Australian National University

Direct Water Electrolysis [2018/RND006]

Mid-Term Activity Report

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Executive Summary

The aim of this project is to address the issues which hinder the potential of III-V semiconductors for photoelectrochemical (PEC) hydrogen generation, namely their high cost and poor stability. Indeed, although they enable the highest energy conversion efficiencies, III-V-based PEC systems typically involve sophisticated growth techniques, expensive co-catalyst materials and short lifetimes. Overcoming these challenges is crucial to promote the commercial prospects of solar hydrogen systems, which have been identified as a key element to the energy transition.

Although the requirement to grow III-V semiconductors by complex epitaxial techniques is hardly avoidable, some research directions have emerged in the last years to reduce the balance of costs of these PEC systems.

(1) The optimisation of the electronic structure with the use of multijunction cells could lead to increased solar-to-hydrogen (STH) efficiencies to counterbalance the fabrication costs.

(2) Efforts are invested in the development of substrate recycling methods for these expensive materials. In particular, the spalling lift-off technique has shown promising preliminary results.

(3) The search for earth-abundant alternatives to noble metal-based co-catalysts is a very active area of research.

(4) The investigation of efficient passivation techniques to improve the stability (hence durability) of PEC systems is continuously enriched with the optimisation of thin-films deposition techniques.

The project thus focusses on the design and development of III-V-based robust integrated solar-driven water splitting systems with >20% Solar to Hydrogen (STH) conversion efficiency and stability over 200 hours, with an emphasis on lowering the balance of system costs.

In this report, we cover the progress made during the first half of the project and highlight key technical results for each of the directions presented above. These results demonstrate that we are on track to complete the project objectives, despite some delays due to the 2020 crises (bushfires, hailstorm damage to facilities and COVID-19 lockdown). Remaining technical challenges include the optimisation of the photovoltaic part of the system and the integration of the multiple strategies explored into a single device.

We further provide insights onto the transferability and commercialisation prospects of the systems we have developed so far. These aspects are to be more carefully examined in the remainder of the project, notably with a technoeconomic feasibility study. We expect that our work will lead to the production of patents and subsequent commercial agreements for solar-driven water splitting systems.

Project Overview

Project Scope

Owing to their excellent optical and electrical properties, III-V semiconductors are ideal candidates for high-efficiency solar-driven water splitting. However, despite remarkable demonstrations in laboratory, III-V-based PEC systems remain a long way from large-scale fabrication and deployment. The two major bottlenecks to this widespread commercial production are the cost and stability of the III-V based systems. III-V structures are indeed typically grown using expensive source materials and demanding, complex, high-maintenance epitaxy techniques such as metal-organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE). Moreover, III-V materials are known to be prone to photocorrosion and III-V-based PEC systems reported in literature have rarely demonstrated operation for more than a couple of hours, making these systems not viable.

This project addresses both challenges by targeting increased STH efficiencies, ensuring the reusability of the substrates, investigating earth-abundant co-catalysts and enhancing the resistance of III-V materials to photocorrosion.

The combination of multiple III-V photoabsorbers in multijunction architectures allows an optimal exploitation of the solar spectrum, leading to higher STH efficiencies that could counterbalance the fabrication costs. However, the growth of an ideal structure for water splitting involves significant technical challenges. More specifically, the ideal electronic configuration to maximise light absorption while enabling spontaneous water splitting correspond to the stacking of highly mismatched materials with specific bandgaps (1.7 and 1.0 eV). The growth of a good quality metamorphic double-junction system thus necessitates the development of complex intermediate buffer layers to bridge the lattice parameter gap. In order to keep such system economically viable, this project aims to develop a relatively simple buffer structure of reasonable thickness providing a defect density low enough for solar-driven operation.

A further goal of the project involves the development of epitaxial lift-off techniques that would allow the exfoliation of the active region of the PEC cell and multiple reuses of the underlying substrate. The spalling technique, in particular, is investigated on GaAs and InP substrates, which are cornerstones of high-efficiency PV and PEC systems. This technique is quite recent and holds promise for cost reduction for III-V systems, not only for solar applications. It is an interesting alternative to the traditional chemical lift-off that often involves toxic and polluting substances for making flexible devices.

Additional cost reduction is expected from the replacement of state-of-the-art noble-metal-based co-catalysts by earth-abundant co-catalysts. Co-catalysts are essential components of PEC systems as they provide a significant boost of the catalytic activity of the photoabsorber. Additional benefits include the enhancement of the charge carrier separation, notably in nanostructures, as well as a relative passivation of the underlying material by favouring the oxygen/hydrogen evolution reaction over photocorrosion. Co-catalysts are typically made of noble metal nanoparticles which are too expensive for widespread commercialisation.

