



Earth-abundant, RoHS-compliant antimony chalcogenide: top cell alternative for silicon tandem cells -2020/RND014

Public Dissemination Report

Acknowledgement: This Project received funding from ARENA as part of ARENA's Research and Development Program – Addressing end-of-life issues and lowering the cost of solar PV.

Disclaimer: The views expressed herein are not necessarily the views of the Australian Government, and the Australian Government does not accept responsibility for any information or advice contained herein.

Lead organisation: University of New South Wales (UNSW)

Project commencement date: 18 September 2020 **Completion date:** 12 September 2023

Date published:

Contact name: Xiaojing Hao

Title: Professor

Email: xj.hao@unsw.edu.au

Phone: +61 2 9385 4018

Table of Contents

Executive Summary.....	3
Project Overview.....	4
Project summary.....	4
Project scope.....	4
Outcomes.....	4
Transferability.....	5
Conclusion and next steps.....	6
Lessons Learnt Report.....	7
Lessons Learnt Report: Solar cell device structure for one-dimension and strong anisotropy antimony chalcogenide.....	7
Lessons Learnt Report: Inorganic hole transport layer for durable and low-cost antimony chalcogenide solar cells.....	9
Lessons Learnt Report: Stability performance of the antimony chalcogenide solar cells.....	10
Lessons Learnt Report: Bifacial and semitransparent antimony chalcogenide solar cells.....	12
Lessons Learnt Report: Antimony chalcogenide/silicon tandem solar cells.....	14
Lessons Learnt Report: Surface passivation to a Cd-free electron transporting layer in antimony selenide solar cells.....	16

Executive Summary

The project aims to improve the cost effectiveness of current mass-market Silicon (Si) solar panels by developing high efficiency Si-based tandem cells with our proposed antimony chalcogenide ($\text{Sb}_2(\text{S},\text{Se})_3$) thin film photovoltaic (PV) material. To achieve lower levelized cost of energy (LCOE) of Si tandem cells than Si cells, while with improved efficiency, the requirement for low degradation rate of Si tandems is also critical. According to International Technology Roadmap for Photovoltaic (ITRPV), a Si-based tandem cell needs to follow the criteria of <2% degradation after the first year of operation and 0.5% per year afterwards. Despite the reported progress on the high bandgap top cells, there is no affirmable top cell solution yet to meet the above requirements of stability, cost-effectiveness and high-efficiency due to either the poor stability, toxicity (perovskite solar cells), and/or scarce constituent (high bandgap Copper Indium Gallium Sulfide, CIGS, solar cells), and/or relatively low performance (high bandgap kesterite solar cells), compromising the possible availability of a fully sustainable thin film PV technology for Si-based tandem cells in a reasonable time-frame. Our project focuses on an alternative top cell which is ultra-thin, uses abundant and Restriction of Hazardous Substances (RoHS)-compliant materials and has long-term stable performance. Besides, it can be manufactured using a highly compatible and cost-effective process thus providing an appealing option for Si-based tandem solar cells.

Successful tandem cell implementation provides a long-term path to ongoing photovoltaic (PV) cost reductions. Project achievements will likely set the agenda for future PV manufacturing & deployment, the latter through associated sustained cost reductions from steadily improving commercial tandem cell efficiency. As stated in ITRPV, Si-based tandem cells are expected to enter mass production after 2021, and their share in the multi-billion solar PV power industry is predicted to reach 5% within next ten years. With 2025-2030 highly likely the market introduction date (Bloomberg¹), Si-based tandem could capture most of the Si market if a durable top cell ultimately increases the efficiency beyond 30%.

During the progress of this project, research towards the set milestones has been conducted. The expected outcome and deliverables in this milestone period have been achieved. The loss mechanism, point defects and carrier dynamics of our state-of-the-art antimony chalcogenide solar cells have been analysed. Based on that, corresponding key step-change technologies required towards 15% efficiency have been identified. The research on these strategies has been carried out, as well as indoor and outdoor testing analysis. Moreover, the fabrication of a bifacial and semitransparent antimony chalcogenide and its application in tandem solar cells in conjunction with a silicon bottom cell have been conducted. All these results have been published in high-impact journals. In addition, the stability performance of antimony chalcogenide and the related antimony chalcogenide/Si tandem solar cells has been tested and analysed.

