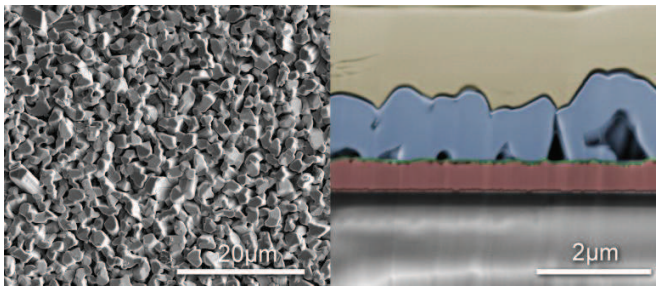

Fig. 2. a) SEM image of the upper surface showing the large micrometer grain structure of Sb_2Se_3 deposited by CSS at 450ºC. b) FIB cross-section of the Sb_2Se_3 layer (blue overlay), deposited on TiO_2-coated (green overlay) TEC (red overlay) glass. Platinum coating is also visible (yellow overlay).

XRD analysis was performed using a Rigaku Smartlab X-Ray diffractometer, and the transmission data was obtained using a Shimadzu solid-spec 3700 UV-Vis Nir spectrophotometer and a profilometer. JV characteristics were taken under AM1.5 illumination from a TS Space Systems Unisim 100 AAA solar simulator and EQE measurements were taken with a Bentham PVE300.

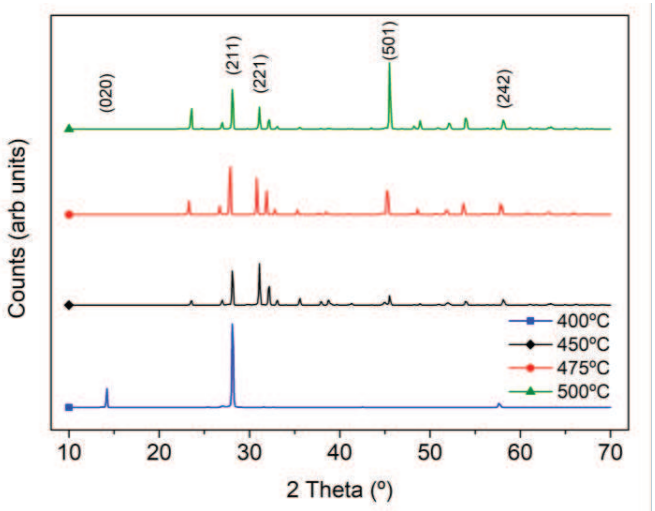

Fig. 3. XRD of Sb_2Se_3 deposited via CSS at source temperatures from 400 ºC to 500ºC. 400ºC is the only temperature with (020) grains, while the presence of (501) is increasingly evident with increasing temperature.

III. Results

Close-spaced sublimation is a technique that generally produces large-grained material. The combination of high-temperature, and low temperature difference between source and substrate, means that island-growth and coalescence is favoured over the growth of many smaller islands and therefore, as can be seen in figure 2a, the grains of material can grow to a diameter of several microns. At lower temperatures, it is possible to form nanorods, which are highly absorbing, but also highly resistive and do not adhere well to the substrate and so are unsuitable for photovoltaic applications. Increasing the temperature of deposition increases the grain size, but this also increases the chance of void formation during coalescence. As can be seen in figure 2b, the grains extend the entire depth of the layer, which should be beneficial to carrier collection as grain boundaries are more likely to be recombination sites. Also visible in figure 2b, is the lack of boundary between the majority of adjacent grains, suggesting either a merging of grains towards the substrate or a grain boundary unable to be distinguished by the SEM. At the TiO_2 surface, there are several voids visible, possibly due to contamination of the surface, strain relief due to lattice mismatch, or simply voids formed during growth. Some of these voids propagate through the entire layer and are likely to increase recombination, and act as shunting pathways between the back-contact and window layers. The main reason for coating the back surface of Sb_2Se_3 with P3HT is to mitigate the deleterious effects of these voids, as the polymer will block these paths and reduce the prevalence of shunting.

Sb_2Se_3 is known to have a 1D ribbon-like crystal structure.[1] Working with this anisotropy will be crucial to the fabrication of high-efficiency devices. Orientating the grains such that charge transport occurs along the covalently-coupled ribbons, rather than relying on hopping between the weakly van-der-waal bound chains is essential for maximal mobility and minimal recombination. XRD was used to examine the crystal structure orientation of the layers deposited at the various temperatures and is shown in figure 3.