Last but not least, the development of efficient passivation techniques is an inevitable requirement for practical applications of PEC systems. Both materials and deposition techniques are being investigated for this purpose and have proven to provide protection over several weeks. More systemic approaches like photoelectrode decoupling and encapsulation are also promising to enable a simplification of the fabrication process and reduced costs.

As the final goal of this project, all the above-mentioned strategies will be combined to realise a high-efficiency, bias-free water splitting via a passivated, co-catalyst-coated tandem III-V PEC cell. Ultimately, this project targets to achieve a STH efficiency above 20% and stability over 200 h.

Project Summary

For this first half of the project, one of the main goals was (1) to design and establish epitaxial growth techniques for double-junction photovoltaic devices with optimal bandgaps for water electrolysis. The major development effort went towards designing a metamorphic buffer that allowed the combination of materials with ideal bandgaps but highly mismatched lattices. Theoretical simulations have shown that a tandem PEC cell combining the 1.7 and 1.0 eV bandgaps is the best candidate to achieve high STH conversion efficiencies, required for commercialisation prospects. We have developed III-V alloys demonstrating these specific bandgaps. Due to their significant lattice mismatch, we have further designed and fabricated a metamorphic buffer structure to bridge the two lattice parameters.

We have also investigated other techniques to make the proposed PEC system more cost-effective and stable: (2) the spalling of III-V thin films to enable substrate recycling, (3) the integration of earth-abundant co-catalysts with III-V cells and (4) the effective protection of III-V cells by either a passivating film or effective encapsulation in a decoupled-photoelectrode configuration. All these developments are fundamental steps toward the realisation of a high-efficiency long-stability cost-effective III-V water splitting system.

More details on the results achieved are provided in the next section.

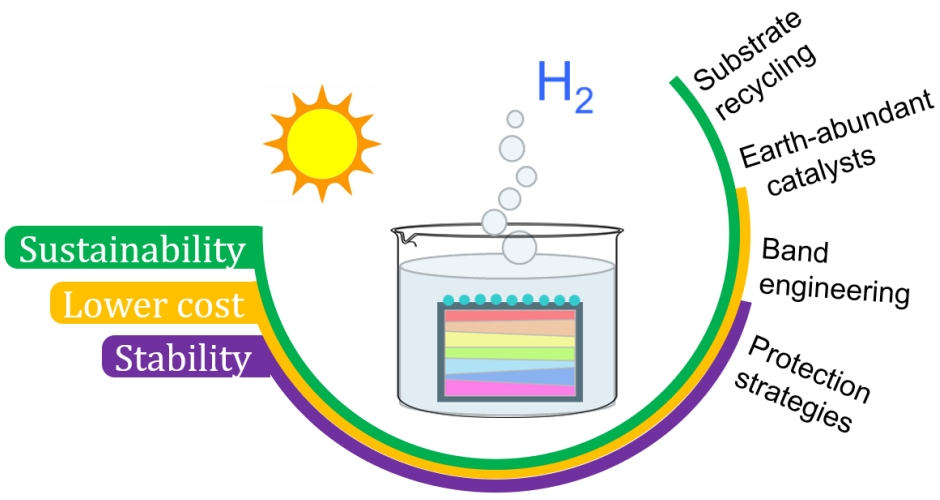

Figure: Recapitulative visualisation of the project goals.

