Project: "Hot Carrier solar cell: Implementation of the Ultimate PV Converter"

Annual Report April 2009

This project is a composite project involving four nodes

- PIs: Gavin Conibeer and Martin Green, University of New South Wales
- PI : Jean-Francois Guillemoles, IRDEP, Paris
- PI: Tim Schmidt, University of Sydney
- PIs: Antonio Marti and Antonio Luque, Instituto de Energia Solar-UPM, Madrid

This first annual report details the work carried out on the project at each node, with this introduction acting as an overview of the whole project.

The project officially started on 1 September 2008, but the sub-contracts for the four nodes were not all signed at the same time. That for IES-UPM came into effect in February 2008 and hence that node has been working longest on the project. Those for the other three nodes were not signed until many months later, such that they have now been working on the project for significantly less time. The effective start date for these nodes is September 2008.

As a result of this staggered start, the reports from the four groups are disparate in length. This disparity in effort to date is only an initial teething problem. As the project develops the differences will smooth out.
An inaugural meeting of all four nodes was held before the project started in Sept 2007 in Madrid. A second meeting is planned for June 2009 in Strasbourg. Several other meetings between two of the partner nodes have taken place in the interim.

There now follows an overview of the main aims of the project followed by the individual reports from each node.

Overview

Hot carrier solar cells offer the possibility of very high efficiencies (limiting efficiency 68% for unconcentrated illumination) but with a structure that could be conceptually simple compared to other very high efficiency PV devices – such as multi-junction monolithic tandem cells. For this reason, the approach lends itself to 'thin film' deposition techniques, with their attendant low costs in materials and energy usage and facility to use abundant, non-toxic elements. [1-5]

The Hot Carrier cell device has the following stringent requirements:

A. Slowing of thermalisation of photogenerated electrons (and holes) in the absorber material.
B. Extraction of these 'hot carriers' to external contacts over a narrow range of energies, such that excess carrier energy is not lost to the cold contacts.
C. In addition, a working device would require integration of the structures used to tackle A and B without compromising their performance.

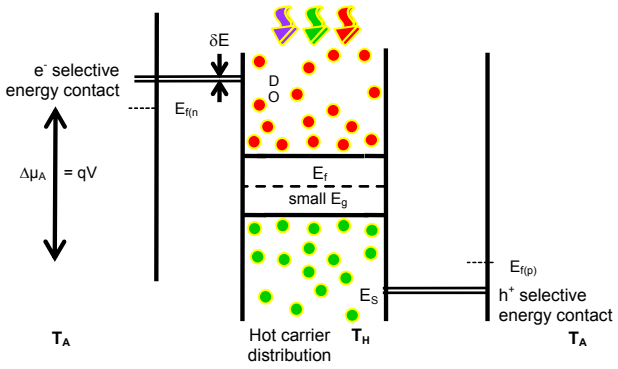

Fig 1: Band diagram of a Hot Carrier solar cell,

The absorber has a hot carrier distribution at temp T_H . Carriers cool isoentropically in the mono-energetic contacts to T_A: their kinetic energy being converted into useable potential energy. [1,2] The difference of the Fermi levels of these two contacts manifests as a difference in chemical potential of the carriers at each contact and hence an external voltage.

The challenges to produce such devices fall into 2 categories: (i) keeping carriers hot without heating the lattice (at least not beyond the selective contacts) and (ii) achieving a fast extraction of hot carriers through a narrow allowed energy range. [1,2] While these challenges are tough, it seems they can be met using newly available materials and more specifically nanostructured semiconductors.

The absorber is conceptually a single layer, homogeneous on the scale of a complete device. Similarly contacts are conceptually relatively simple effectively 2D structures. This conceptual simplicity of construction of the whole device would lend itself to thin film or related techniques.

A great strength of this project is that it synergistically combines the significant experience in all three generations of photovoltaics at the University of New South Wales (UNSW), with that on intermediate band cells and QD characterisation at Instituto de Energia Solar (IES-UPM), with the pioneering work on Hot Carrier cells at IRDEP, Paris, in conjunction with UNSW and with the excellent optical expertise and facilities at Sydney University (USyd).

Project Tasks

The tasks for the first major part of the project aim to model fabricate and characterise quantum dot nanostructures to demonstrate slowing of hot carrier cooling in a Hot Carrier cell absorber material.
Detailed theory and modelling will be used to identify promising structures with the materials available. Test structures for both the absorber and contacts will be fabricated and subjected to rigorous spectroscopic analysis, effectively disassembling the processes in the solar cell and providing a feedback loop into the theoretical effort. Conventional photovoltaic device assessment will be used to evaluate successful test structures.

Task 1. Modelling

- Earlier 1D modelling will developed and extended to include full 3D folded phonon dispersions with calculation of Joint DOS at IRDEP using ab-initio input data of force constants from UNSW.

Also the mechanisms for the control of the anharmonic phononic interactions will be modelled using molecular dynamics at IRDEP with parameterisation provided by ab-initio density functional calculation at UNSW.

Task 2: Stranski-Krastanov MBE/MOVPE growth & characterisation of periodic QD arrays:
A mismatch in QD and matrix acoustic impedance should give complete gaps in the phonon dispersion. Correctly tuned gaps can prevent phonon decay by the Klemens mechanism.[4,6]

- Various systems will be tried, with the option for ternary or even quaternary strain compensation layers to give independent control of confinement and acoustic impedance.
- Growth will be carried out via external collaborations for all of ESI-UPM, UNSW and USyd for MOVPE and IRDEP for MBE. This multiple approach will be necessary because individual MOVPE or MBE machines are dedicated to a small number of material systems. Some small fraction of funding is requested for this area, but the bulk of the growth will be carried out as part of existing and other projects within the groups.
- It is not intended to grow III-nitrides as part of the project. The difficulty of this being acknowledged. However samples of InN and GaN have been procured and are being measured by TR-PL to prove the concept of blocked Klemens decay.

Task 2a: Characterisation:

- Carrier cooling rates and charge transport mechanisms will be determined at a new ultrafast laser spectroscopy laboratory at Sydney University (USyd). Dual Optical Parametric Amplifiers (OPA) provide two 150fs laser pulses that are independently tuneable (189nm-2.5μm). Using the technique of up-conversion spectroscopy, carrier dynamics can be studied with a 150fs time resolution in a wide range of materials, with absorption thresholds that span the solar spectrum. Conventional photon counting techniques will be used to assess carrier dynamics on time scales from 1ns upwards. This will determine the carrier dynamics, investigating both the mechanism and effectiveness of the QD nanostructures in slowing the carrier thermalisation times from a few ps to the several hundred ps required for efficient operation of the Hot Carrier cell.
- AFM, HR-TEM and XRD of the QD nanostructures at UNSW, Measurement of phonon bottleneck effects and other QD array properties will be carried out at the Instituto de Energia Solar (IES-UPM).
- Extended range high resolution Raman will be used to map phonon dispersions and evidence for Brillouin zone folding from folded peaks and peak doublets [7] through a collaboration at IRDEP.