The successful completion of these milestones and the conclusion of the research activities and outcomes will guide the further development of high efficiency antimony chalcogenide and the related antimony chalcogenide/Si tandem solar cells under this project. The lessons learnt will also help the research community and industry apply the strategies and techniques generated from this project in other PV research and development activities.

Project Overview

Project summary

This project aims to reduce the cost of silicon photovoltaics (Si PV) through improved cell efficiency by developing a novel top cell option for Si-based tandem cells. Antimony chalcogenide is one of few >10% efficiency high bandgap PV candidates which is Restriction of Hazardous Substances (RoHS)-compliant, has only earth-abundant constituents benign to Si properties, and stable performance. It can be synthesised at moderate processing temperatures (<400 °C) and only requires ultra-thin (300-400 nm) absorbers. Consequently, it has the ideal properties for a top cell as long as 20% efficiency can be achieved.

In this project, UNSW works with its partners to maximise the full potential of antimony chalcogenide starting from our 10% world-record efficiency for an antimony chalcogenide solar cell. The roadmap towards 20% efficiency has been proposed with combined experimental/theoretical exploration, identified key step-change strategies regarding absorber, interfaces and architectures, which are currently limiting antimony chalcogenide solar cells.

Project scope

This project implements a bottom-up research and development approach, starting from our 10% benchmark efficiency antimony chalcogenide ($\text{Sb}_2(\text{S,Se})_3$) established by the project team, exploits the consortium's expertise to maximise the full potential of antimony chalcogenide, providing an appealing alternative top cell with excellent merits for Si-based tandem solar cells. With the well-established device model on the basis of the 10% efficiency antimony chalcogenide, solutions towards 15% efficiency antimony chalcogenide during the course of this project and ultimately towards 20% in the next 5 years have been identified. Associated effective experimental solutions have been developed in this project, paving the pathway for high efficiency Si/ $\text{Sb}_2(\text{S,Se})_3$ tandem cells and the roadmap for upscaling the technology. This has been realised with combined experimental / theoretical exploration, identified key step-change strategies regarding absorber, interfaces and architectures, which are currently missing activation steps for antimony chalcogenide solar cells.

Outcomes

A comprehensive device simulation with the characterisation input from our fabricated antimony chalcogenide solar cells has been performed to understand the loss mechanism of our state-of-the-art antimony chalcogenide solar cells. Based on advanced material and device characterisations, device physics analysis, and device simulation, the core limiting factors for high efficiency antimony chalcogenide solar cells have been identified. The band alignment at the absorber/electron transport layer (ETL) interface and absorber/ hole transport layer (HTL) interface, and the doping density of both ETL and HTL are important factors for creating strong electric field in the absorber. Therefore, the strategies for achieving high efficiency antimony chalcogenide solar cells are identified. The work on exploring suitable hole transport layer materials and processing approach has been published and the study of comparing different electron transport layers is ready for submission as well.

Point defects are a vital aspect which restricts the advancement of antimony chalcogenide solar cells. A systematical investigation has been conducted on the fundamental point defect mechanism through deep-level transient spectroscopy and transient absorption spectroscopy. In specific, the point defects in antimony chalcogenide materials with different ratios of anions (S^{2-}/Se^{2-}) and cations/anions ($Sb^{3+}/S(e)^{2-}$), as well as the thermally driven transformation were characterised and analysed, paving a path towards advanced performance of antimony chalcogenide solar cells by minimising the defect concentration.