Key highlights

Theoretical studies have identified the ideal bandgap combination for water splitting to be 1.7 / 1.0 eV for the top / bottom cells. This combination could correspond to the lattice-matched $Al_{0.44}In_{0.56}As$ / $In_{0.80}Ga_{0.20}As_{0.44}P_{0.56}$ system (grown on InP) or to the lattice-mismatched $In_{0.32}Ga_{0.68}As_{0.34}P_{0.66}$ / $In_{0.27}Ga_{0.73}As$ system (grown on GaAs). We have explored both options to achieve the desired bandgap combination. We studied all candidate materials and achieved the targeted bandgap values for $In_{0.80}Ga_{0.20}As_{0.44}P_{0.56}$, $In_{0.32}Ga_{0.68}As_{0.34}P_{0.66}$ and $In_{0.27}Ga_{0.73}As$ but showed that the theoretical bandgap value of $Al_{0.44}In_{0.56}As$ was overestimated. We have thus decided to pursue the lattice-mismatched double-junction cell. Following this, we have designed and grown an $In_{0.32}Ga_{0.68}As_{0.34}P_{0.66}$ / $In_xGa_{1-x}P$ / $In_{0.27}Ga_{0.73}As$ metamorphic structure. We have studied various design parameters of the $In_xGa_{1-x}P$ step-graded buffer such as growth temperature, pause time, misfit grade and overshoot layer composition. After a first round of optimisation, we were able to reach a 10^8 cm^{-2} threading dislocation density for a total buffer thickness of 3 µm. Although this threading dislocation density is high, it corresponds to a relatively thin buffer with simple design. Moreover, contrary to the best metamorphic buffers reported in the literature, we have chosen an Al-free route to ensure a better operation in an aqueous solution. Obviously, finer tuning of the buffer thickness is required to reduce the roughness and dislocation density but our preliminary results demonstrate the feasibility of an Al-free metamorphic structure with ideal bandgaps.

Among the various techniques available to produce high-quality III-V thin films, we have identified spalling as one of the most promising. This technique makes use of mechanical stress to detach a crystalline layer from a substrate. Spalling has recently been used with good results for Si, Ge, GaAs and GaN films. We have thus investigated the spalling of large-area InP films and demonstrated the potential of this technique for reduced-cost III-V systems. The obtained InP thin (< 20 µm) films proved of high quality, even after multiple spallings from the same substrate. We have further demonstrated that the fractured surface could be tailored to introduce texture, which is beneficial for anti-reflection properties. We have also studied the influence of induced strain on the electronic properties of the spalled film. Although the thickness of the spalled films should be slightly reduced for application to metamorphic double-junction solar cells, these results show excellent promise for this cost-effective substrate recycling technique. Moreover, they constitute highly promising results for any other type of flexible electronics application.

In terms of co-catalysts, we have developed $NiFe(OH)_x$ and $NiMo_x$ to drive oxygen evolution reaction and hydrogen evolution reaction, respectively, at high catalytic efficiencies. We have integrated these earth-abundant co-catalysts onto Ni foil with commercial III-V solar cells and demonstrated an enhanced water-splitting performance for a GaAs photoanode. The photoelectrode demonstrated record performance, not only for GaAs photoanodes but for any single-junction photoanode. More importantly, we have fabricated an unassisted water splitting PEC system made of two commercial GaAs solar cells in series with the Ni foil-supported earth abundant co-catalysts. This system achieved the highest STH efficiency reported for a single-junction PEC device with earth-abundant electrocatalysts and the second-highest for any single-junction PEC device. The long-term stability of the artificial leaf was also maintained for over 9 days, which is the second-longest duration reported in the literature for a PEC water splitting device. In the future, the co-catalysts will be integrated directly on the metamorphic double-junction solar cell developed in this project.

Concerning the improvement of III-V cells stability, we have investigated two approaches. For the first one, we have developed an efficient sulfide layer for passivation of InP and demonstrated its efficiency in protecting InP nanostructures. The passivated photocathodes proved to be highly stable for over 24 h of testing, compared to a few minutes only in the absence of passivation. Moreover, the photocathode performance was improved both in terms of light absorption and catalytic efficiency. The other approach we have studied consisted in the decoupling of the photoactive and catalytic components of a PEC system. We have thus integrated commercial III-V solar cells with catalysts. This decoupled configuration allowed us to encapsulate the solar cells, providing them extended protection, while maximizing the catalytic efficiency and offering more flexibility in the choice of catalysts.

While further work is still needed to integrate the above-mentioned strategies into a functional PEC system with high efficiency, these results represent significant technological advances made in enabling cost-effective stand-alone solar water splitting systems.

Difficulties experienced

Like for many research teams across the world, 2020 has been a challenging year due to COVID-19. In addition, bushfire smoke has significantly restricted our access to the University over the 2019-2020 Summer. Furthermore, significant damages that occurred at ANU during the hailstorm of January 2020 have necessitated substantial repair work and lengthy administrative procedures. The repair work was additionally delayed by the COVID-19-related lockdown, lengthy delays in procurement times of items for repair and travel restrictions for contractors to repair the facilities. Overall, we have been unable to use the MOCVD reactors for about ten months in 2020 and other chemical and characterisation laboratories for several months as well. The pandemic crisis has also restricted us from participating in conferences and knowledge sharing activities, including face-to-face meetings with our partners/collaborators.

