



[2-A005 The Hot Carrier Solar Cells]

Project results and lessons learned

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Executive Summary

The goal of this project was to demonstrate proof-of-concept Hot Carrier solar cells toward the development of a high efficiency, low cost device. The HC solar cell is a promising advanced photovoltaics or so called “third generation” concept which aims to tackle the major loss in conventional solar cells that most of the energy of high energy blue photons in the solar spectrum is lost as heat before the electrons excited by the photons can be extracted as an electrical current. These photo-excited “hot” carriers (carriers with energy above the fundamental energy level of the solar cell – the ‘band gap energy’) lose their excess energy as heat or lattice vibrations in a few trillionths of a second. The limiting efficiency of the HC solar cell is 65% for non-concentrated solar radiation, whereas it is more than 85% for maximally concentrated sunlight.

The main anticipated outcomes of this project were:

- The distribution of the lattice vibration energies in real material systems - phononic dispersion model.
- HC solar cell efficiency model using practical absorber and special ‘Energy Selective Contacts’.
- Process to deposit highly ordered monolayer and multilayers of nanoparticles.
- Improved energy selectivity for Energy Selective Contacts.
- Integration of HC absorber and energy selective contacts.
- Market assessment of the technology.

The project has successfully delivered all of these outcomes and has met the milestones. The progress of this project has been reported through milestone reports.

Absorber materials in bulk and nanostructured form, which have potentially long thermalisation time constants, have been theoretically and experimentally investigated. Thin films of indium nitride (InN) which is an ideal absorber material due its large phonon gaps and low electronic band gap and its chemical analogues were investigated. In addition, high quality III-V semiconductor quantum dots and quantum wells were fabricated in collaboration with partners in Japan and the USA. We have developed a nanoparticle deposition facility using Langmuir-Blodgett (LB) techniques to deposit a highly ordered array of nanoparticles (NPs). The technique was further developed to incorporate multiple layers by a sequential deposition technique.

For Energy Selective Contacts (ESCs), double barrier structures consisting of quantum dots (QDs) or a quantum well (QW) in an insulating dielectric oxide or nitride matrix were investigated. The QDs/QWs provide a discrete energy level between two insulating barriers which is expected to give conduction of carriers strongly peaked at these particular energy levels, but much lower at other energies – hence selecting a particular energy level. The position of the peak and the selectivity can be tuned by carefully choosing the QD size and the insulating barrier thickness of the contacts. ESC structures included $\text{SiO}_2/\text{Si QD}/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{Si QW}/\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3/\text{Si NP}/\text{Al}_2\text{O}_3$.

Complete HC solar cell devices combining absorber and energy selective contacts have been fabricated with thin film deposition methods. Solar cell characteristics of these devices have been measured with illuminated current vs. voltage (I-V) curves. The devices have shown power generation, demonstrating the collection of hot carriers with an ESC thus demonstrating HC solar cell performance.

Project Overview

Project summary

The aim of this project was to demonstrate the proof-of-concept Hot Carrier (HC) solar cells, an important step toward developing cost-effective, high efficiency solar cells. In order to achieve this, the two main components of the HC solar cell, absorber and energy selective contacts, have been separately investigated, both theoretically and experimentally. Optimised structures were combined together to develop a complete HC solar cell device.

Project scope

Over the last decade the cost of the generation of photovoltaic electricity has significantly decreased. In fact in some countries, it is cheaper than the retail price of electricity from fossil fuel based generation. However, for mass implementation of photovoltaics at the scale of terra Watts needed to replace fossil fuel generation completely, the cost has to further reduce, such as to be similar to or lower than the 'wholesale' price of fossil fuel based electricity. The most promising way to achieve this is to increase the efficiency of solar cells. This not only reduces the cost of the solar cell generation itself but also the relative costs of the balance of systems (BOS) cost for a given generation capacity. As for a fixed 1KW system, the installation area decreases with increase in the efficiency of the solar cells. This BOS cost is now a significant cost component of a PV system (60-70%) and hence needs to be addressed in order to reduce the cost of electricity delivered by PV systems. The conventional single junction solar cell efficiency is limited to about 31% due to unavoidable losses, the major ones being the non-absorbance of the sub-bandgap photons and thermalisation of carriers generated by high energy photons. This project has aimed to address these issues by developing a new type of solar cell device, called the Hot Carrier solar cell that has a theoretical efficiency limit of about 65% at one sun and about 75% at 1000X concentration or 85% at maximal concentration. Although the theoretical concept has existed for several years, there was not any practical demonstration. This is because it demands stringent requirements on the two crucial components, namely the absorber and the energy selective contacts. In this project we have investigated a range of materials and structures for their suitability as absorbers or as energy selective contacts. Potential materials were fabricated and characterised with advanced characterisation techniques. The most promising absorbers and contacts were integrated together to realise a proof of concept HC solar cell devices.