A bifacial and semitransparent antimony chalcogenide solar cell has been fabricated by employing ITO as the back contact. The underlying mechanism behind the operation of a single-junction bifacial solar cell was investigated and revealed. Furthermore, an innovative characterisation technique for performance enhancement by exploiting albedo and the capability of absorbing light with sequentially increased tilt incident angles is developed. Additionally, a 4-terminal tandem solar cell was assembled by stacking the bifacial and semitransparent antimony chalcogenide solar cell onto a silicon heterojunction solar cell. They were bonded by transparent epoxy glue. A polydimethylsiloxane film with random, pyramidal textures was introduced at the top surface of the tandem cell to minimise the reflection loss. The performance and quantum efficiency were investigated and analysed.

Indoor and outdoor testing has been conducted on mono-facial, single-junction antimony chalcogenide solar cells. This testing included an evaluation of performance using a low-power LED light source, as well as an analysis of the optoelectronic parameters in relation to varying light intensity and power levels. Furthermore, the degradation of these cells when exposed to outdoor sunlight at different tilt angles was also characterised.

Accelerated stability test has been conducted on the antimony chalcogenide solar cells and the related antimony chalcogenide/Si tandem solar cells. The effect of the test condition on the device performance has been investigated. The unencapsulated antimony chalcogenide and the related antimony chalcogenide/Si tandem solar cells show acceptable stable performance under some test conditions like damp heat. But under other test conditions like thermal cycle and humidity freeze, the device suffers severe delamination, which indicates the thermal stability of the device structure needs to be carefully studied and the strategies for addressing the delamination need to be developed.

The market potential and commercialisation plan of antimony chalcogenide thin film solar cell technology as well as $Sb_2(S,Se)_3/Si$ solar cell have been evaluated. The practical potential, challenges and strategies towards the commercialisation of $Sb_2(S,Se)_3/Si$ tandem cells have been identified based on the manufacturing cost, conversion efficiency, long term stability, upscalable manufacturing method studied during the project.

Transferability

The technical challenges that the project seeks to address are relatively specific to antimony chalcogenide solar cell technology and related Si-based tandem solar cells. However, the achievements and lessons learnt can be applied to other projects which involve other chalcogenide thin film technology, top cell options to Si-based tandems. Tandem solar cells are currently widely studied as they are the pathway to higher efficiencies. Many projects are investigating the potential of perovskite/Si tandem cells as well as III-V compound semiconductors/Si tandem systems both in Australia and worldwide.

Knowledge sharing within UNSW is through regular meetings and seminars, as well as internally produced documents that detail specific processes. We also have a fortnightly antimony chalcogenide meeting, where all researchers present and discuss their results. We also have regular seminars which go into more details about specific research topics. All group members regularly attend conferences, visit research institutions and industries, and give talks at a variety of forums to both specialist and lay audiences. Journal publications have been published in high-impact journals by the research team relating to the innovations developed over the course of this project. In addition, significant results like breaking world record efficiency are also featured in media releases.

Conclusion and next steps

In conclusion, this project has been able to achieve all of its technical milestones. The importance of these milestones is that achieving them indicates the feasibility of the approaches being undertaken. The project has been successful in establishing the leading position of Australia in thin film PV technology as well as Si-based tandem cells development. However, there are still many remaining challenges for tandem cell technology to become commercially available. We will continue to work with our partners established during this project to further promote the chalcogenide thin film technology as well as the tandem concept.

Ultimately, the benefit of the project will be to facilitate and accelerate the development of commercially produced tandem devices on a large scale, which in turn will drive a reduction in the cost of renewable energy. The benefit to the Australian energy system lies in lower cost solar energy generation which will be passed on to domestic and industrial consumers. Given that solar energy is set to dominate electricity production in Australia in the near future (and already dominates newly installed electricity capacity) and the massive growth in renewable energy demand that will arise from both a switch away from coal and gas, and an electrification of the transport system, such a cost reduction will translate to a significant economic benefit

Lessons Learnt Report

Lessons Learnt Report: Solar cell device structure for one-dimension and strong anisotropy antimony chalcogenide

Project Name: Earth-abundant, RoHS-compliant antimony chalcogenide: top cell alternative for silicon tandem cells

