

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

Annual Report April 2010

This project is a composite project involving four nodes

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- PI: Jean-François Guillemoles, Institut de Recherche et Développement sur l'Energie Photovoltaïque, Paris (IRDEP)
- PI: Tim Schmidt, University of Sydney (USyd)
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This second annual report details the work carried out on the project at each node, with this introduction acting as an overview of the whole project.

As reported last year, the disparate timings of the start of the project in the different nodes has meant that the work at IES-UPM has been going on for nine months longer than the other nodes. Hence the report here for IES-UPM is their final report whilst those of the other three nodes are their second annual reports.

The inaugural meeting of all four nodes was held before the project started in September 2007 in Madrid. The first annual meeting was held in May 2009 in Strasbourg and the second annual meeting is planned for September 2010 in Valencia. Several other meetings between two of the partner nodes have taken place during the project.

There now follows an overview of progress on the project followed by the individual detailed reports from each node.

Introduction and Background

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.

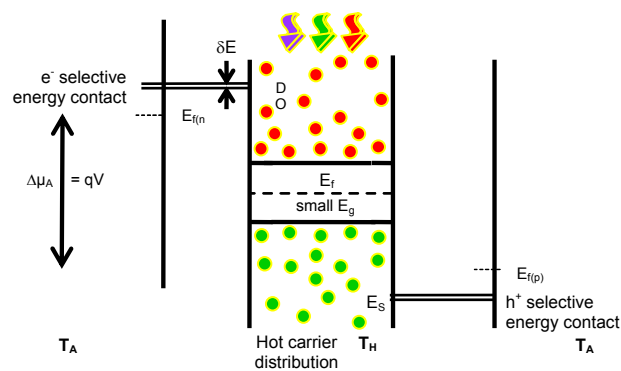


Fig 1: Band diagram of a Hot Carrier solar cell,

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 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).

References:

- [1] Green MA, “Third Generation Photovoltaics”, (Springer Verlag, 2003).
- [2] Würfel P, Sol Energy Mats & Sol Cells, 46(1997) 43.
- [3] Ross R and Nozik AJ, J. Appl Phys, 53 (1982) 3318.
- [4] Conibeer G et al, Solar Energy Materials and Solar Cells, 2009, 93, 713.
- [5] Guillemoles J-F et al, PVSEC (Shanghai, 2005) 375.

Overview of Progress, May 2009 to April 2010

Progress towards both of the twin aims of developing a Hot Carrier absorber with slowed carrier cooling and characterising resonant tunnelling structures using quantum dots for energy selective contacts, has been made in the past year.

Photogenerated hot carriers in an absorber lose their energy principally through emission of optical phonons. The subsequent blocking of the decay of these optical phonons by modification of an absorber material's phonon dispersion maintains a 'hot phonon' population and reduces carrier cooling. Previous work in this project has shown this to be the optimal method to achieve slowed carrier cooling.

In the past year, modelling of the phonon energies in bulk compound materials has been developed further with DFT input to the vibronic modes of binary compounds at the UNSW node. As with the simpler modelling based on elemental mass this shows a strong dependence of large phononic gaps for the large mass difference compounds. For several of these the phononic gap is large enough to block the decay of optical phonons and hence reduces the main route of carrier cooling. Experimental verification of this has been obtained in the time resolved photoluminescence data from the USyd node which show a slower carrier cooling rate in the large phononic gap of InP as compared to that in the zero phononic gap of GaAs. The fitting of this data to characteristic temperatures has been carried out at the IRDEP, USyd and UNSW nodes, allowing full evolution of the carrier dynamics. Further analysis of different incident photon energies has allowed the contribution of side valley scattering to carrier dynamics in both materials to be incorporated in a more complete picture. This important proof of concept is now allowing the characterisation of other bulk materials such as InN with a large phononic gap and small electronic gap and the very large phononic gap of some Bi and Sb compounds. Other development of characterisation has been carried out at the IES-UPM node for techniques including UV quantum efficiency measurement and low temperature measurement to suppress background phonon noise in hot carrier absorber measurements.

In parallel, work on modelling of the mini-gaps in the phonon dispersion for nanostructures has been carried out at UNSW and IRDEP. These mini-gaps can emulate the phonon blocking mechanism of the large phononic gap materials for correctly engineered nanostructures of more abundant materials, potentially more suitable for large scale implementation – these include nanostructures based on Group IV alloys. The modelling shows that complete gaps in reciprocal space can be achieved for high symmetry superstructures, particularly FCC and Diamond superlattices using small (1nm) quantum dots in a light material matrix. Further work has been carried out on computing the phonon lifetimes in such nanostructures. At UNSW a perturbative method based on the anharmonic decay function of optical phonons is used to compute the density of states and hence the probability of a decay and the lifetime of the initial state. At IRDEP a more computer intensive but more accurate approach using molecular dynamics of the whole system is used to compute the lifetimes with excellent agreement for bulk materials such as silicon. These analyses allow prediction of the carrier cooling rates in such materials which will be used to predict the time resolved photoluminescence results when these nanostructure materials are fabricated and characterised.

Further progress has been made on fabricating coherent nanostructure arrays of gold nanoparticles using colloidal dispersion at UNSW. Good 2D crystallinity has been demonstrated in TEM imaging, Fourier Transform and electron diffraction measurements. Development of multi-layer structures, use of silicon, tin and core shell nanoparticles and characterisation of the phonon modes using Raman is now underway. The alternative route to coherent nanostructure arrays using Stranski-Krastinov growth of III-V quantum dot nanostructures has been carried out by our collaborators at the University of Tokyo. Samples

of InAs QDs in a GaAs matrix have been supplied and will soon be characterised using Raman at UNSW and tr-PL at USyd.

Modelling of energy selective contacts (ESCs) has been carried out at IRDEP with the result that efficiency is seen not to be strongly dependent on the degree of selectivity – an important result technologically. Measurement of ESCs has been facilitated at IES-UPM by the use of low temperature I-V measurement to suppress phonon noise and photoreflectance measurement of resonant selective features. The degree of equivalence of ESCs with Intermediate Band cells has also been investigated at IES-UPM.

More sophisticated models of the overall efficiency of Hot Carrier cells have been developed at IRDEP and UNSW. That at IRDEP uses measurable material properties with the only variable input being the thermalisation time. At UNSW the electronic band structure of a real potential hot carrier absorber material (InN) is used to calculate the thermalisation rates and the impact ionisation and Auger recombination rates in an efficiency model. Both models give more specific and realistic estimates for Hot Carrier cell efficiencies than earlier models. These can now be applied to the bulk and nanostructure materials used in other parts of the project.

The elements of slowed carrier cooling in an absorber, energy selective contacts, fabrication of quantum dot nanostructures and calculation of overall efficiencies have all made progress in the past year, with strong complementarity and synergy demonstrated between the four nodes of the project. The next year will see exploitation of the techniques and structures so far developed to make further progress towards the still challenging goal of a working Hot Carrier cell.

Full descriptions of these projects are given in the following detailed reports from each node.

**Project: “Hot Carrier solar cell:
Implementation of the Ultimate PV Converter”**
Institution: University of New South Wales, Sydney, Australia
Annual Report April 2010

Abstract

The UNSW node of the Hot Carrier Solar Cell project is investigating absorbers which slow the rate of carrier cooling - an essential element of a successful cell. This work includes modelling the limiting efficiencies of cells using real material properties and modelling the phonon dispersions of ordered arrays of quantum dots. The object of the latter 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 three 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. Calculating the limiting efficiencies of cells with specific electronic, and later with specific phononic properties.
3. Fabrication and characterisation of ordered quantum dot arrays. Colloidal dispersion of capped nanocrystals to form 2D supercrystal arrays. These are being characterised for their modulation of phonon dispersions and for the effects of this modulation on the rate of carrier cooling.