Task 3. Colloidal dispersion of core shell QDs:
A ‘soft’ QD shell should maximise the Bragg reflection effect and hence open up large gaps in the phonon dispersion. [4,5] Colloidal dispersion chemistry techniques for the fabrication of “core shell” nanocrystals will be developed from an existing project at IRDEP using special precursors enabling a good control over surface chemistry during growth and hence

shape, size, stability, crystallinity and electronic activity. Size selection will be improved using an independently developed procedure. These will be deposited using dipping and Langmuir-Blodgett techniques at UNSW to give self-organisation of nanocrystals into a regular array by attraction of hydrophilic groups of controlled molecular weight on their surfaces. Thus achieving the control of nanocrystal size, density and spacing required for "phononic engineering".

Task 4. Solid state self-assembled Si and Sn QD nanostructures in dielectric matrices:
Particularly for Sn, the acoustic impedance mismatch in such a system is high. The challenge will be to achieve the uniformity in QD spacing and size required to give the gaps in the phonon dispersion. Incorporation of a QD shell will also be investigated. This will involve the further development of a very significant amount of expertise at UNSW in self assembled Si nanocrystal structures in dielectric matrices, which has recently been extended to Sn nanocrystals as part of other projects.

The proposed approach with the various approaches to QD formation is illustrated in Fig 2.

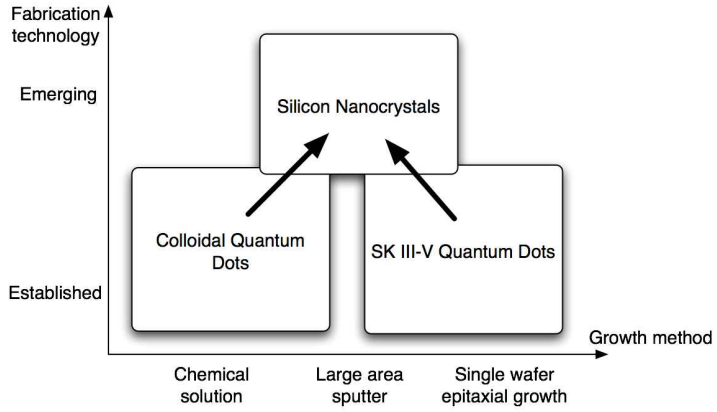

Fig 2: Transfer to thin film technology:

When and if the carrier cooling by restriction of phonon modes concept is proved by TR-PL measurements of the III-V S-K QDs and/or Colloidal QDs, an integral part of the project will be to feed the nanostructure design parameters into thin film fabrication of QDs.

This will build heavily on expertise on Si and Sn QD technology grown by thin film sputtering and PECVD techniques in Si dielectrics that has been established at UNSW over the last several years. The principle issues are likely to be regularity of spacing and to a lesser extent the size uniformity of QDs. The information gained from the sensitivity analysis of the high quality QD arrays will feed into the minimum requirements for these.

In parallel a new programme at UNSW (already being established independently) and an existing one at IRDEP, will further develop the core shell aspects of colloidally grown QDs. These techniques are amenable to potentially very low cost and low temperature deposition techniques, with self assembly of QD spacing and size an integral part of the technique.

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Institution: University of New South Wales, Sydney, Australia

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Abstract

The UNSW node of the Hot Carrier Solar Cell project is investigating the phonon dispersions properties of ordered quantum dot arrays. The object is to determine the potential to modify the allowed phonon energies such as to block the decay of optical phonons, this being the principle decay mechanism for hot photo-generated carriers in an absorber material.

This will then offer the possibility of producing a material which substantially decreases the rate of carrier cooling in an absorber and hence allows carriers to be extracted whilst still hot and hence produce a higher external voltage. Thus also boosting the efficiency of such a 'Hot Carrier solar cell' very significantly.

The investigation has two main themes:

1. Modelling of the phonon dispersions in three dimensions of these quantum dot nanostructures. This will allow the phonon properties of various material combinations to be modelled and assessed.
2. Fabrication of ordered quantum dot arrays. This is being carried out using colloidal dispersion of capped nanocrystals. Once fabricated these arrays will be characterised for both their modified phonon dispersions and their ability to slow the rate of carrier cooling.

Administration

Personnel

[All personnel are members of the ARC Photovoltaics Centre of Excellence, supported by the Australian Research Council.]

Principal Investigators:
Dr. Gavin Conibeer – Deputy Director, Photovoltaics Centre of Excellence (CoE)
Prof. Martin A. Green – Research Director, Photovoltaics Centre of Excellence

Investigators:
Dr. Dirk König – Research Fellow, GCEP, CoE
Dr. Shujuan Huang – Postdoctoral Fellow, GCEP, CoE
Dr. Santosh Shrestha – Postdoctoral Fellow, GCEP, CoE
Dr. Lunmei Huang– Postdoctoral Fellow, GCEP, CoE (from Feb 2009)

Postgraduate Students, CoE:
Mr. Christopher Flynn (PhD)
Ms. Lara Treiber (PhD)
Mr. Pasquale Aliberti (PhD)
Mr. Andy Hsieh (PhD)
Mr. Robert Patterson (PhD)
Mr. Binesh Puthen Veettil (PhD)

Equipment *(funded on other projects)*

Femtosecond laser for TR PL – located at JLUS, Sydney University
Computer cluster – upgraded to 340Gflops
Langmuir-Blodgett deposition apparatus

Organisation

The UNSW node of the project is organised into sections on:

Hot carrier dynamics and phonon dispersion modelling;
Fabrication of quantum dot arrays - colloidal dispersion;

1 Introduction

The concept underlying the hot carrier solar cell is to slow the rate of photoexcited carrier cooling, caused by phonon interaction in the lattice, to allow time for the carriers to be collected whilst they are still at elevated energies ("hot"), and thus allowing higher voltages to be achieved from the cell, as shown schematically in Figure 1. [1,2,3] It thus tackles the major PV loss mechanism of thermalisation of high energy photogenerated carriers. In addition to an absorber material that slows the rate of carrier relaxation, a hot carrier cell must allow extraction of carriers from the device through contacts which accept only a very narrow range of energies (energy selective contacts).

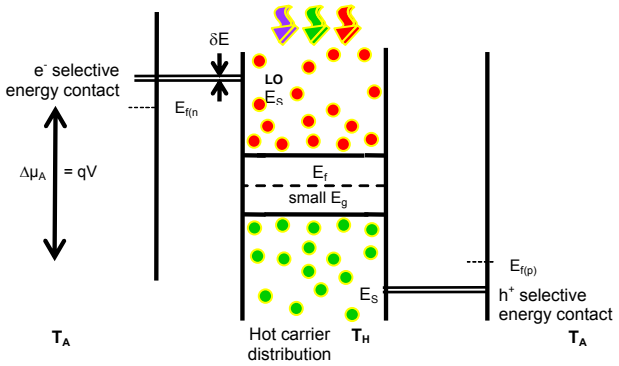

Figure 1: Band diagram of the Hot Carrier cell.