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	NSW

Background

Objectives or project requirements

Antimony chalcogenide ($\text{Sb}_2(\text{S},\text{Se})_3$) is a unique one-dimension material with high absorption coefficient ($>10^5 \text{ cm}^{-1}$) and benign grain boundaries. The strong anisotropy of carrier transport imposes a serious limit on carrier mobility. The complicated deep defects lead to low minority carrier lifetime and low effective doping. In a word, $\text{Sb}_2(\text{S},\text{Se})_3$ is a near-intrinsic material with very low carrier diffusion length. This requires development of a specific device structure to accommodate the special properties of antimony chalcogenide.

Process undertaken

Detailed device simulation has been undertaken based on the optical and electrical properties of the state-of-the-art $\text{Sb}_2(\text{S},\text{Se})_3$. The main loss mechanism of the solar cell performance has been identified based on the simulation results and the strategies for achieving high efficiency antimony chalcogenide have been proposed.

Key learning

According to the special optical and electrical properties of the antimony chalcogenide material, p-type semiconductor - intrinsic semiconductor- n-type semiconductor (p-i-n) structure is the most suitable device structure. With a very thin (about 300 nm) and fully depleted absorber, the carrier separation and transport efficiency can be greatly promoted by the built-in electric field spreading into the entire absorber.

Implications for future projects

In order to realise a strong electric field in the absorber in the identified p-i-n device structure, the electron transport layer and hole transport layer should have large Fermi level energy difference or high doping density, respectively. Therefore, seeking alternative electron transport layer and hole

transport layer or modifying current layers are vital for achieving high efficiency p-i-n device structure solar cells.

Lessons Learnt Report: Inorganic hole transport layer for durable and low-cost antimony chalcogenide solar cells

Project Name: Earth-abundant, RoHS-compliant antimony chalcogenide: top cell alternative for silicon tandem cells

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	NSW

Background

Objectives or project requirements

Exploring alternative inorganic hole transport layer to expensive organic materials is vital in reducing the cost and producing durable thin film solar cells. The widely used hole transport layer in p-i-n structure solar cells are usually inorganic materials, e.g., Spiro-OMeTAD (full name: 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene). These materials are usually expensive and not stable. In addition, the deposition techniques for these materials are difficult to be compatible with high output production line for solar modules. Therefore, inorganic, low-cost and stable materials with desirable optical and electrical properties for hole transport layer are highly demanded in developing antimony chalcogenide solar cells.

Process undertaken

Manganese sulfide (MnS) hole transport layer has been explored and used in antimony chalcogenide solar cells. The material properties have been investigated and modified via changing the evaporation process and heat treatment conditions. The solar cell performance and parameters related to the MnS hole transport layer have been studied.

Key learning

The manganese sulfide (MnS) hole transport layer works well in the antimony chalcogenide p-i-n structure solar cells, especially after proper heat treatment. The device applying MnS hole transport layer demonstrates comparable performance as those with high-cost and low-stability Spiro-OMeTAD hole transport layer. In addition, the durability of the device with this inorganic hole transport layer shows much better performance than those with organic hole transport layer.

Implications for future projects

The manganese sulfide (MnS) has been proved suitable for p-i-n structure devices as a hole transport layer, which can be further explored in similar solar cells like perovskite. Moreover, the deposition method for MnS can be scalable thermal evaporation, which is not a limitation for its large-scale application anymore.

Lessons Learnt Report: Stability performance of the antimony chalcogenide solar cells

Project Name: **Efficient Earth-abundant, RoHS-compliant antimony chalcogenide: top cell alternative for silicon tandem cells**

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	NSW

Background

Objectives or project requirements

The stability performance is a vital aspect of a high-efficiency solar cell because it determines the lifetime of the final product and the leveraged cost of energy. Although antimony chalcogenide itself is a stable material, the stability of the solar cell is affected by the multiple functional layers and their interaction during operation. To realise commercialisation of a solar cell technology, the stability performance must be evaluated. Therefore, at the early stage of the development of antimony chalcogenide solar cells, the accelerated stability test needs to be performed to guide the research on how to improve the stability of the solar cells.