Administration

Personnel

[All personnel are members of the ARC Photovoltaics Centre of Excellence (CoE), which is supported by the Australian Research Council.]

Principal Investigators:

Assoc/Prof. Gavin Conibeer – Deputy Director, Photovoltaics Centre of Excellence
Prof. Martin A. Green – Research Director, Photovoltaics Centre of Excellence

Investigators:

Dr. Dirk König – Research Fellow, GCEP, CoE
Dr. Shujuan Huang – Research Fellow, GCEP, CoE
Dr. Santosh Shrestha – Lecturer, CoE
Dr. Lunmei Huang – Postdoctoral Fellow, GCEP, CoE (until July 2009)
Dr. Ivan Perez-Wurfl – Research Fellow, CoE

Students, CoE:

Mr. Christopher Flynn - PhD (completed July 2009)
Ms. Lara Treiber - PhD
Mr. Pasquale Aliberti - PhD
Mr. Andy Hsieh - PhD
Mr. Robert Patterson - PhD
Mr. Binesh Puthen Veetil - PhD
Mr. Fred Qi - PhD (from March 2010)
Mr. Yu Feng - U/Grad thesis project (from Sept 2010)

Equipment (funded on other projects)

Femtosecond laser for TR PL – located at JLUS, Sydney University
Computer cluster – upgraded to 650Gflops
Langmuir-Blodgett deposition apparatus

Organisation

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

Hot carrier dynamics and phonon dispersion modelling;
Limiting Hot Carrier Cell efficiency modelling;
Fabrication of quantum dot arrays for absorbers with slowed carrier cooling;

Introduction

An ideal Hot Carrier cell would absorb a wide range of photon energies and extract a large fraction of the energy to give very high efficiencies by extracting ‘hot’ carriers before they thermalise to the band edges. Hence an important property of a hot carrier cell is to slow the rate of carrier cooling to allow hot carriers collected whilst they are still at elevated energies (‘hot’), and thus allowing higher voltages to be achieved from the cell and hence higher efficiency. A Hot Carrier cell must also only allow extraction of carriers from the device through contacts which accept only a very narrow range of energies (energy selective contacts or ESCs). This is necessary in order to prevent cold carriers in the contact from cooling the hot carriers, i.e. the increase in entropy on carrier extraction is minimized [1]. The limiting efficiency for the hot carrier cell is 65% at 1 sun and 85% at maximum concentration – very close to the limits for an infinite number of energy levels [2,3,4]. Figure 1 is a schematic band diagram of a Hot Carrier cell illustrating these two requirements.

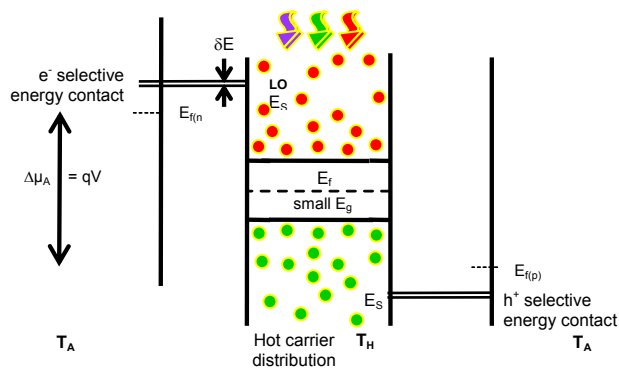


Figure 1: Band diagram of the Hot Carrier cell: showing absorption of carriers in a narrow bandgap absorber material, which must exhibit slowed carrier cooling, and energy selective contacts to extract hot carriers with a minimum increase in entropy.

Carrier cooling progresses by the interaction of hot carriers with the lattice to emit optical phonons. Interruption of the decay of these optical phonons into acoustic phonons can maintain the ‘hot phonon’ population and allow scattering back with the electron or hole gases, thus slowing down the rate of cooling. Methods to maximize this ‘hot phonon bottleneck’ effect are the subject for the work of the UNSW node of the project.

Progress May 2009 – April 2010

In the past year a sophisticated model of the limiting efficiencies of Hot Carrier cells has been developed, which includes the electronic properties of real materials for the absorber and reasonable materials and device properties with the current state of the art. Theoretical work on carrier cooling and interaction with phonons in absorber materials has developed into three dimensional modeling of phonon decay. There has also been a significant development in the measuring of slower carrier cooling in some III-V materials supporting the theoretical models for phonon decay. Development of QD nanostructures using Langmuir-Blodgett deposition of nanoparticles has made significant progress, with 2D crystals demonstrated by Fourier Transform analysis of TEM.

Modeling of Hot Carrier cell 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 the Klemens mechanism, in which the optical phonon decays into two acoustic phonons of half its energy and of equal and opposite momenta [5]. The build up of emitted optical phonons is strongly peaked at zone centre both for compound semiconductors due to the Frölich interaction and for elemental semiconductors due to the deformation potential interaction. The strong coupling of the Frölich interaction also means that high energy optical phonons are also constrained to near zone centre even if parabolicity of the bands is no longer valid [6]. This zone centre optical phonon population determines that the dominant optical phonon decay mechanism is this pure Klemens decay.

Phononic Properties of Bulk Materials

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, possibly large enough to block operation of this Klemens mechanism, which can be termed a 'phononic band gap'. Work previously presented [7] using a simple 1D force constant model indicated that GaN, InN and InP all have large phononic band gaps, which are close to those found experimentally [8]. This work has now been complemented by high accuracy Density Functional Theory (DFT) computation [9] of diatomic molecules consisting of two elements forming binary compounds potentially useful for hot carrier absorbers. These diatomic molecules were Hydrogen-terminated, with the wave number of the standing symmetric vibration then corrected for the attached H atoms, yielding the optical phonon wave number at the Brillouin zone centre. Despite the rather simple assumption of emulating a bulk phase with a H-terminated diatomic molecule, the match to data in the literature is good [8].

The ratios of phononic properties are shown in Figure 2. The data for $E_O - E_A / E_A$ indicate the potential to block Klemens decay. Those compounds with values greater than 1.0 have no available acoustic phonon energy at half the optical energy and so will prevent Klemens decay. The data for $E_O(\text{Max-Min}) / E_A$ indicate the potential for reducing energy loss through Ridley decay, in which a zone centre phonon decays into a non-zone centre optical phonon and an acoustic phonon of matching momentum. Low percentages show a small amount of energy can be lost via this route because the narrowness of the optical phonon dispersion is a small fraction of the acoustic phonon energy.