Transferability

Although the innovations made and challenges addressed in this project are more specific to PEC water splitting systems, they are broadly applicable to other optoelectronic devices, not restricted to PV cells and electrolysers. In particular, the spalling technique is of interest for any field involving III-V thin films (flexible electronics). The vast catalysis field, notably active industrially, also shares our interest for the development of earth-abundant co-catalysts. Finally, efficient passivation is a challenge faced by any (opto)electronic system with commercialisation prospects. We anticipate that the material/device designs with the highest commercial potential will be patented and subsequent commercial agreements will be sought for their widespread use.

Knowledge sharing within the project occurs through fortnightly meetings, seminars, as well as internally produced documents that detail specific processes. The project partners participate in regular meetings to discuss new results and specific challenges. The chief investigators and other researchers involved in the project attend conferences, visit research institutions, and give talks at a variety of forums for both specialist and non-specialist audiences, within the limits of COVID-19 restrictions. For example, one of the project members gave a public webinar in December last year, hosted by the Australian National Nanofabrication Facility.

Finally, we have conveyed the knowledge gathered during this project in two review articles illustrating promising directions for PEC systems. The first one, focused on III-V materials, has been published in ACS Energy Letters (Tournet, J., Lee, Y., Karuturi, S.K., Tan, H.H. and Jagadish, C., 2020. III–V Semiconductor Materials for Solar Hydrogen Production: Status and Prospects. ACS Energy Letters, 5(2), pp.611-622). The second one, focused on the spalling technique, has been published in ACS Applied Electronic Materials (Lee, Y., Tan, H.H., Jagadish, C. and Karuturi, S.K., 2021. Controlled Cracking for Large-Area Thin Film Exfoliation: Working Principles, Status, and Prospects).

Commercialisation prospects

A detailed technoeconomic feasibility study is one of the main goals of the remainder of the project and will provide a more detailed analysis of the commercialisation prospects of the different

strategies developed. We are also currently investigating different designs of direct water splitting reactors that could use commercial solar cells.

Conclusions and next steps

The project has been successful so far in developing the foundations of a cost-effective III-V PEC system by tackling various challenges met by III-V semiconductors in this context. However, the integration of these individual components into an operational device satisfying the requirements of high efficiency and long stability for commercialisation prospects remains to be achieved. Our work in the second part of the project will be focussed on this integration. We will also pursue the optimisation of the photovoltaic tandem cell to further increase the efficiency of the PEC device. Moreover, to better inform future work on this technology, we will also undertake a technoeconomic feasibility study of spalled tandem solar water splitting systems.

Ultimately, the benefit of the project will be to facilitate and accelerate the development of commercial technologies for solar hydrogen generation by developing robust integrated stand-alone systems with >20% STH conversion efficiency and long-term stability, providing widespread potential for renewable hydrogen exports from Australia.

List of publications related to the project

Published:

Lee, Y., Yang, I., Tan, H.H., Jagadish, C. and Karuturi, S.K., 2020. Monocrystalline InP Thin Films with Tunable Surface Morphology and Energy Band gap. *ACS Applied Materials & Interfaces*, *12*(32), pp.36380-36388.
https://doi.org/10.1021/acsami.0c10370

Tournet, J., Lee, Y., Karuturi, S.K., Tan, H.H. and Jagadish, C., 2020. III–V Semiconductor Materials for Solar Hydrogen Production: Status and Prospects. *ACS Energy Letters*, *5*(2), pp.611-622.
https://doi.org/10.1021/acsenergylett.9b02582

Lee, Y., Tan, H.H., Jagadish, C. and Karuturi, S.K., 2020. Controlled Cracking for Large-Area Thin Film Exfoliation: Working Principles, Status, and Prospects. *ACS Applied Electronic Materials 2020, in press.*
https://doi.org/10.1021/acsaelm.0c00892

Butson, J.D., Narangari, P.R., Lysevych, M., Wong-Leung, J., Wan, Y., Karuturi, S.K., Tan, H.H. and Jagadish, C., 2019. InGaAsP as a Promising Narrow Band Gap Semiconductor for Photoelectrochemical Water Splitting. *ACS Applied Materials & Interfaces*, *11*(28), pp.25236-25242.
https://doi.org/10.1021/acsami.9b06656

Under revision:

Narangari, P.R., Butson, J., Tan, H.H., Jagadish, C. and Karuturi, S.K., 2020. Wafer-Scale Fabrication and Surface Engineering of InP Nanowires: Stabilised InP Nanowire Photocathodes for Efficient Water Reduction. *Nano Energy*.