Process undertaken

Accelerated stability test has been conducted on the antimony chalcogenide solar cells and the related antimony chalcogenide/Si tandem solar cells. The effect of the test condition on the device performance has been investigated.

Key learning

The unencapsulated antimony chalcogenide and the related antimony chalcogenide/Si tandem solar cells show acceptable stability performance under some test conditions like damp heat. But under other test conditions like thermal cycle and humidity freeze, the device suffers severe delamination, which indicates the thermal stability of the device structure needs to be carefully studied and the strategies for addressing the delamination need to be developed. From another perspective, the delimitation mechanism under accelerated test conditions may imply the failure state of the tandem solar cell, which could provide knowledge on how to recycle the end-of-life Si-based tandem solar cells.

Implications for future projects

The core materials in the solar cell may behave durable, for example, antimony chalcogenide material in this project. However, the solar cell is produced with multiple materials and these materials may interact with each other during working conditions and environment and become unstable or cause

solar cell degradation. Therefore, the durability of the solar cell has to be monitored from the beginning of the research and development.

Moreover, the test conditions that lead to failure state of the antimony chalcogenide and the related antimony chalcogenide/Si tandem solar cells can be recorded and utilised when considering recycling the tandem solar cells at their end-of-life stage.

Lessons Learnt Report: Bifacial and semitransparent antimony chalcogenide solar cells

Project Name: **Efficient Earth-abundant, RoHS-compliant antimony chalcogenide: top cell alternative for silicon tandem cells**

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	NSW

Background

Objectives or project requirements

High-efficiency antimony chalcogenide thin film solar cells have historically been mono-facial and opaque due to the use of metal contacts for both substrate and superstrate configurations. Consequently, they cannot meet the requirement of semitransparency for BIPV windows and top cells in tandem solar cells and the capability of performing well under non-normal and diffuse incident light. Semitransparency and bifaciality are crucial features for thin film solar cells to function in the aforementioned fields.

Process undertaken

A single-sided bifacial and semitransparent $\text{Sb}_2(\text{S,Se})_3$ solar cell was fabricated by employing ITO as the back contact capping on the MnS hole-transporting layer (HTL). The underlying mechanism behind the operation of a single-junction bifacial solar cell was investigated and revealed.

Key learning

ITO and the ultra-thin n-i-p structure provide high transmittance at the long wavelength region. Despite the unfavourable Schottky junction and increased interface defect density, a satisfactory power conversion efficiency with only front illumination is achieved. On the other hand, though the varied carrier kinetic with rear illumination has a negative impact on the power conversion efficiency (PCE), the internal ultrathin fully depleted absorber layer enables it to remain at a satisfying level, contributing to great bifaciality. As a result, our bifacial and semitransparent antimony chalcogenide solar cells can gain great enhancement in PV performance by exploiting albedo of surroundings and show exceptional capability in absorbing non-normal incident light.

Implications for future projects

The first bifacial and semitransparent structure for antimony chalcogenide collectively highlights the significant potential of antimony chalcogenide for widespread applications due to their adjustable bandgap, up-scalable deposition methods, semitransparent properties, and ability to effectively absorb non-vertical incident light.

In addition, innovative characterisation techniques on performance enhancement by exploiting albedo and the capability of absorbing light with sequentially increased tilt incident angles are developed. This technique is highly applicable for a comprehensive assessment of the performance of all bifacial solar cells.

Lastly, the substitution of the gold contact with an ITO back contact has not only significantly reduced costs but also improved the capability to capture non-vertical incident light. This structural modification has the potential to be adopted by other thin-film solar cells.