The device has two stringent requirements:

This project aims to tackle the cooling of carriers by emission of phonons in an absorber material. In particular it seeks to modify the decay of optical phonons into acoustic phonons (i.e. heat in the lattice) using ordered quantum dot arrays, in much the same way as an ordered array of different refractive index materials modifies the photon dispersion in a composite photonic material.

Since the start of this project in Sept 2008, earlier work on 1D modelling of phononic modes in QD superlattices has been extended to full 3D modelling. Work is also continuing on methods to fabricate the required ordered QD arrays using Langmuir-Blodgett deposition of nanoparticles. Parallel work on Energy Selective Contacts is continuing as part of projects funded from other sources. When both projects reach maturity at a later stage they will be combined in a working device.

2 Progress Sept 2008 – April 2009

Work has only started officially on this project from Feb 2009 on signing of contracts. However reported here is work back to Sept 2008, the official start of the project.

2.1 Modelling of quantum dot arrays for Hot Carrier Absorbers

Carrier cooling in a semiconductor proceeds predominantly by carriers scattering their energy with optical phonons. This builds up a non-equilibrium 'hot' population of optical phonons which, if it remains hot, will drive a reverse reaction to re-heat the carrier population, thus slowing further carrier cooling. Therefore the critical factor is the mechanism by which these optical phonons decay into acoustic phonons, or heat in the lattice. The principal mechanism by which this can occur is for the optical

phonon to decay into two acoustic phonons of half its energy and of equal and opposite momenta. [4]

In some bulk semiconductors, with a large difference in their anion and cation masses, there can be a large gap between the highest acoustic phonon energy and the lowest optical phonon energy. This can be termed a "*phononic* band gap" referring to the disallowed *phonon* energies caused by a periodic modulation of *atomic force constants*. [5] [This is analogous to the "*photonic* band gap" which arises from the disallowed *photon* energies caused by a periodic modulation of *refractive indices*.] In a few cases – e.g. InN, GaN, BiN, AlSb & SnO – this gap is larger than the highest acoustic phonon energy and hence prevents operation of the Klemens optical decay mechanism described above. In a few others – e.g. InP – the gap is almost this large. We are using time resolved photoluminescence to in vestigate the carrier cooling rates in these materials.

The most promising materials with phononic gaps larger than or close to 1 are GaN, InN and InP. Some inconclusive evidence for slowed carrier cooling exists in these materials (see [5] for further detail). Also InN is the only one of these materials with a band gap (at 0.7eV) which is small enough for it to be a good absorber material in a Hot Carrier cell. However, its preparation is difficult and In is a rare element, hence it would be useful to find alternative materials to achieve slowed carrier cooling.

Reduced dimension phononic structures:

The work in the group is in modelling a similar prevention of the Klemens' optical phonon decay mechanism in less exotic materials (possibly based on elemental semiconductors), by exploiting the Bragg reflection that occurs at the mini-Brillouin zone boundaries of nanostructure superlattices. This reflection opens up mini-gaps in the phonon dispersion for those acoustic phonon energies which satisfy the Bragg condition. In 2008 we have extended the 1D force modelling of phononic dispersions to 3D modelling.

All neighbour approach: DFT force constants:

One approach we have used for this uses a force constant model with diagonalisation to include 3D effects. [6] This uses input force constant values calculated separately using the Phon code [7] and a full electron density functional ab-initio approach, see Figure 2.

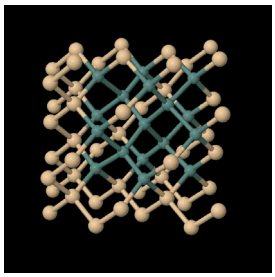

Figure 2: DFT representation of a Si QD in a Ge matrix, using a harmonic approx. and long range force constants.

This takes into account precisely the force constants for all neighbours within the cut-off radius at the LDA-DFT level. A cut-off radius of 9.5 Å is taken for the integration of force constants in real space. Including the full calculated long range force

constants, the full phonon dispersion for the crystal can be reproduced very accurately compared with the experimental values [6]. A mass approximation was used, i.e. neglecting the dependence of the force constants upon composition.

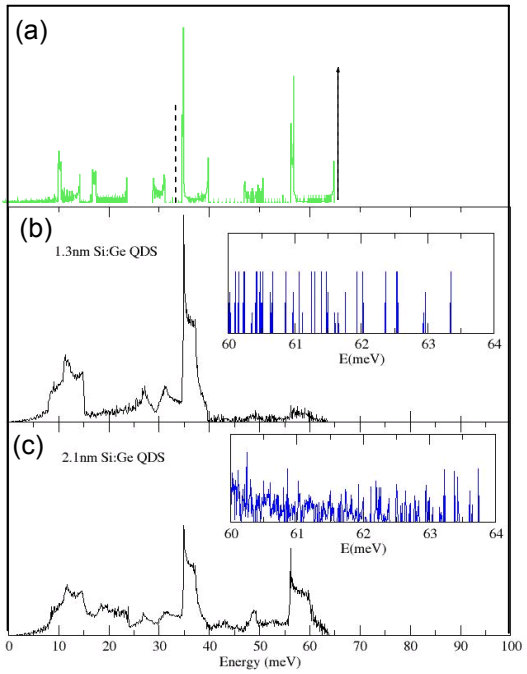

Figure 3: (a) 1D calculated phonon DOS for Si/Ge MQW. Maximum phonon energy and ½ this max. aligned with a minigap are indicated.
3D DOS for QD arrays with Si dots of (b) 1.3 nm and (c) 2.1 nm. Insets show detail over the 60-64 meV range with several mini-gaps in each case [3].

Figure 3 shows the calculated total phonon DOS for a Si:Ge MQW and for Si:Ge QD arrays with Si QDs of 1.3nm and 2.1 nm. The shapes of the total phonon DOS are very similar to the mixed behaviour of bulk Si and bulk Ge (not shown). However, the QD superlattice does show very discrete phonon energies, due to Bragg reflection at the mini-Brillouin zone edges in 3D (as seen in the inserted figures in Figure 2) with complete gaps which decrease as the QD size increases. These gaps are smaller than those in the QW structure. This indicates that the big gaps in 1D are difficult to obtain just by phonon confinement in nanostructures, because of the broadening of allowed energy levels in 3D.