At 400ºC, there is a peak at ~14.2º which is assigned to (020) orientated ribbons lying parallel to the substrate surface while at higher temperatures, this peak is absent. All the material deposited at higher temperatures exhibits two strong peaks at ~31.1º and ~28.1º, corresponding to (221) and (211) orientations respectively. These are the perpendicular and intermediate orientations conducive to efficient charge extraction in a cell. The peak at 45.5º is absent at 400ºC but grows with increasing temperature, and corresponds to (501) orientated material. This is indicative of the higher substrate temperatures inducing reorganization and re-evaporation from the surface.

A UV-Vis spectrophotometer was used to measure the optical transmission of the material, as shown in figure 4, and the band-gap, inset in figure 4, was extracted from a tauc plot. The bandgap increases by 0.04 eV from 1.14 eV at 400ºC to 1.18 eV at 475ºC. These values are consistent with literature, the former generally matching nanostructured thin films while the latter more consistent with to bulk samples and theoretical calculations.[8] The smaller grains and nanorods of the lower temperature sample are not small enough to be affected by quantum confinement and more work is needed to understand the factors affecting the bandgap of Sb_2Se_3 to determine if, for example, the stoichiometry is different with differing levels of selenization occurring at different temperatures.[9]

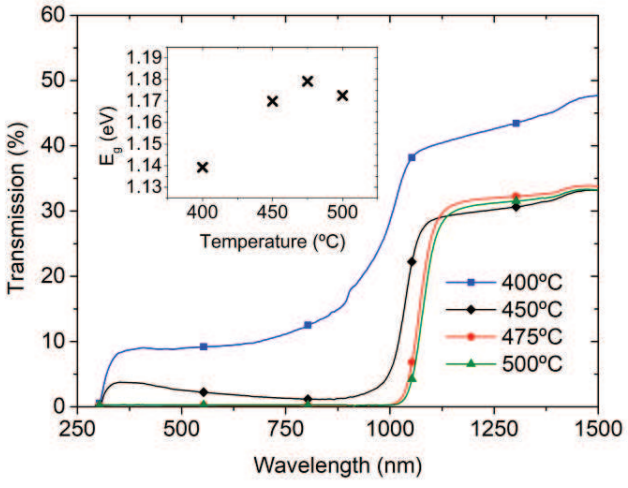

Fig. 4. Transmission curves of Sb2Se3 layers deposited via CSS at varying source temperatures. The bandgap at each temperature extracted from a tauc plot is also included (inset).

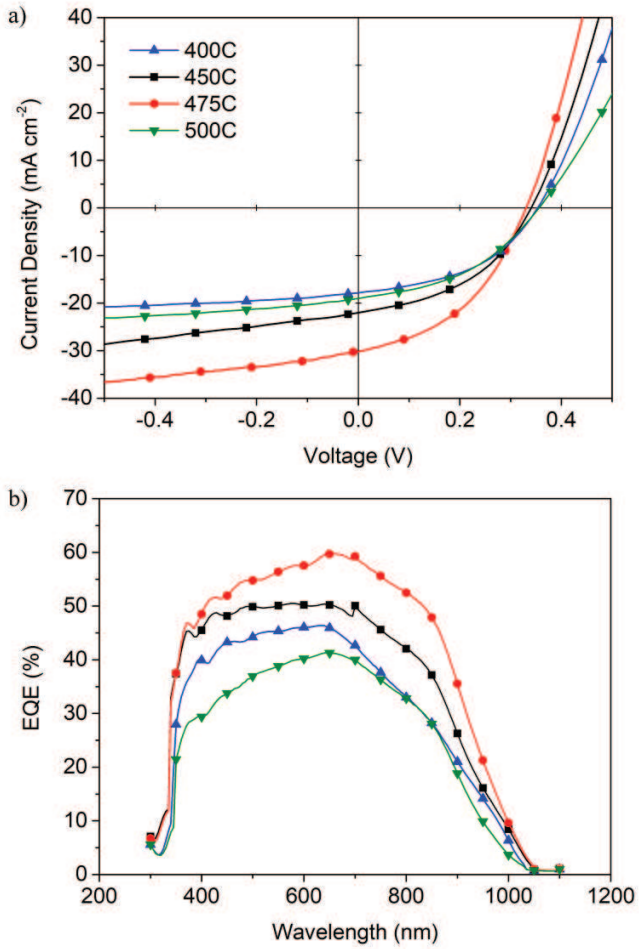

Fig. 5. a) JV and b) EQE curves for highest efficiency device contacts for cells produced using CSS Sb_2Se_3 at temperatures varying from 400 to 500ºC.