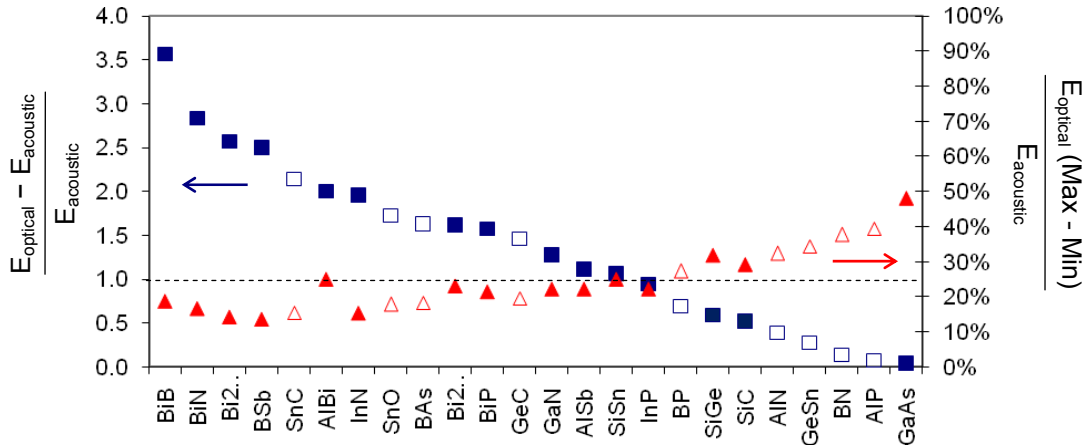


Figure 2: Ratios of phononic band gap energy values for various binary compounds: ■ & □ energy gap between acoustic and optical modes normalised to acoustic frequency; ▲ & △ energy dispersion of optical modes. Filled Symbols (■ & ▲) refer to DFT calculations of diatomic ‘molecules’ fed into a 1D diatomic chain model whereas Open Symbols (□ & △) refer to calculations based on simple elemental masses. The dashed line indicates the point at which the phononic gap equals the maximum acoustic phonon energy.

In Figure 2 it can be seen that the compounds with a large ratio of mass number have the largest phononic gaps. They also tend to have the smaller loss by Ridley decay because the optical phonon dispersion decreases as mass ratio increases. The bismuth compounds have particularly large gaps. However any of the compounds to the left of InP on the abscissa have a gap larger than the acoustic phonon energy and hence will not allow Klemens decay, although a margin for error in the imperfect crystallinity of real materials is likely to be advantageous. Other factors such as the ease of fabrication of the compounds and their quality and the abundance of the elements involved are likely to decide which of these are optimal. The III-V zinc-blende and wurtzite materials fit the first of these criteria with the ability to be fabricated with fairly high quality. InP and GaAs are currently being compared for their carrier cooling properties, as detailed elsewhere in this report. InN is an interesting candidate with its wide phononic gap but also narrow electronic bandgap (0.7eV) needed to facilitate absorption [11]. The bismuth compounds and some of the arsenides and antimonides have large gaps but are not currently grown as high quality crystals, although experiments are now being carried out on Bi₂S₃, the results of which will be reported in next year’s report. Others of interest are the group IV compounds SiC, SiGe, GeSn, SiSn, GeC and SnC, as discussed in [6]. Of these only SiC exists as a real material, but it has too small a phononic gap. The Sn compounds in particular do look interesting, if a way can be found to fabricate them. This is the subject of other ongoing work which will also be reported next year. SnO is a real material although not a stoichiometric compound on which further work is also planned.

Measurements for slowed carrier cooling

Time resolved photoluminescence (tr-PL) has been used to measure the carrier cooling rates in some materials. This is reported in the section of this report from the University of Sydney. In summary this work compares the cooling rates in InP and GaAs. This semiconductor pair make for a good comparison of the effect on phononic bandgap on carrier cooling, because they have similar electronic bandgaps (1.35 and 1.45eV respectively) but very different phononic bandgaps (see Figure 2), with that for InP just large enough to block Klemens decay. The results of this work (see Sydney University section) show that InP does indeed exhibit slower carrier cooling than GaAs, strongly supporting the hypothesis of the suppression of Klemens decay.

Modeling of phononic bandgaps in QD superlattice structures

In coherent nanostructure superlattices Bragg reflections at the mini-Brillouin zone boundaries, due to modulation of the vibronic properties. Suitably engineered, such phononic mini-gaps can be used to produce a similar prevention of the Klemens optical phonon decay mechanism in less exotic materials than those discussed in the previous section - possibly based on elemental semiconductors.

Studies of Quantum Dot (QD) superlattices (SLs) and other nanostructured materials using a semi-empirical force constant model within the rigid ion approximation are ongoing. Recent results include the computation of phonon lifetimes in one symmetry direction from an arbitrary three-dimensional (3D) phonon dispersion, as well as the discovery of a few highly constrained geometries in which phonon decay via the Klemens mechanism is inhibited. In addition, lifetime computations show that phonon band gaps of insufficient size to inhibit the Klemens mechanism can nonetheless give rise to substantially increased phonon lifetimes if the bandgaps force the phonon decay path into regions of the Brillouin Zone (BZ) with very low density of states. Both situations should slow phonon decay and in turn yield longer hot carrier lifetimes, which is a desirable property in the hot carrier solar cell absorber material.

Results were obtained for FCC or Diamond SLs with single element QDs and matrix materials. Force constants were scaled to match with literature values for group IV elements such as silicon out to third nearest neighbour interactions. Mass differences between the QD and matrix materials were set at 1:7 to simulate a bulk material with a large phonon bandgap such as InN. Typical QD sizes for solid state systems range from between 1-2 nm.

FCC SLs with heavy, overlapping QDs show phonon band gaps sufficient to inhibit first order (Klemens) phonon decay. Simulations of the “highly constrained” geometry, where QD overlap was large enough such that at superlattice interstitial sites the matrix material was reduced to only a few light atoms, produced a few high energy, highly degenerate phonon bands. The high energy bands are a result of these periodically placed light elements vibrating at high frequencies, largely decoupled from the heavier matrix. The degeneracy of the phonon bands appears to be the result of the symmetrical placement of the light elements in real-space, resulting in very similar energy and momentum states for each of these atoms in the BZ.

Figure 3 shows the large phonon band gap for the FCC SL arrangement in the three major symmetry directions, indicating a complete gap in reciprocal space. Simulations of the inverse situation, with small light quantum dots and heavy matrix material at the interstitial sites, shows that this result is general and scalable to larger SL unit cell dimensions – a very important result for the possibility of fabricating such structures.

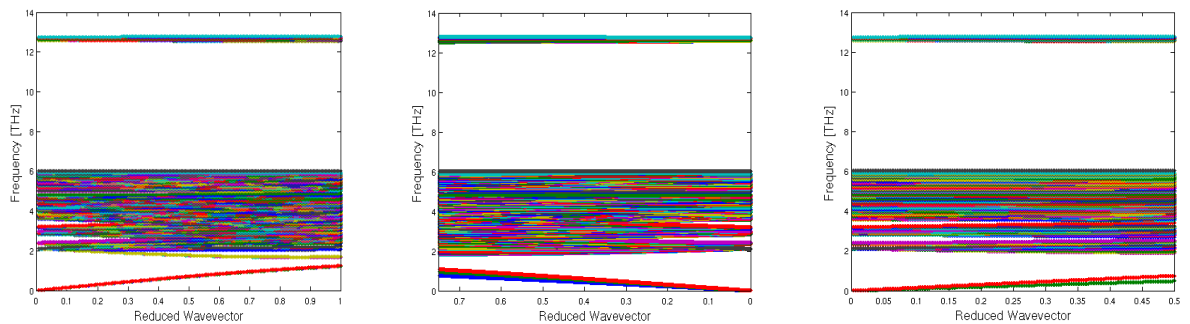


Figure 3: FCC SL of QDs showing a complete phonon bandgap large enough to inhibit Klemens decay in all major symmetry directions ($\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$).