Outcomes

In this project we have theoretically and experimentally investigated absorber and energy selective contacts and combinations of these for the demonstration of proof of concept Hot Carrier solar cell. The project has achieved all the milestones and project outcomes. This work has generated 12 journal publications and a similar number of conference proceedings. The main outcomes of this project are briefly described below:

Phonon modelling: A model able to predict the phonon dispersion of specific III-V materials and a number of nanostructures has been developed. This is able to map phonon dispersions and also phonon decay rates based on density of states.

Hot carrier solar cell efficiency modelling: A model to calculate the limiting efficiencies of a III-V based HC solar cell has been developed. This model is based on conservation of energy and balance of particle number that takes into account the effects of the actual impact ionization (II) and Auger recombination (AR) rates. Furthermore, several properties of the absorber material and Energy Selective Contacts (ESCs), such as electronic dispersion curves and absorption coefficients, have been considered in the calculation. This model represents a great improvement in the calculation of HC solar cell limiting efficiency values, since previous models were based on ideal material and used either a particle conservation approach or ideal infinitely fast II-AR theory. The modelling framework has been further improved to allow investigation of the effects of non-ideal ESCs on the device performance. The improved model has been applied to an InN based HC solar cell with InN/InGaN ESCs.

Nanoparticle deposition system: A deposition facility for colloidal nanoparticles has been established using a Langmuir-Blodgett (L-B) system for fabrication of uniform arrays of nanoparticles. This facility has been used to deposit close-packed single layers and multilayers of size-uniform nanoparticles for absorber and energy selective contacts, for example Si and PbS.

Hot carrier lifetime of absorber materials: Time Resolved Photoluminescence (TRPL) measurements have been performed on several bulk III-V semiconductor materials in order to investigate the relation between phononic properties and hot carrier relaxation times. Comparison of hot carrier transients in InP and GaAs showed a slower cooling in InP which has the wider phononic bandgap. TRPL experiments have been performed on several high quality bulk InN samples grown by collaborators. These measurements showed that carrier cooling in InN is strongly affected by material quality and growth technique. Carrier lifetimes in L-B deposited closely packed Si and PbS nanoparticles has also been investigated. A model has been developed to interpret the TRPL data and to extrapolate the equivalent hot carrier temperature from PL spectra. For non-luminescent samples ultrafast transient absorption (TA) has been used to investigate hot carrier cooling times.

Fabrication of Energy selective contacts: Double barrier resonant tunnelling structures consisting of silicon QW in aluminium oxide matrix and germanium QW in germanium nitride matrix have been investigated for Energy Selective Contacts (ESCs). While the former combines the stability and abundance of Si and Al, the later can possibly be made at a much lower temperature due to the much lower melting temperature of Ge compared to Si. All of these structures were grown by thin

film deposition techniques employing RF sputtering. Process parameters have been varied to optimise the material properties to improve resonant tunneling through these structures.

Proof of concept Hot carrier solar cell device: Complete HC solar cell devices combining absorber and energy selective contacts have been fabricated with thin film deposition methods. Devices were fabricated on either n-type or n⁺-type Si wafer. A 140nm layer of sputtered hafnium nitride (HfN) is deposited as the absorber. Then a variety of top layers were deposited as energy selective contacts. On one group of samples, a thin layer of Si or of Ge was sputtered. The other group had double barrier resonant tunnelling contacts with either Ge or Si QW between Al₂O₃ barriers. All these thin film layers were deposited by a low cost sputtering method. Contacts were made with Au on the back and either Al or In/Ag on the front. Solar cell characteristics of these devices have been measured with illuminated I-V. Both types of devices show power generation. The measurements are very repeatable. This demonstrates collection of hot carriers from the front of the device with an ESC. Carriers are thus collected at the voltage of the ESC which is elevated above the band gap of the absorber (HfN band gap is zero or very small). This thus demonstrates HC solar cell performance.

Market assessment: Market assessment of the Hot Carrier solar cell has been performed. Cost and energy payback times (EPBT) of HC solar cells for two device architectures, thin film deposition and roll-to-roll solution processed fabrications, have been calculated. The results show that the cost of thin film based HC solar cells is very high compared to commercial silicon photovoltaics. However, the cost for solution processed HC devices could be lower than silicon solar cells.

Transferability

Many research groups in Australia and worldwide aim to develop high efficiency thermoelectric (TE) devices. The conversion efficiency of TE materials is related to their temperature dependent 'figure of merit' ZT. Restriction of heat flow through the materials is a promising approach to increase the figure of merit of thermoelectric materials, and hence to improve the energy conversion efficiency. Wide phonon gap materials and resonant tunnelling structures investigated in this work for HC absorbers and energy selective contacts are highly relevant to TE devices as they can limit the thermal dissipation and help improve the efficiency.