Lessons Learnt Report: Antimony chalcogenide/silicon tandem solar cells

Project Name: **Efficient Earth-abundant, RoHS-compliant antimony chalcogenide: top cell alternative for silicon tandem cells**

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	NSW

Background

Objectives or project requirements

Owing to the suitable bandgap and high transmittance at long wavelengths, the bifacial and semitransparent antimony chalcogenide solar cells are applicable as top cells in tandem solar cells to increase the overall efficiency and energy yield. Transmitted light beyond the absorption spectra of antimony chalcogenide can be efficiently absorbed by a bottom cell with a narrow bandgap, such as a silicon solar cell. Therefore, antimony chalcogenide/silicon tandem solar cells are expected to be developed.

Process undertaken

A 4-terminal tandem solar cell was assembled by stacking a bifacial and semitransparent antimony chalcogenide solar cell onto a silicon heterojunction solar cell. They were bonded by transparent epoxy glue. A polydimethylsiloxane film with random, pyramidal textures was introduced at the top surface of the tandem cell to minimise the reflection loss. The performance and quantum efficiency were investigated and analysed.

Key learning

Without substantive extra expense, the feasibility of the proposed tandem structure was verified. Silicon bottom cell can actually absorb the long-wavelength light transmitted through the antimony chalcogenide top cell, and then provide additional photoelectric conversion. Therefore, the 4-terminal tandem solar cell achieved a great power conversion efficiency, breaking the efficiency record of single-junction antimony chalcogenide solar cells with ease.

Implications for future projects

The successful trial and the impressive power conversion efficiency of antimony chalcogenide/silicon tandem solar cells underscore the significance of advancing the development of bifacial and semitransparent antimony chalcogenide solar cells as well as tandem solar cells. Moreover, there exists significant potential for further optimising the initial tandem cell design and fabrication process to attain even higher efficiency levels. One promising avenue for enhancement is the utilisation of a silicon bottom cell that is specifically tailored in terms of size and structure to match

the tandem configuration, thus reducing edge recombination and improving overall performance. Furthermore, the bandgap of the antimony chalcogenide top cell can be fine-tuned by adjusting the selenourea dosage, ensuring a better alignment with the silicon sub-cell's bandgap and consequently enhancing tandem efficiency.

Lessons Learnt Report: Surface passivation to a Cd-free electron transporting layer in antimony selenide solar cells

Project Name: **Efficient Earth-abundant, RoHS-compliant antimony chalcogenide: top cell alternative for silicon tandem cells**

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar PV
State/Territory:	NSW

Background

Objectives or project requirements

Up to now, high-efficiency antimony selenide solar cells have always used CdS as an electron transport layer. However, the parasitic absorption caused by CdS reduces the light absorption of the antimony selenide absorber layer while the toxicity of Cd largely limits its practical applications. Thus, it is of great significance to replace CdS substrates and develop efficient Cd-free antimony selenide solar cells. In this regard, metal oxide semiconductors are desirable to be used as electron transporting layers for antimony selenide solar cells.

Process undertaken

SnO₂ was adopted as the electron transporting layer in antimony selenide solar cells. Furthermore, InCl₃ solution was used for surface passivation on SnO₂, followed by a post-annealing treatment. Subsequently, antimony selenide films were deposited through a thermal evaporation deposition. The underlying mechanism behind the performance improvement of InCl₃ treatment was investigated.

Key learning

The InCl₃-modified SnO₂ not only significantly improved the crystallinity of antimony selenide films and increased the grain size, but also optimised the band alignment between SnO₂ and Sb₂Se₃. Furthermore, the deep-level defects in antimony selenide were reduced, and thus prolonged the carrier lifetime of the absorber layer. As a result, the efficiency of the solar cell got a significant improvement, which is the highest power conversion efficiency among completely Cd-free antimony selenide solar cells prepared by vacuum thermal evaporation.

Implications for future projects

A straightforward and efficient surface treatment method for enhancing the performance of Sb₂Se₃ solar cells deposited on metal oxide substrates is presented. This method significantly improves the viability of SnO₂ as an electron transport layer, paving the way for the development of highly efficient Cd-free Sb₂Se₃ solar cells. The absence of cadmium in this composition holds the promise of large-scale applications.