Similarly constrained Diamond SLs also show bandgaps, though there is less degeneracy. In this case long phonon lifetimes are obtained since the fastest decay path that conserves energy and momentum is forced through some part of the BZ where the phonon density of states (DOS) is low. Typically the overall phonon decay path is made up of a few decay steps involving high and low energy phonons. In the simulations, any low energy phonon decay products were considered to be “lost.” High energy phonon decay products, those still above significant phonon bandgaps, were allowed to continue to decay. In the example case shown in Figure 4, the first very fast phonon decay yields a high energy phonon for which only slow decays are possible. In detail the first stage is the decay of the LO phonon into a LA phonon (Step 1) and a TO phonon (Step 2), this is a Ridley decay event. Since these must happen simultaneously the rate is determined by the slow Step 2. This is slow because of the low DOS to which it couples. The next stage (Step 3) is further decay of the TO phonon to two LA phonons by an off centre Klemens decay. This is fast, but the overall rate is determined by Step 2 – 22ps in this case. Under these circumstances phonon lifetimes can be increased by two orders of magnitude [10].

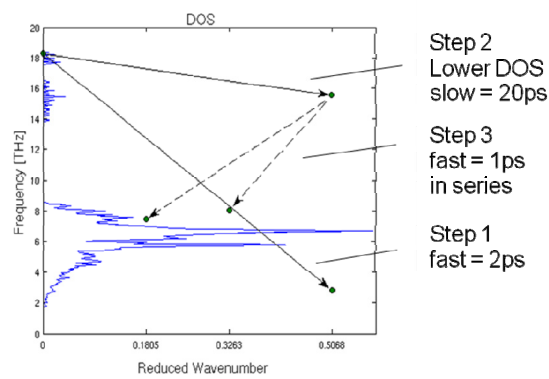


Figure 4: HCP SL of QDs showing the rates of in-series phonon decay mechanisms, with their calculated rates.

Present modelling of phonons in nanostructures includes investigations of core-shell geometries and nano-porous materials. Phonon dispersions of simple cubic (SC) SLs of core-shell QDs show large phonon bandgaps for light shell thicknesses on the order of a monolayer. Nano-porous materials with gas filled pores also show potential as candidate hot carrier absorber materials. In these mixed-phase materials the modulation of the force constant comes from difference in bond strength between the covalently bonded light absorber material and the gas phase interacting via dipole-dipole potentials. Figure 5 shows some exploratory simulations for mixed phase absorber materials in a few different approximations.

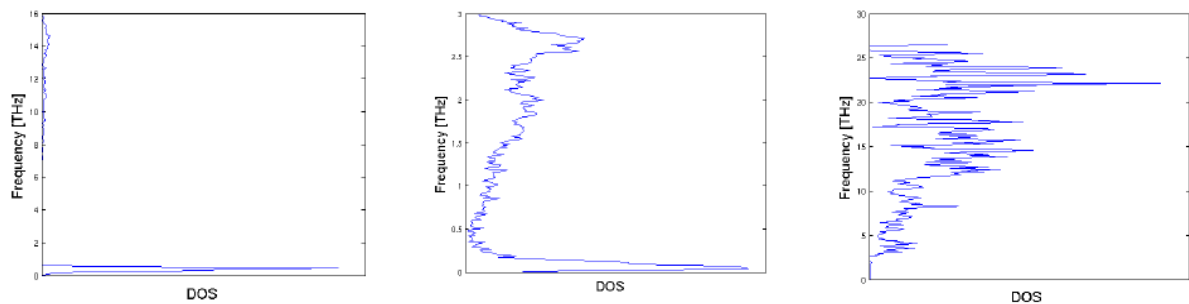


Figure 5: [Left] – DOS with complete Klemens gap for solid-gas nanoporous system where the atoms are ordered and interact via harmonic potentials. [Centre] – DOS with gas particles pseudo-randomly arranged and interacting via dipole forces. [Right] – DOS for single element solid system where the pores contain vacuum.

Hence the rate decay analysis shows that slow decay rates can occur even if complete gaps are not big enough to prevent Klemens decay. In addition core shell structures look promising in tailoring phononic properties further.

Modeling of Hot Carrier Solar Cell Efficiency

Earlier work has modeled the ideal limiting efficiency for HCSCs [2,3,4]. But for a real device a number of the ideality assumptions must be given up. Indium Nitride (InN) has been suggested as a potential material for a HCSCs because of its narrow electronic band gap for absorption of a wide range of photon energies, whilst also having a wide phonon band gap, which is good for suppression of phonon decay – the main mechanism for carrier cooling [11]. Some evidence for slowed carrier cooling is given in the literature, from transient absorption measurements [12]. The work presented here is on further development of the limiting efficiency of HCSCs with a bulk InN absorber modeled by removing most of the ideality assumptions previously used and also including in the calculation the real InN dispersion relations and thermalisation velocities.

Previous reports proposed two different approaches to calculate HCSCs theoretical efficiency; one is based on particle conservation (PC) [4] and the other assumes rapid rates of impact ionization and auger recombination (II-AR) [3] and is further expanded in [2]. These models are not suitable for describing the general behavior of real materials for HCSC converters, but can only be applied under particular conditions. A third model [13] has recently been put forward using finite II and AR rates, and thus combining elements of both the PC and II-AR models. The current model described here also combines the PC and AR-II models, but in such a way that II and AR rates are determined by the specific band structure of the absorber material – this being another step forwards in realism. The detailed band structure of wurtzite bulk InN has been considered to perform computation of carrier densities, pseudo-Fermi potentials and II-AR time constants.

The HCSC has been treated as a system which can interact with the external environment through particles and energy exchange. Hot electrons and holes are extracted to the external circuit through energy selective contacts (ESCs) which are considered to be ideal. For simplicity a common temperature for hot electrons and holes has been assumed and energy distributions only differ for quasi-Fermi potential.

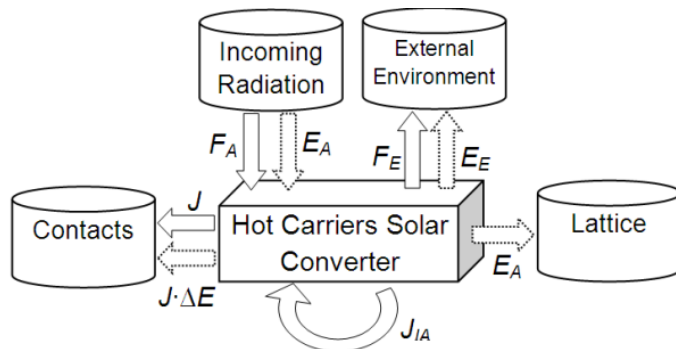


Figure 6: Schematic representation of energy and particle fluxes used in the model - (particle fluxes - full arrow, energy fluxes- dotted arrow).

Figure 6 shows energy and particle fluxes involved in the hot carrier device operation. The incoming particle flux from the sun can be approximated with blackbody radiation at 6000K; fluxes to the external environment are due to radiative emission and interaction with the lattice related to optical phonon emission. The E-k relationship for high purity wurtzite InN have been calculated in [14] using the empirical pseudopotential method. Results of the calculations illustrate that in the energy range of interest for solar cell modeling, InN shows two separated bands at the Γ point and a satellite band at the M-L symmetry point, along the Σ

crystal direction for the conduction band. For the valence band the calculation confirms two main bands with a point of degeneration at Γ , which can be identified as heavy and light hole bands, with a separate split-off band also present. A multivalley approximation for the bulk InN band structure which takes into account the three lowest conduction band minima (Γ_1 , Γ_3 and M-L), and the three lowest hole valleys for the valence band, has been used in our model.