The energy selective contact technology is a similar approach to the multiple barrier resonant tunnelling concept used in quantum cascade lasers. The thin film approach to resonant tunnelling structures demonstrated in this project could offer a lower cost fabrication route for such quantum cascade structures which usually require high cost epitaxial III-V growth.

Conclusion and next steps

In this project we have successfully demonstrated proof of concept HC solar cell devices. In this process, the project has also delivered other important outcomes such as a HC solar cell efficiency model, a phonon dispersion model, and fabrication processes for energy selective contacts based on Si, Ge QW in Al₂O₃ matrix. Knowledge gained in this project will guide further development of this technology as well as high efficiency thermoelectric devices and other applications of ESCs. Further

work will include use of epitaxial growth such as Atomic Layer Deposition to improve the quality of absorber and energy selective contacts, as well as optimisation of device integration/ metallisation to improve overall device performance. This will be of great benefit in developing the science and engineering in the Australian research community and in potential development of commercial products for Australian and collaborators' manufacturing potential.



Lessons Learned

Lessons Learned Report: Si quantum dot based energy selective contacts

Project Name: The Hot Carrier solar cell

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

Key learning

Energy selective contacts based on Si quantum dots, obtained by annealing of a silicon-rich oxide layer between dielectric materials, are not practical due to technological limitation of making the quantum dots with narrow size distribution. This results in broadening of the resonance peak which has a negative effect on the efficiency of HC solar cells.

Implications for future projects

Future projects should use alternative materials and structure for energy selective contacts. Langmuir-Blodgett techniques can be used to deposit a highly ordered array of uniformly sized NPs. Quantum well resonant tunnelling structures are more practical to realise due to better control on well thickness.

Background

Objectives or project requirements

One of the objectives of this project was to fabricate energy selective contacts. It is required to extract carriers from the HC absorber within a narrow energy range to minimise thermalisation loss.

Process undertaken

One of the approaches considered to realise energy selective contacts was by using Si QDs in SiO₂ by thermal annealing of SiO₂/SRO/ SiO₂ (SRO = silicon rich oxide) thin layer. This structure was chosen due to the high abundance of Si and our from our prior experience. Although evidence of resonant tunnelling was obtained, the observed half width of the resonance peak was more than 400 meV, which is an order of magnitude larger than the recommended value.

An alternative approach, by using QW instead of QD, was used because the thickness of the well can be precisely controlled. Although QWs only offer energy selection in one dimension unlike QDs

which offer total energy selection, precise control of thickness can overcome the broadening of resonance peak due to the size distribution of QDs. Using $\text{Al}_2\text{O}_3/\text{Si QW}/\text{Al}_2\text{O}_3$, energy selectivity results with 6 times better selectivity than our previous results from $\text{SiO}_2/\text{Si QD}/\text{SiO}_2$ structures were achieved.

Lessons Learned Report: InN based hot carrier solar cells

Project Name: The Hot Carrier solar cell

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

Key learning

Theoretically InN, using a combination of InN as an absorber and $\text{In}_x\text{GaN}_{1-x}/\text{In}_y\text{N}_{1-y}/\text{In}_x\text{GaN}_{1-x}$ as energy selective contacts, is the best material of choice for HC solar cells. However, with the current technology, InN-based HC solar cells are not practical to make due to difficulty in growing these materials with sufficiently good quality.

Implications for future projects

Future projects should use alternative materials for absorber and energy selective contacts. For absorber, transition metal nitrides such as HfN and Zirconium nitride may be used. These materials have large phonon gaps suitable to suppress the Klemens phonon decay mechanism and thus create a phonon bottleneck and slowing carrier cooling.

Background

Objectives or project requirements

One of the objectives of this project was to make an InN HC absorber and $\text{In}_x\text{GaN}_{1-x}$ energy selective contacts. This combination was expected to give the best performance although not practical for mass-implementation due to the low abundance of indium.

Process undertaken

One of our principal strategies for developing a hot carrier solar cell absorber is the study and use of group III-V material compounds, both in bulk form and in multiple quantum well superlattice structures. InN owes its large phononic band gap to a large difference between cation and anion masses. It also possesses a small electronic band gap for increased photon absorption, and so is an ideal absorber. To improve material crystalline quality (and thus slowing down hot carrier thermalisation rates) films were deposited by some of our collaborators using state-of-the-art molecular beam epitaxy deposition processes such as Energetic Neutral Atom-beam Lithography/Epitaxy (ENABLE) and Metal Modulated Epitaxy (MME). However, it has been difficult to integrate absorber and energy selective contacts due to their different processing conditions.

Therefore, alternative materials such as colloidal Si NPS, and HfN thin films have been investigated as absorber materials. For energy selective contacts $\text{Al}_2\text{O}_3/\text{Si (Ge) QW}/\text{Al}_2\text{O}_3$ has been used.