Cells were fabricated with Sb_2Se_3 deposited at temperatures of 400, 450, 475, and 500ºC. The J-V characteristics of the peak cell pixel from each 5×5 cm sample plate are shown in figure 3a, with the peak and average parameters also shown in table 1. The best cell performance was achieved using a deposition temperature of 475ºC, mainly due to the increase in J_{sc}. This increase is likely to be due to the improved charge collection from a thicker film and larger grains. The increased thickness of the film is also the likely cause of the drop in V_{oc} due to higher series resistance. Sb_2Se_3 film thickness increased from ~1.1 µm for 400ºC to ~8.5 µm for 475ºC with the film at 500ºC reducing to ~4.0 µm. The increasing chance of void formation at the highest temperature limits the performance, in addition to material loss due to re-evaporation, and therefore the current is reduced for the 500ºC deposition. As the source temperature becomes too high, the substrate reaches a temperature high enough that the rate of re-evaporation from the surface actually reduces the total amount of material deposited. The most consistent limiting factor in all devices is fill-factor, probably caused by a low shunt resistance due to

TABLE I
AVERAGE DEVICE PERFORMANCE PARAMETERS (FROM ~56 DEVICES FOR EACH TEMPERATURE)

	Av. η (%)	Av. V_{OC} (V)	Av. J_{SC} (mA/cm^2)	Av. FF (%)
400ºC	1.43 ± 0.77	0.34 ± 0.06	10.76 ± 4.69	36.41 ± 5.88
450ºC	1.94 ± 0.86	0.31 ± 0.03	15.62 ± 6.23	39.08 ± 2.48
475ºC	3.56 ± 0.49	0.36 ± 0.15	25.74 ± 3.04	40.81 ± 7.69
500ºC	1.29 ± 1.12	0.34 ± 0.03	9.79 ± 7.31	33.61 ± 8.37

TABLE II
PARAMETERS FROM THE CONTACTS HAVING HIGHEST EFFICIENCIES

	Peak η (%)	Peak V_{OC} (V)	Peak J_{SC} (mA/cm^2)	Peak FF (%)
400ºC	2.84	0.36	17.86	44.19
450ºC	3.25	0.34	22.99	41.63
475ºC	4.32	0.33	30.19	43.38
500ºC	2.86	0.36	19.01	41.79

voids and a high series resistance due to a thick absorber layer. It is notable how high the current is at 475ºC with an 8.5 µm thick absorber layer and reinforces our confidence in the potential of this material.

The external quantum efficiencies (EQE) for each peak cell are shown in figure 3b. The wide-bandgap TiO_2 window layer allows much of the low wavelength light into the cell and so produces a relatively square EQE curve at high energies. However, more interesting is the shallow gradient of the EQE curve at the band-edge. This suggests that the thicker films could be reducing the charge extraction efficiency towards the back surface of the cell where longer wavelengths are more likely to be collected. Also, while the large grains and 1D ribbon-like structure may minimize grain boundary defects, it appears likely that there are still many defects present within the material which, results in a significant Urbach-tail. This would also be a significant factor in limiting the V_{oc}. Therefore, to achieve higher efficiencies, there is still significant work to do on identifying defects and defect passivation is likely to be required if they cannot be eliminated during growth.

IV. CONCLUSION

We have demonstrated Sb_2Se_3-based solar cells grown via a CSS technique with very promising performance characteristics. The large, micron-sized, grains produced using this technique have been shown capable of generating and allowing the extraction of high currents, as demonstrated by the maximum J_{sc}. The absorber material has grains spanning the entirety of the layer perpendicular to the substrate and which appear to merge towards the substrate, suggesting benign boundaries. Grain orientation has been shown to be tunable by altering deposition conditions and the desirable (211) and (221) orientations maximised. The peak performance of 4.32% achieved using the CSS method has attained a significant fraction of available current i.e. ~72% of the 42 mA cm^{-2} Shockley-Queisser limit (SQL), whereas the voltage for the best device falls far short (~44% of the possible 0.75 V for the SQL) The slope of the EQE at longer wavelengths at the band-gap suggests significant Urbach-tailing and indicates the presence of defects within the material that require further investigation and passivation before solar cells made with this material can achieve their full potential.

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