The influence of AR-II on the efficiency of the HCSC has been taken into account by modifying the expression for the total current from the cell. Such a modeling approach allows consideration of the effects of II-AR for all operating conditions of the cell. AR-II rates have been calculated considering highly probable three particles processes for bulk InN, and neglecting high k-vector mechanisms [15].

Figure 7(a) shows the dependence of the calculated maximum efficiency as a function of the extraction energy ΔE , for the three different concentration ratios and the absorber thickness $d_{abs} = 50$ nm. A thermalisation constant $\tau_{th} = 100$ ps has been used, as a reasonable compromise between values recently reported [12].

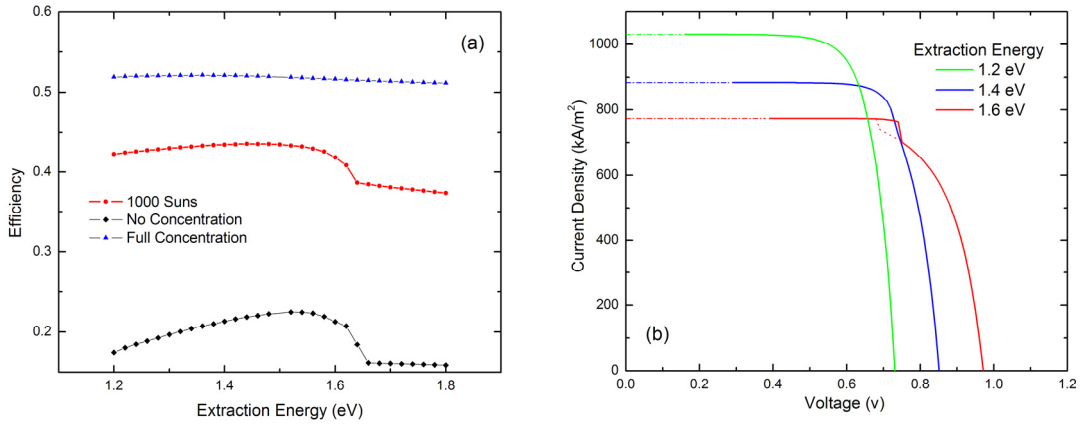


Figure 7: (a) HCSC efficiency as a function of carrier extraction energy level. Parameters used are: thermalisation time = 100 ps, concentration = 1000, lattice temperature = 300K and absorber layer thickness = 50 nm. (b) Current Density and a function of voltage for different extraction energies (ΔE) for ESCs.

We have found that for 1000 suns the efficiency curve reaches a peak value of 43.6% for a hot carrier extraction energy of 1.44 eV. Maximum efficiencies of 52% and 22.5% have been calculated for full concentration and non-concentrated spectra, respectively. Figure 7(b) shows J-V relations for three different extraction energies. The value of V_{OC} increases when the extraction energy is increased. In fact, as the carrier temperature T_C is very high in open circuit conditions, the V_{OC} is strongly related to ΔE . The short circuit current decreases monotonically as a function of extraction energy due to the increase in Auger recombination.

In summary results from this modeling work show that if a real material is considered, efficiency calculations of HCSC efficiency limits lead to considerably lower values than results obtained in other reports, where ideal absorbers are considered. This implies that the gain in efficiency that can be achieved using bulk materials as absorbers in HCSCs is limited due to fixed phononic properties. The efficiency is found to depend critically on the thermalisation time. However the figure used of 100ps for thermalisation time, whilst based on a reasonable extrapolation of current experiment, is not necessarily the highest for InN. It is also quite possible that either higher quality or cubic InN or other bulk materials or nanostructures can have longer thermalisation times. Hence the fact that an efficiency of 43.5% can be obtained with a bulk absorber is an optimistic outcome which encourages

further investigation on phononic properties of semiconductors to slow down carrier cooling and achieve a more significant efficiency gain.

Fabrication of highly ordered nanoparticle arrays for Hot Carrier absorbers

In parallel with the work on modeling phonon modulation in QD superlattices, methods are being investigated to fabricate highly ordered QD arrays. These include colloidal dispersion of mono-disperse nanoparticles obtained from a collaboration with the Indian Institute of Science and characterization of III-V in-situ QD arrays grown at the University of Tokyo on another collaboration.

Colloidal dispersion of nanoparticles

Colloidal dispersion of nanoparticles of very monodisperse size is known to produce uniform nanoparticle arrays [16]. It also offers the potential to incorporate core shell QDs. As discussed in the section on superlattice modeling and in [11] core shell QDs offer a way to significantly change the phonon modulation in a superlattice because the core and shell can be of materials of very different force constant, directly leading to a strong phonon confinement.

In the last year experimental work has continued on methods to fabricate highly ordered QD arrays using Langmuir-Blodgett (LB) deposition of nanoparticles. The LB technique (Figure 8) allows for the formation of ordered monolayers at an air-water interface using whilst exploiting the self-organization mechanism of colloidal dispersion. Compression of the monolayer is monitored via measurements of surface pressure (SP), see Figure 9. This reaches a maximum at the highest density of nanoparticles in the plane, corresponding to a highly organized 2D crystal structure. This technique allows transfer of ordered monolayers and multilayers onto a wide range of solid substrates such as glass or Si wafers [16].

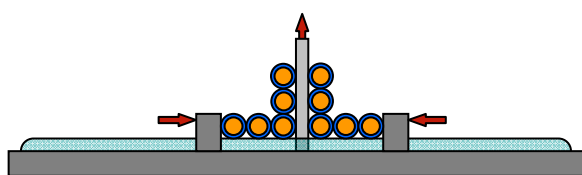


Figure 8: Schematic diagram of the LB apparatus used to fabricate a monolayer of encapsulated nanoparticles.

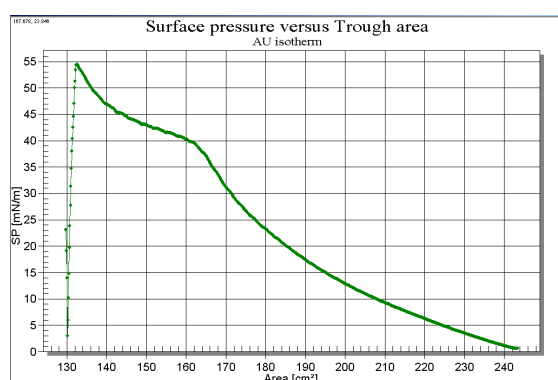


Figure 9: Surface pressure isotherm of Au nanoparticle on the water surface. The maximum SP, of 55mN/m at 132cm², corresponds to the maximum packing in the plane and a high degree of 2D crystallinity.

Work has focused on optimising the deposition parameters to achieve the required ordered monolayer of gold (Au) nanoparticles. The Au nanoparticles are supplied by the Indian Institute of Science. They are 3.5±1.1 nm in diameter and functionalized with dodecanethiol molecules. Figure 9 shows the full surface pressure of the trough with the Au nanoparticle as

a function of the barrier position. This isotherm gives information on the interaction between the nanoparticles on the water surface, indicating the phase change of the monolayer. When the compression reaches the hump around 40 mN/m, the monolayer starts to buckle and overlap. We have made a series of depositions at different surface pressures in order to study the nanoparticle arrangement. Figure 10 shows TEM images of the Au nanoparticle monolayer transferred at 20 and 30 mN/m, clearly showing the improvement of the nanoparticle order. The coverage of the nanoparticles was estimated from a number of TEM images, which indicate that the coverage increases significantly with increasing surface pressure. Fast Fourier transform (FFT) analysis of TEM images has been carried out to investigate the degree of ordering in the nanoparticle monolayers. An example of the FFT from Figure 10(b) is shown in Figure 11. This clearly shows six spot-like features suggesting a highly ordered 2D hexagonal structure. The nearest centre-to-centre distance measured from this FFT is 5.9 nm, which gives the average gap between the nanoparticles as 2.4 nm. This is in good agreement with two times the length of the dodecanethiol molecules. The remaining defects in the arrangement are thought to be caused by the large deviation in nanoparticle size dispersion.