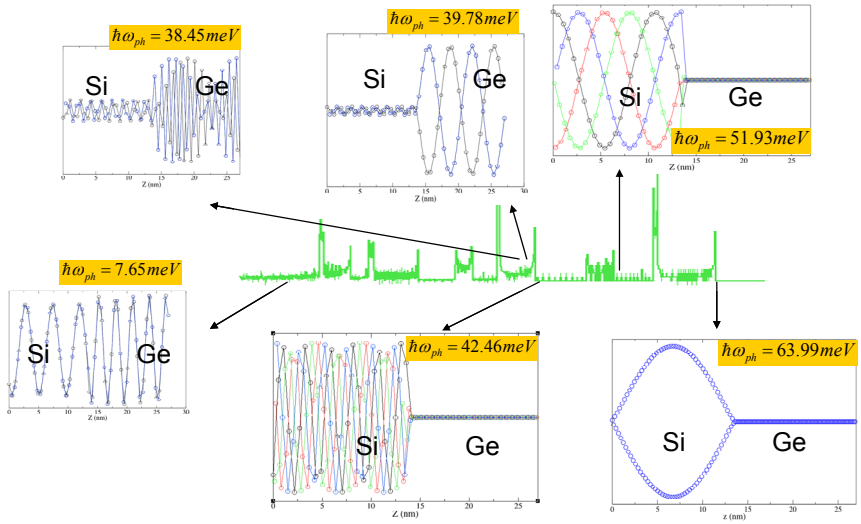

Figure 4: The calculated phonon displacement amplitude for a Si:Ge QW system. The ratio of contributions from the Si and the Ge parts is seen to vary for different phonon frequencies as denoted by the green DOS plot.

Phonons consist of the displacement of atoms in atomic planes. The amplitude of this displacement can be modelled as shown for a Si:Ge quantum well superlattice in Figure 4. For different values of the phonon frequency - as demoted by the green plot of the phonon density of states – there are different contributions t the overall phonon amplitude from the vibration of planes of Si atoms or planes of Ge atoms. For the highest frequency and hence highest energy phonons only the light Si atoms contribute (bottom right Figure 4). This is the highest energy optical mode. Whereas for lower energies the heavier Ge atoms becme more dominant. For instance for the graph at top middle of Figure 4, the mode is almost completely dominated by Ge atm vibrations. This corresponds to the highest energy acoustic mode. For other points in the DOS both types of atom contribute. The advantage of this analysis is that it can indicate which modes and hence energies will be localised and confined in a particular layer and which will propagate. The confined modes will not contribute to a spreading of energy through the material from phonon decay and hence a material designed with decay phonons at these energies should retain a longer phonon lifetime and hence slow carrier cooling.

Rigid ion model on a model material superstructure

In an alternative approach phonon dispersion curves are obtained from numerical calculations within the rigid ion model. They have been performed on QD superlattices of various geometries. A sample geometry is shown in Figure 5 in which diamond structured nanocrystals arranged in a superlattice in a hexagonal close packed structure. [8]

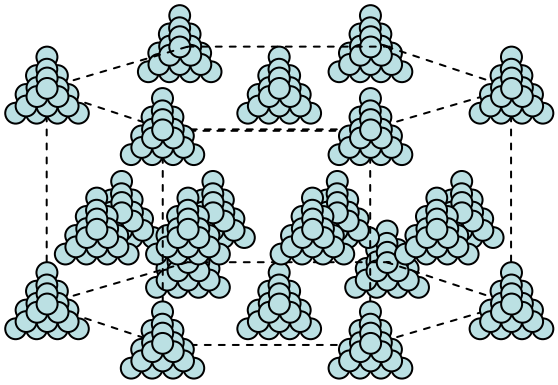

Figure 5: Diamond sub-lattice Nanocrystals in an HCP superlattice ordered array.

The dispersion relation covering the minimum area of the Brillouin Zone necessary to capture all unique modes was calculated numerically. The remainder of the modes may be obtained from symmetry operations. Dispersion calculations were carried out using a rigid ion model. Where possible, force constants were obtained from the literature. Where it was not possible to find material parameters, scaled factors consistent with known force constants were used. The resultant phonon dispersions from such a calculation in the major symmetry directions for the structure in Figure 5 are shown in Figure 6.

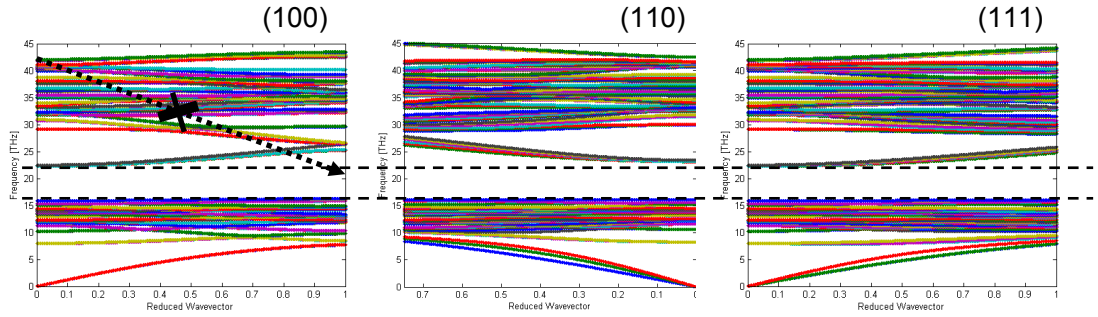

Figure 6: Folded zone phonon band diagram for a few typical symmetry directions for a model simple cubic QD superlattice made from materials with the diamond symmetry. Note the small but complete bandgaps that exist in the symmetry directions shown. Places where phonon decay are likely to begin are at the zone centre (k=0) and zone edge (k=π/a or k=1).

Complete gaps in the dispersion in reciprocal space are seen for a not too narrow region at approximately half the maximum phonon energy. If such a structure could be fabricated perfectly it should prevent the Klemens decay, indicated by the arrow in Figure 6. Once the phonon dispersion has been obtained, all phonon processes that lead to phonon decay can be evaluated to produce a lifetime. Lifetimes will computed from Time Dependent Perturbation Theory.

2.2 Fabrication and characterisation f ordered nanoparticle arrays for Hot Carrier solar cell absorbers

As reported in [9], we have initiated experimental work on fabrication of highly ordered arrays of nanoparticles for use as the absorber materials for Hot Carrier solar cells. Work has been concentrated on surface functionalisation of silicon nanoparticles (SiNPs) in order to achieve close control of the spacing between particles, which should allow modification of the phonon dispersion.

Organosilane chemistry has been used in an attempt to functionalise Si nanocrystals. If successful, the formation of a Si-O-Si bond should occur as depicted in Step 2 of the reaction mechanism of Figure 7.