Lu, H., Tournet, J., Dastafkan, K., Liu, Y., Hau Ng, Y., Karuturi, S.K., Zhao, C. and Yin, Z., 2021. Noble-metal-free Multicomponent Nanointegration for Sustainable Energy Conversion. *Chemical Reviews.*

Under review:

Tournet, J., Butson, J.D., Narangari, P.R., Dontu, S., Lysevych, M., Karuturi, S.K., Tan, H.H. and Jagadish, C., 2020. Narrow-bandgap InGaAsP solar cell with TiO_2 carrier-selective contact. *IEEE Journal of Photovoltaics*.

In preparation:

Butson, J., Sharma, A., Chen, H., Wang, Y., Lee, Y., Tricoli, A., Zhao, C., Tan, H.H., Jagadish, C. and Karuturi, S.K., 2020. Surface-Structured Ni-based Catalyst Foils Enabling Highly-Efficient Ultra-Stable Photoelectrodes.

Lessons Learnt report

Lesson learnt 1: Optimisation of metamorphic buffers

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar Hydrogen
State/Territory:	ACT

Background:

Objective or process requirements

To fabricate a monolithic double-junction solar cell with ideal electronic bandgaps for water splitting, a metamorphic buffer is needed to bridge the lattice parameter gap between the two subcells. This metamorphic buffer aims at engineering the strain relaxation between the two active regions in order to minimise the defect density, more particularly the threading dislocation density which has a significant impact on the solar cell performance. It is a highly complex structure made of multiple layers of specific graded compositions and requires high precision.

Key learnings

We faced difficulties in optimizing the metamorphic buffer design and growth without *in-situ* and *in-operando* characterisation tools. Metamorphic buffers are indeed complex structures for which each layer has to be carefully optimised in terms of composition and strain relaxation. This is very challenging to do with great accuracy relying only on external post-growth techniques such as X-ray diffraction or optical/electron microscopy. We managed to establish a growth strategy by combining a multitude of *ex-situ* characterisation techniques but we acknowledge that the use of *in-situ* tools such as multiple optical beam stress sensor (in the case of MOCVD) of reflection high-energy electron diffraction (in the case of MBE) would have been more convenient and accelerated our progress.

Implications for future projects

It is imperative in future projects to better estimate time delays that could occur from the lack of specific equipment. To save more time, it would also be beneficial to better identify and prepare all the required available characterisation systems before establishing the growth plan. Obviously, this is a complex task in a shared facility with numerous users, but could be eased with better communication.

Knowledge gap

Based on our experience in III-V films epitaxy and lattice-mismatched growth, we were able to quickly apprehend the fundamentals of metamorphic buffers. Interactions with peers have helped us make further progress. Some knowledge gaps regarding highly technical considerations for characterisation (e.g. reciprocal space mapping or dislocation analysis by electron microscopy) remain, on which we are progressing. COVID-19 has made it more difficult to fill these knowledge gaps as experts are not mobile as they usually are but we have still benefited from good contacts in the III-V solar community.

Publications/patents:

N/A

Lesson learnt 2: Quaternary alloy homogeneity

Knowledge Category:	Technical
Knowledge Type:	Technology
Technology Type:	Solar Hydrogen
State/Territory:	ACT

Background:

Objective or process requirements

A significant part of milestone 2 targeted the development of III-V materials with ideal bandgaps for water splitting, *i.e.* 1.7 and 1.0 eV. These bandgaps can be achieved by alloying III-V elements into a single compound. However, most quaternary compounds present significant miscibility gaps, making them unstable and prone to phase segregation. The use of non-equilibrium growth techniques, such as MOCVD, allows to circumvent the miscibility gap. Yet, the material quality remains extremely dependent upon growth conditions (temperature, V/III ratio, pressure, growth rate, substrate orientation and offcut, *etc*).

Key learnings

We faced difficulties in optimizing the growth of photovoltaic-grade quaternary alloys. This is due to the extreme sensitivity of the quaternary materials to the growth parameters. The recent laboratory closedowns due to bushfires, hail damage and COVID-19 have significantly delayed our progress in this optimisation, which routinely requires numerous growth runs and characterisations.

Implications for future projects

It is imperative in future projects to better estimate these risks and establish a growth plan that considers the possibility that the MOCVD reactor might not be available for long periods of time.

Knowledge gap

N/A

Publications/patents:

N/A