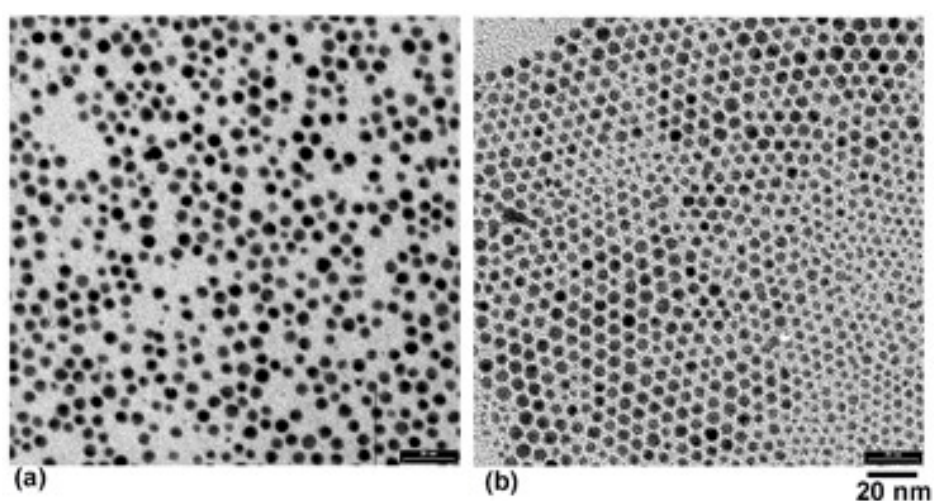


Figure 10: TEM images of Au nanoparticle monolayers deposited at surface pressures of 20 mN/m (a) and 30 mN/m (b).

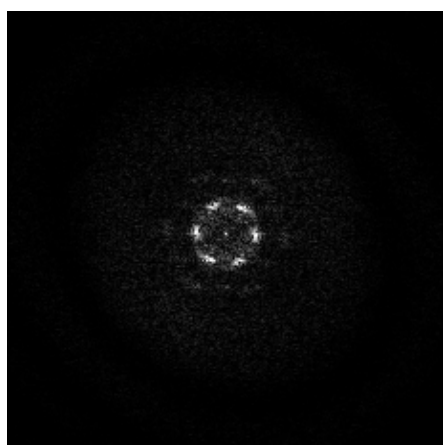


Figure 11: FFT from the TEM image of Au nanoparticle monolayer deposited at 30 mN/m.

Future work will concentrate on the fabrication of highly ordered multilayer structures and the investigation on the phononic properties using Raman and time resolved photoluminescence (tr-PL). Also other materials such as Si NPs will be investigated.

III-V quantum dot arrays

An alternative route to coherent nanostructure arrays is to use growth of III-V quantum dot nanostructures in the Stranski-Krastinov mode. At the University of Tokyo Prof. Okada is able to control size and to a lesser extent spacing of MBE grown QDs on lattice mismatched substrate. Multi-layer QD superlattices with a high degree of size uniformity are enabled through addition of strain balancing layers. Samples of such InAs QDs in a GaAs matrix have been supplied to UNSW on this collaboration. Modelling of similar superstructure geometries at UNSW, using the same 3D force constant model described above, indicate that such superstructures should demonstrate small mini-gaps at zone centre, see Figure 12.

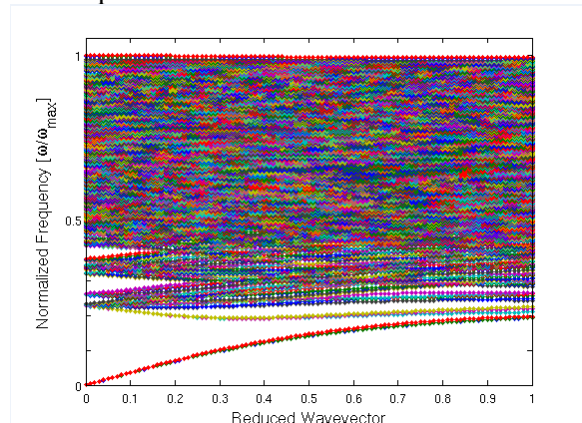


Figure 12: Phonon dispersion in $\langle 100 \rangle$ for 2nm spherical InAs QDs in a GaAs matrix, using the rigid ion force constant model described above. The InAs QDs are arranged in a simple hexagonal superlattice with the QDs just touching. This model has a very similar geometry, although a different scale, to samples supplied from the University of Tokyo.

The small gaps in the phonon dispersion at zone centre shown in Figure 12 should in principle be observable using Raman spectroscopy. The gaps are small in both the energy and momentum directions because of the small difference in mass between InAs and GaAs. Measurements using high resolution Raman to investigate these mini-gaps have just started. Once such predictions can be validated, other superstructures with larger mini-gaps in the positions required to block phonon decay will be designed at UNSW and fed back to the growth of such superstructures at the University of Tokyo. Raman at UNSW and tr-PL at USyd will then be used to characterise their phonon mini-gaps and carrier cooling.

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

Methods to slow the rate of carrier cooling in potential Hot Carrier cell absorber materials are focused on interruption of optical phonons decay by modification of phononic bandgaps.

In bulk materials the phononic bandgap of a range of binary compounds is modeled using both DFT calculations and element mass calculations. With the result that a large mass difference in the constituent atoms gives a large phonon gap. Compounds containing Bi or N have particularly large gaps. tr-PL measurement of carrier cooling of some III-V materials supports this suppression of optical phonon decay model.

Nanostructures can also exhibit such gaps through Bragg reflection at mini-zone boundaries. 3D modeling using a rigid ion force constant model, indicates that an FCC superstructure for 1nm QDs in a FCC array can realize complete blocking of phonon decay. Whereas perturbation analysis of less symmetric superstructures, such as a Diamond structure, shows that much slower phonon decay rates are possible even without complete blocking of optical phonon decay, because of a reduction in the number of available states.

Modeling of Hot Carrier solar cell efficiencies has progressed with a model using the real electronic properties of the promising candidate for an absorber, InN. Results show limiting

efficiencies around 50%. Although this is somewhat disappointing, it does depend critically on the phonon lifetime used. Improved quality of materials and a switch to nanostructured materials is expected to improve this lifetime and hence increase efficiency.

QD superlattice nanostructures are being fabricated using Langmuir-Blodgett deposition of colloiddally dispersed Au nanoparticles. TEM and FT analysis show good 2D crystallinity.

Further work will include development of the superstructure modeling to include core-shell structures and the role of interfaces. DFT input for the force constants will be used. Carrier cooling measurements using tr-PL will be carried out on new bulk and nanostructure materials modeled as having strong potential to block phonon decay. These will include colloiddally dispersed superlattices of Si, Sn and core shell nanoparticles and tailored Stranski-Krastinov III-V QD superlattices. The work on limiting efficiency calculations will be improved in sophistication to incorporate the detailed phononic structures of target materials. Growth of colloiddally dispersed Si and possibly Sn nanoparticle arrays will be combined with Raman, tr-PL and diffraction methods to determine phonon dispersion modulation.