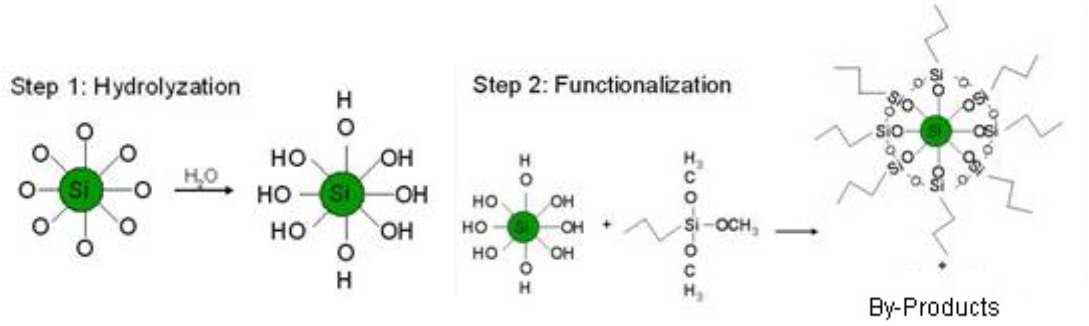

Figure 7: SiNPs functionalisation: Step 1, hydrolysation of SiNP powder with water; Step 2, addition of capping agent (TMOPS) to hydrolysed SiNPs with resulting f-SiNPs and unwanted by-products.

Following Step 2, the functionalised nanocrystals were washed in a 1:3 ratio with water, shaken by hand and allowed to settle overnight resulting in two phases – the top layer formed a transparent brown solution containing functionalised nanocrystals and cyclohexane and the bottom phase formed a transparent solution containing water and the unwanted by-products, as shown in Figure 8.

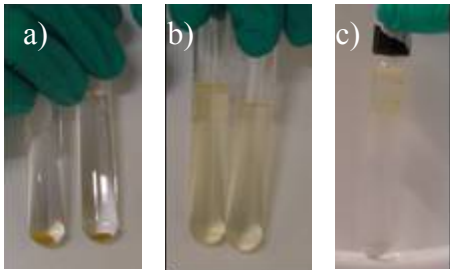

Figure 8: a) Step 1 reactants, phase separation between polar hydrolyzed H_2O-Si solution and non-polar cyclohexane solvent; b) Step 2 products, miscible solution of functionalised Si nanocrystals; c) products after washing, phase separation.

Characterisation of the top layer has been carried out using TEM, FTIR and NMR to confirm the presence of this Si-O-Si bond, however, none of these have provided conclusive results since the byproducts have not been completely removed and have thus affected the results seen in the characterisation methods. Investigation on separating of functionalised Si nanocrystals using other methods such as centrifuging is ongoing. Also, we have begun exploring the use of other nanocrystals, with narrower band gaps and hence greater absorption, to fabricate highly ordered arrays

which would be useful for our investigation of the phononic structures and slowed carrier cooling effects.

A Langmuir-Blodgett (LB) deposition system for fabrication of highly ordered nanoparticles monolayers has now been commissioned, as shown in Figure 9. The LB technique will allow deposition of 2D ordered arrays of nanoparticles with the particle spacing determined by the molecular weight of the capping material.

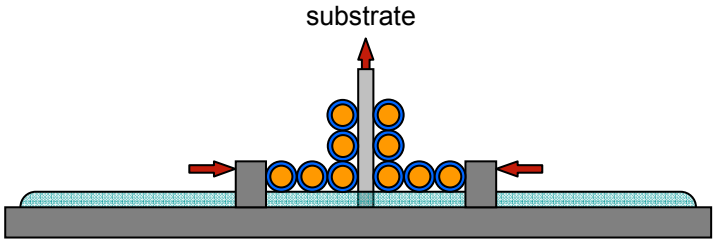

Figure 9: Schematic of the LB apparatus used to fabricate a monolayer of encapsulated nanoparticles.

3 Summary of Progress and Plans for the next stage of the project

Modelling of slowed carrier cooling structures has seen the extension of a 1D model to 3D modelling of phonon dispersions of QD nanostructures. Two different methods are used. One using ab-initio calculation of force constants the other using a high level force constant model. These two approaches to modeling phonon dispersions in 3D will be used to model various conceived nanostructures. They will allow an estimation of the allowed phonon energies and hence the potential for slowing carrier cooling.

Fabrication of periodic QD superlattice nanostructures has begun with work on capping Si nanoparticles. The Langmuir-Blodgett deposition set-up is now ready to fabricate regular 2D arrays of QDs, initially of Si and then f other materials.

As reported in the report from the node at Sydney University, the time resolved photoluminescence laser system (JLUS) is now operational and producing good results. We are now measuring test materials and at a later stage will be able to look for evidence of slowed carrier cooling in the QD nanostructure arrays.

4 Publications

- R. Patterson, M. Kirkengen, A. Hsieh, G. Conibeer, M.A. Green, G. Conibeer, “Modelling of QD superlattices for Hot Carrier cell absorbers”, Proc. Int. Solar Energy Society, Asia Pacific region, Conf., Sydney (2008).
- L. Treiber, C. Bumby, S. Huang, G. Conibeer, 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain (2008).
- G.J. Conibeer, N. Ekins-Daukes, D. König, E-C. Cho, C-W. Jiang, S. Shrestha, M.A. Green, Solar Energy Materials and Solar Cells, “Progress on Hot Carrier solar cells”, In Press, Corrected Proof, available online Dec 2008.

5 Contacts

Dr. Gavin Conibeer: g.conibeer@unsw.edu.au
Prof. Martin Green: m.green@unsw.edu.au

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Project: “Hot Carrier solar cell: Implementation of the Ultimate PV Converter”

Institution: Institut de Recherche et Développement sur l'Energie Photovoltaïque (IRDEP)

Annual Report April 2009

Investigators
Jean-François Guillemoles, Research director
Christophe Domain, research engineer
Par Olsson, research engineer
Lun Mei Huang, post-doctoral researcher
Arthur LeBris, Graduate researcher
Ali Umrani, undergraduate researcher
François Barrat, undergraduate researcher

Abstract

In this very beginning of the project, we could get started on our main tasks of the first year, namely modeling of carrier extraction and of blocking of thermalization pathways through phononic engineering in nanostructures.

Introduction

IRDEP's contribution in the course of the first year of the project deals with modeling of selective energy contacts and of the phonon modes in nanostructured semiconductors relevant for carrier thermalisation. In this first semester after the project started, we have begun the modeling studies.

Slowing the hot carrier cooling to allow hot carriers to be extracted with high energy is the key strategy for hot-carrier solar cell. The 'hot phonon bottleneck effect' in the low dimensional quantum structures provides a very promising way to harvest the hot carrier energy. In this study, the phonon modes in Si/Ge nanostructures: superlattice, multiple quantum wires, and multiple quantum dots have been calculated by ab-initio force constant method. Within our calculation method, the phonon properties due to low dimensional structures were correctly captured. The phonon propagation and confinement were investigated in order to understand the possible effect on the phonon-electron and phonon-phonon scattering for the application in hot carrier solar cell.