Publications in past year of project

Refereed Journal papers:

1. G. Conibeer, N.J. Ekins-Daukes, J-F. Guillemoles, D. König, E-C. Cho, C-W. Jiang, S. Shrestha and M.A. Green, "Progress on Hot Carrier Cells", *Solar Energy Materials And Solar Cells*, 2009, 93, 713.
2. G Conibeer, R Patterson, L Huang, J-F Guillemoles, D König, S Shrestha, MA Green, "Modelling of hot carrier solar cell absorbers", *Solar Energy Materials and Solar Cells*, accepted December 2009, In Press, corrected proof available online February 2010.
3. D. König, K. Casalenuovo, Y. Takeda, G. Conibeer, J.F. Guillemoles, R. Patterson, L.M. Huang, M.A. Green, "Hot Carrier Solar Cells: Principles, Materials and Design", *Physica E*, in press, 15th Jan. 2010; <http://dx.doi.org/10.1016/j.physe.2009.12.032>.
4. Y. Takeda, T. Ito, T. Motohiro, D. König, S. Shrestha, G. Conibeer, *Journal of Applied Physics*, 105, (2009) 074905, "Hot carrier solar cells operating under practical conditions".

Un-refereed Conference papers:

5. G. Conibeer, R. Patterson, P. Aliberti, L. Huang, J-F. Guillemoles, D. König, S. Shrestha, R. Clady, M. Tayebjee, T. Schmidt, M.A. Green "Hot Carrier solar cell Absorbers", 24th European PVSEC, Hamburg (Sept. 2009) 1BO.8.3 on CD-ROM.
6. R. Patterson, M. Kirkengen, Binesh Putten Veettil, D. König, M.A. Green, G. Conibeer, "Phonon Lifetimes in Model quantum dot superlattices", 24th European PVSEC, Hamburg (Sept. 2009) 1CO.9.6 on CD-ROM.

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7. G. Conibeer, N.J. Ekins-Daukes, J-F. Guillemoles, D. König, E-C. Cho, C-W. Jiang, S. Shrestha and M.A. Green, "Progress on Hot Carrier Cells", *Solar Energy Materials and Solar Cells*, 2009, 93, 713.
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10. R. Patterson, M. Kirkengen, Binesh Putten Veettil, D. König, M.A. Green, G. Conibeer, "Phonon Lifetimes in Model quantum dot superlattices", 24th European Photovoltaic Solar Energy Conference, Hamburg (Sept. 2009) 1CO.9.6 on CD-ROM.
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**Project: “Hot Carrier Solar Cell:
Implementation of the Ultimate Photovoltaic Converter”
Institution: Institut de Recherche et Développement sur l'Energie
Photovoltaïque (IRDEP)**

Annual Report April 2010

Investigators

All investigators are member of IRDEP but not necessarily under contract with CNRS, in which case they are not supported by the grant.

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Abstract

In this second year of the project, we have worked on the thermalization issue of hot carriers on two aspects: (i) searching new materials based on Si with increased phonon lifetimes, which was approached by computing these lifetimes by molecular dynamics modeling of the lattice, and (ii) evaluating thermal losses in the absorber or via the electrical contacts by a model. Si Bulk phonon lifetimes could be well reproduced and we are now in position of attacking Si based nanostructures. The modeling of the thermalisation in bulk samples gave access to the experimental value of thermalisation rates. Finally, first results on modeling of the thermalisation in the contacts showed that the contact selectivity may not be as drastic as initially thought, and that 100 meV selectivity (achieved in QD lasers) might be enough.

On the experimental side, we have worked with the USyd node to extract thermalization data from the TR PL experiments, and we have characterized by Raman the vibration modes of core-shell Qdots.

Results, May 2009 – April 2010

The efforts were divided in two parts:

- a) finding new materials based on Si where reduced thermalisation would be possible. As our previous work indicated, this is largely dependent of the relevant phonons lifetimes. This was pursued using modeling of the response of various Si nanostructures to the emission of phonons such as those emitted by a hot electron cooling down.
- b) assessing the extent to which thermalisation is an issue in experimental materials and structures.

Phonon lifetime

A hot electron ensemble cooling down will emit very specific phonon modes due to restrictions in energy and momentum conservation. These phonon modes are another word for lattice vibration modes. The crystal lattice then rings (like a piano) at a very specific tone (15 THz for bulk Si, the zone center LO mode, see figure below). Like in a piano, the intensity of the mode (the sound of a note) decreases in time as more and more of the vibration energy of the mode is passed to other modes (other notes): this is the so called anharmonic interaction, causing a finite lifetime of the vibration modes. As long as the energy is mainly in the initial mode, it can still be given back with a good probability to electrons. It is not so with the decayed modes. The phonon lifetime is ultimately what will limit the thermalisation of the electrons in the system and is therefore the most important quantity. Unfortunately, few data are available for bulk materials, and even less in nanostructures. Because very difficult measurements have to be performed, sometimes the data published are not even reliable. Therefore we set to compute these values using state of the art, accurate, techniques.

As was shown in the previous report, vibration modes of nanostructured lattices, even containing a large number of atoms, can be simulated very accurately using ab initio techniques where forces between atoms are computed at the quantum mechanical level using DFT (Density Functional Theory) formalism. IRDEP developed a code that was then communicated to UNSW to obtain the modes in nanostructures such as Si-Ge

These vibration modes are then a good starting point to obtain the phonon lifetimes by either a perturbative approach (a path followed by UNSW) or directly using molecular dynamics: because lattice vibrations consist of periodic motion of atoms, a Fourier transform of their motion will give the modes' vibrational frequencies and their decay in time (the Fourier transform is actually carried out on the velocity autocorrelation function). This is the path that was followed at IRDEP, in spite of being very computer intensive (simulations were carried out on an IBM Blue Gene supercomputer, with 40000 CPUs) because it is the most accurate method available.

The method was tested successfully on silicon lattice (see fig. below). Not only the fundamental frequency of the zone center LO mode could be reproduced accurately, but its lifetime was found to fit existing data. The method is currently being tested on various nanostructures to check for lifetime improvements.