The other path for loosing hot carrier energy is that of carrier collection through energy non selective contacts: thereby additional heat (and therefore possible work) is lost to the contacts when hot carriers in the absorber exchange with cold carriers in the

contacts. Energy selective contacts , i.e. contacts that allow carriers to be transported at a single energy level, are a central concept of the device [Ross 82, Wurfel 97]. We have also started to study the influence of the non selectivity of the contacts on the final performance of the solar cell.

Results

The energy loss rate of a carrier - also known as the thermalization rate of the carrier - is determined by both the rate at which the carrier's energy is lost by optical-phonon emission and the rate at which the carrier gains energy from optical-phonon absorption. This latter rate can be significant in low dimensional quantum structures since the phonon emitted by energetic carriers can accumulate in these structures due to the phonon spatial confinement. The phonon densities in confined semiconductor are typically well above those of the equilibrium (called hot), phonons will be reabsorbed by the carriers. This phenomenon of reabsorption of hot phonons is referred to as the 'hot-phonon-bottleneck effect', which is an important effect for many low dimensional semiconductor electronics performance [Othonos1998]. Moreover according to the anharmonicity of crystal, the emitted LO phonon in semiconductor shows typical a few picoseconds to about 10 ps life time, afterwards, LO decays to two or several lower energy phonons based on energy and momentum conservations. These decayed LO phonons are not available for absorption by carriers anymore, in this case clearly, the lifetimes of the optical phonons are very important in determining the total energy loss rate for carriers {DasSarma1992}.It has been recognized that the Klemens channel {Klemens1966}, one optical phonon decays to two longitudinal acoustic (LA) phonons, is the dominant mechanism for many semiconductors.

The phononic engineering by using low dimensional confined structures and mass difference effect are being used to design certain phononic structures as good hot carrier absorber {Conibeer2006, Conibeer2008, Conibeer2005, Guillemoles2005} were Klemens decay channel is made impossible through specific modifications of the phonon dispersion curves (curves that relate energy and momentum of the vibration spectrum) : phonon thermalization would then violate energy and momentum conservation .

In the present work, the phonon dispersion and phonon in 1, 2, 3 dimensional confinement in superlattice, multiple quantum wires (MQWR), and multiple quantum dots(MQD) are theoretically calculated by ab-initio calculated force constant method applied to Si-Ge nanostructures : not only they are actually technically interesting, but also because we can confine our discussion on the mass effect on the phonon modes due to the lattice similarity between crystal Si and Ge. The effect of mass difference between matrix elements and confined structures is discussed. The character of calculated phonon modes in quantum structures are expected to be used to the full calculation on phonon-phonon and phonon-electron dynamics in these structures.

In this study, all the nanostructures are repeated periodically to form a 3D superlatice so that periodic boundary condition can be used

The full force field derived from displacement of the supercell atoms can be accurately calculated from ab-initio DFT method. In this paper, we used the so-called PHON code {Alfe98} and full electron DFT calculation code VASP{Kresse 93, Kresse 96} to get the full force constant matrix.

At this stage, phonon dispersion have been calculated for pure Ge system and Si-Ge zinc blende structure alloys within the mass approximation. Fig. 1 shows our calculated phonon dispersion curves of pure Si, Si-Ge zinc blend structure, and pure Ge bulk phonon dispersion curves compared with experimental Si and Ge bulk material results. As can be seen, the ab-initio calculated Si phonon dispersion shows very good agreement with experimental values. The Ge phonon dispersion calculated by mass approximation also shows good agreement with experimental result {Dolling 1963, Tubino 72,Weber 77}, only slight deviation is found for part of high energy acoustic modes. The optical phonon frequencies for Si-Ge modes in Si-Ge zinc blend structure are also consistently in agreement with the experimental values {Alonso 89}.

The method being thus validated, the computation of vibration modes of Si-Ge nanostructures could start. Dots, wires and wells of various sizes could be simulated (up to a few thousand atoms) and their dispersion curves obtained. The corresponding results are being processed. Beyond a few thousands atoms in the unit cell (few nanometers in characteristic size), the dispersion curves become very similar to that of bulk materials, so that we have focused our studies on nanometer scale nanostructures.

2- Carrier extraction

The modeling of hot carrier solar cells has been extended to include losses through energy non selective contacts. The complete model is in progress, but preliminary results are that up to 10 meV width of contacts, the efficiency losses are negligible.

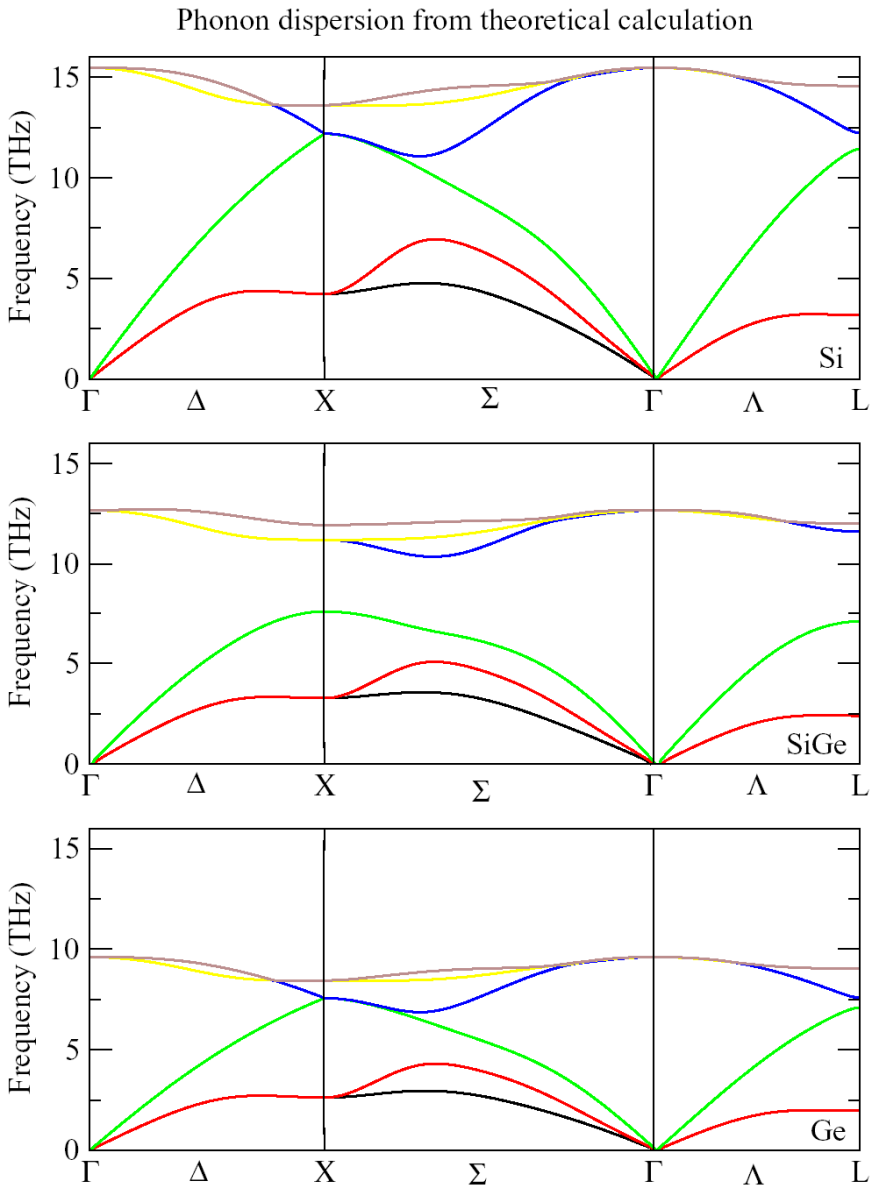

Figure 1: Phonon dispersion curves for Si, Si-Ge alloy and Ge along high symetry lines of the Brillouin zone, as calculated in the present work.

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Contacts

Jean-François Guillemoles : jf-guillemoles@enscp.fr

Hot Carrier Solar Cell:
Implementation of the Ultimate Photovoltaic Converter
(University of Sydney node)

Investigators
Timothy W. Schmidt, Senior Lecturer; Dr Raphaël Clady, Postdoctoral Fellow; Murad J. Tayebjee, Graduate Researcher, Chemistry, The University of Sydney, Australia;
N. J. Ekins-Daukes, Lecturer, Department of Physics and Grantham Centre for Climate Change, Imperial College, London, UK.

Abstract

We have built a new laboratory for the characterization of materials for the Hot Carrier Solar Cell, to be manufactured in the other nodes of this international project. The femtosecond laser laboratory is housed at The University of Sydney and was funded by greater than $1m by The University of Sydney and The University of New South Wales, with matching contributions from the Australian Government. We have measured hot carrier lifetimes in GaAs and InP at a range of temperatures, showing the lifetime of the carriers to be related to the population of quanta in the acoustic modes of the sample, as expected from the Klemens optical phonon decay mechanism. While the interpretation of these results is ongoing, the laboratory is ahead of schedule in the context of the project.

Introduction

The Hot Carrier Solar Cell is a third generation photovoltaic device which seeks to circumvent the Shockley-Queisser limit by extracting carriers (electrons and holes) at energies far exceeding the bandgap of the material. The carriers are characterized by a temperature greater than that of the lattice and are thus termed “hot carriers”.

A rigorous characterization of materials for use as absorbers in a hot carrier cell requires the ability to observe hot carriers, and measure their cooling rates. Electrons and holes in most materials cool on the picosecond time-scale – one millionth of one millionth of a second (10^{-12} s). This exceeds the speeds of even the most modern electronics, so measurements on hot carriers require the use of ultrafast spectroscopy.

The Joint Laboratory for Ultrafast Spectroscopy (JLUS) was commissioned in 2008 with over $1m of funding from The University of Sydney, The University of New South Wales, and the Australian Government. The laboratory is directed by Dr Timothy Schmidt and is managed by Dr Raphaël Clady. The laboratory is equipped with a Clark MXR femtosecond laser which puts out 1.5 mJ 780nm laser pulses at 1000 Hz. The pulses has a duration of about 150 fs. This “mother” beam is split into two parts to pump two TOPAS optical parametric oscillators. These devices allow us to independently tune the 780 nm, near-infrared pulses across the solar spectrum, from 200 nm to 2200 nm. These tuned femtosecond laser pulses are used to clock the carrier cooling times in candidate hot carrier absorbers.

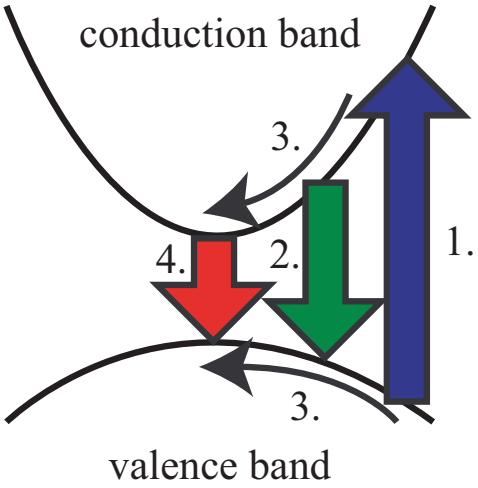

Figure 1: (1) electons are pumped at an energy above the band gap. (2) Carriers radiatively recombine as they, (3) cool through optical phonon emission. Finally, (4) cooled carriers radiatively recombine near the bandgap energy.

Background

The hot carrier cell represents a paradigm shift in photovoltaic research, seeking to break the conventional cost vs performance relationship that exists in conventional photovoltaic devices. Existing first generation, single-threshold photovoltaic convertors are typically manufactured to give energy conversion efficiencies between 10-20% but the large quantity of semiconductor material used leads to a high cost per Watt. Emerging second generation technologies achieve low manufacturing cost by depositing semiconductors directly onto inexpensive substrates, such as glass or metal foil, but at the expense of efficiency; most technologies achieve efficiencies of between 5-10% in production. Our technology is based on cheap manufacturing costs of second generation cells, but with the aim to attenuate some of the energy loss mechanisms inherent in single-threshold devices, extracting electrons at a higher voltage than normally achieved with silicon. Our research is thus "outside the square" of most photovoltaic research. It is ambitious, yet if successful will be paradigm-shifting in its impact.

Results

Figure 1 illustrates the sequence of events which occur after femtosecond illumination of a semiconductor material. Within 200fs or so, the carrier-carrier scattering distributes the electrons and holes throughout the conduction and valence bands respectively, acquiring a characteristic temperature in excess of the lattice temperature. These carriers immediately start to emit photoluminescence with a spectrum which reflects the distribution of carriers in the respective bands, and therefore the carrier temperature. This spectrum cools down to the steady-state photoluminescence spectrum typical of carriers at the lattice temperature. By measuring the spectrum at a series of time-delays after the pump laser pulse, or equivalently by measuring the time-decay of each photoluminescence wavelength, the time-dependent dynamics of the carriers is revealed.

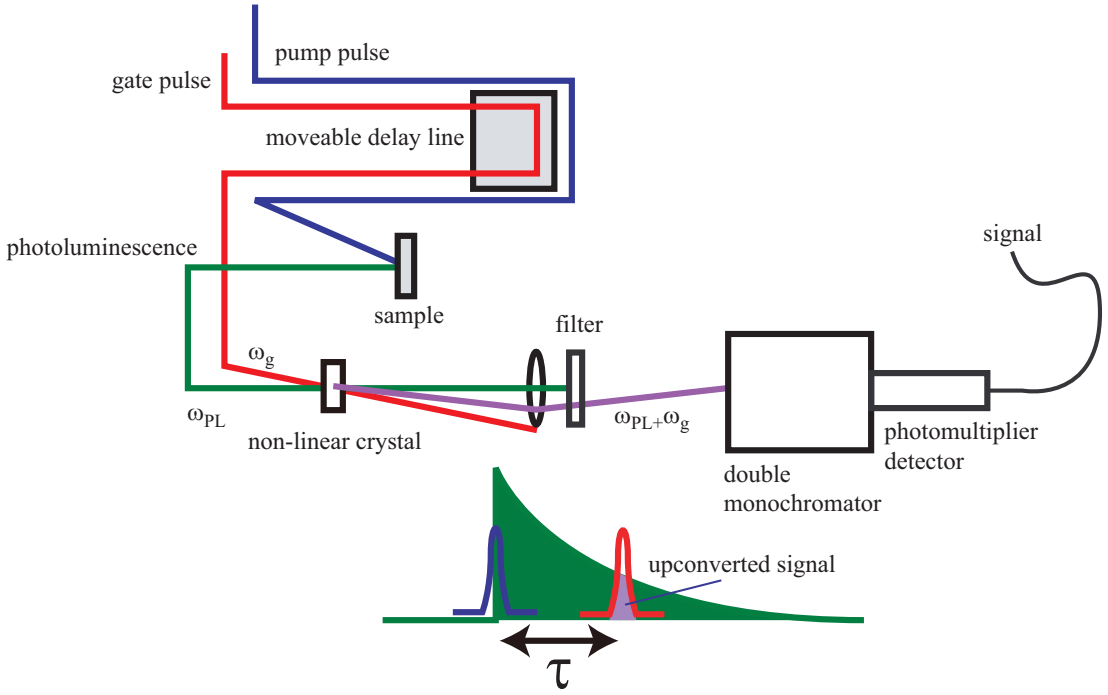

Figure 2: Schematic of time-resolved photoluminescence experiments.

The actual experiment is illustrated in Figure 2. A 150 fs laser pulse excites the sample. The resulting photoluminescence (PL) is focussed into a non-linear crystal. One wavelength component of the PL is upconverted by sum-frequency mixing with a gate laser pulse. The intensity of this upconverted signal is proportional to the PL intensity, so the gate pulse acts as a 150 fs "shutter", taking a snapshot of the intensity of the PL at a given time for a given wavelength. Scanning the time-delay and the wavelength reveals the carrier dynamics. We perform these experiments using a commercial Halcyone spectrometer from Ultrafast Systems (Florida).

We have performed a series of TRPL experiments on GaAs and InP at temperatures from 80K to 310K. A portion of the time-resolved spectrum is given in Figure 3. The scattered last peak is from the front window of the cryostat, and thus reaches the non-linear crystal a few picoseconds before the PL. The PL itself rapidly cools down towards the bandgap, with the hottest carriers only living for a few picoseconds at most. After 10s of picoseconds the carriers have cooled down to 80K, and emit only near the bandgap. We have observed the same carrier cooling at a series of lattice temperatures. At higher lattice temperatures, the cooling is significantly faster. The Klemens anharmonic coupling mechanism is enhanced by the number of quanta in the acoustic modes into which the optical photons decay. Classically, this is interpreted as a higher temperature lattice sampling the more anharmonic part of the nuclear potential energy surface. As such, the observation that carrier cooling takes place faster at higher lattice temperature is in support of the present proposal to attenuate carrier cooling by phononic engineering of the hot carrier absorber materials.

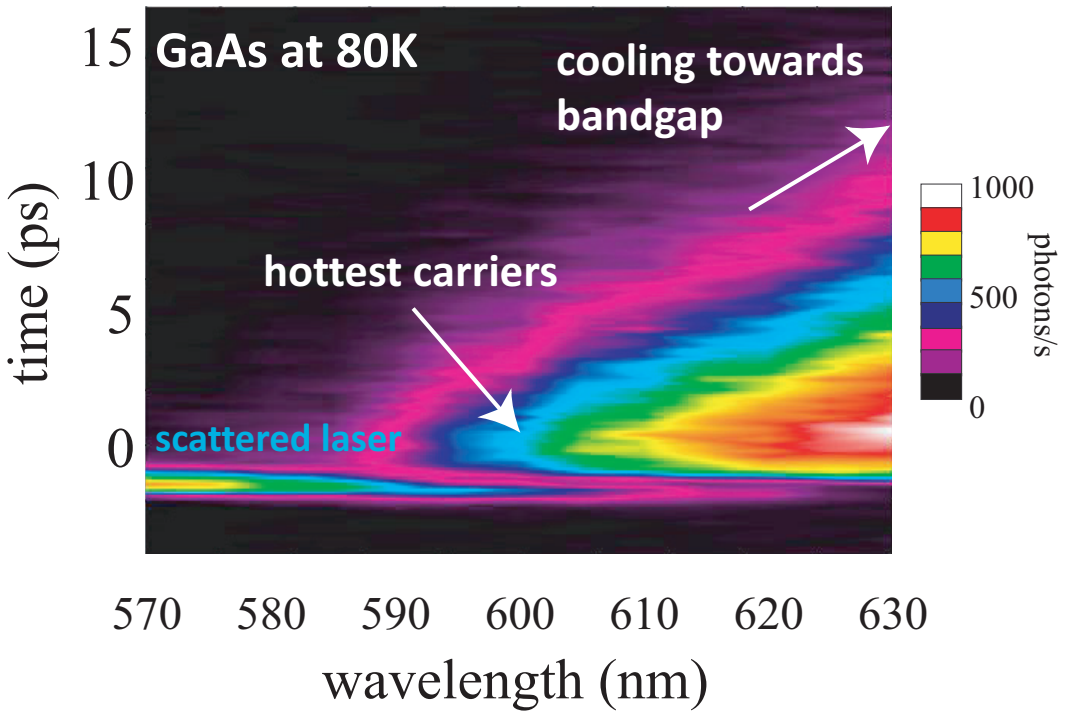

Figure 3: A portion of the TRPL of GaAs at 80K after illumination with a 150fs, 460nm laser pulse. The hottest carriers are very short-lived, on the order of a few picoseconds.

Conclusions

The TRPL experiment has been setup within the Joint Laboratory for Ultrafast Spectroscopy, a joint facility of USyd and UNSW. We have tested the experiment by performing a range of experiments on GaAs and InP, and are ready to characterize the candidate hot carrier absorbers, providing vital feedback to the other nodes of the project. Our initial experiments lend support to the underlying premise of this project – that control of the phonic structure of the hot carrier absorber will lead to control of the carrier cooling rates.

The successful outcome of this project will be the realization of a solar cell, made from abundant and cheap materials, which exceeds 50% conversion efficiency. This will substantially reduce the cost of clean and sustainable photovoltaic energy and thus contribute greatly to greenhouse gas abatement.

Contacts

Provide email contact information for principal investigators.

Timothy W. Schmidt: t.schmidt@chem.usyd.edu.au