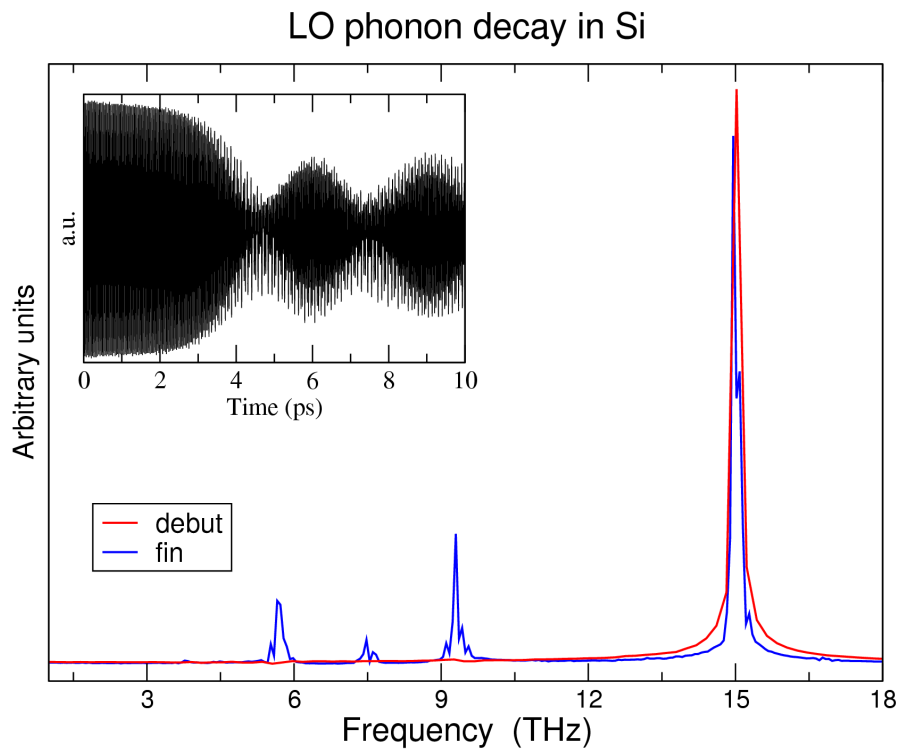


Figure 1: The oscillations show the velocity autocorrelation function (VAF) of the atoms in the lattice. By a Fourier transform, the main vibration modes can be extracted and their evolution in time followed.

Extracting thermalization rates from data

The operation of a hot carrier solar cells is outlined below (figure 2). The main difference with a standard photovoltaic device is that whereas in the former the excess photon energy (difference between photon energy and absorption threshold) is dissipated as heat and does not contribute to the electrical power delivered (it is actually a nuisance), a hot carrier solar cell attempts to collect as much of the incoming power as possible.

To do so, as much of the incoming photon energy as possible must be delivered and maintained in the electron population before it is collected through the contacts, therefore all energy dissipation to the semiconductor lattice must be accounted for and kept within a minimal boundary. There are 2 main losses :

- in the absorber itself, e.g. by phonon emission. This is the loss addressed by nanostructures and phononic crystals, as it is governed by the emitted phonon lifetime.
- in the contacts, when highly excited electrons give their energy to the “cold” electrons either when injected in the contact or when electrons from the contact

are injected in the absorber. This loss can be minimized by having a barrier for electron exchange and by having energy selective contacts.

In this part of the work we have tried to measure the thermalization rate in the absorber. In this aim, we have used time resolved photoluminescence data.

Our goal is to use these data to evaluate the losses incurred in hot carrier solar cells, and more specifically, to obtain the dependence of the free energy loss rate as a function of carrier temperature. This function can then be used in a device model developed earlier and summarized below.

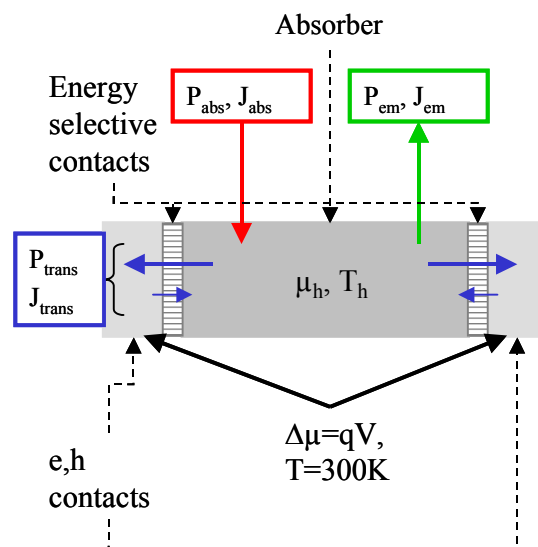


Figure 2: A hot carrier type of photovoltaic converter absorbs an incoming photon flux and power (resp. J_{abs} and P_{abs}), and re-emits photons (resp. J_{em} and P_{em}), while a fraction of the current and electrical power is collected through selective energy contacts (J_{trans} , P_{trans}). T_h and T are the temperatures in the absorber and in the contacts resp., while μ_h and μ are the electron-hole pair chemical potentials.

All quantities described above appear in the balance equations for particle and for energy, and are known a priori, with the exception of Q_{th} , the thermalization rate in the absorber:

$$J_{abs} - J_{em}(\mu_h, T_h) + J_{trans}(\mu_h, T_h) - \Delta\mu = 0$$

$$P_{abs} - P_{em}(\mu_h, T_h) + P_{trans}(\mu_h, T_h, \Delta\mu) + Q_{th}(T_h) = 0$$

The USyd node measured time resolved PL on GaAs and on InP samples with an excellent resolution and shared the data with us. Following earlier studies, we have assumed that the electron system is in quasi-steady state and that it can be described by a temperature and a chemical potential. Indeed, fitting the data confirmed that the assumptions are very reasonable.

Fitting the high temperature part of the spectrum yields the electron temperature (see description in the USyd section) as a function of time. Introducing the heat capacity of the electron gas enabled us to obtain the kinetic energy of electrons, and its derivative versus time gives the energy loss per electron. This function can be used in the equations above to model the operation of a hot carrier solar cell. Unsurprisingly, these losses are large in the bulk samples tested, but we are now in a position to investigate nanostructured samples. As expected, InP has a much reduced (about 10 times lower) thermalization rate as compared to GaAs, as expected from their published respective LO phonon lifetimes.

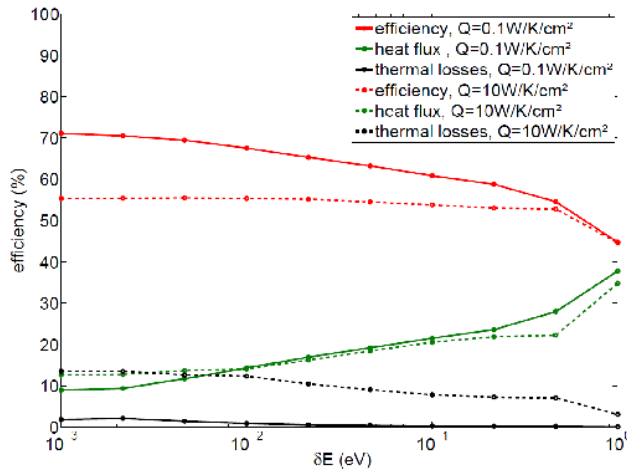


Figure 3: Hot carrier solar cell efficiency (red), thermal losses (power transferred to the lattice) (black) and heat flux at the contact (green) vs contact width in the case of partially thermalized carriers under maximal solar flux concentration and for a band gap of 1 eV. Full lines: slow thermalization ($Q=0.1$ W/K/cm²), dashed lines: fast thermalization ($Q=10$ W/K/cm²).

Moreover, efforts have been made to model realistic selective energy electric contacts. Although the results need further in-depth analysis, preliminary findings confirm that contacts do not have to be unrealistically selective, and that 100 meV selectivity might be enough. An important finding is that the design of the contacts is very dependent on the thermalisation rate in the absorber (figure 3).

Progress

Although most of the work carried out in this period was concerned with bulk materials, it was necessary to validate the methods to lay the ground for the studies on quantum wells and quantum dots. We are now in a position to search nanostructures with extended phonon lifetimes, to use TR-PL measurements for extraction of thermalization rates and use those to design hot carrier solar cells.

Future Plans

In the next period it is planned to investigate nanostructures for increased LO phonon lifetime both in terms of modeling and in terms of characterization, using samples prepared in the framework of other programs. Nanostructured samples will be investigated by TR-PL at U Syd, and it will be very interesting to obtain their thermalization rates. The losses through electric contacts are being currently investigated in more details and the priority is to validate the results in the coming weeks.

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**Project: “Hot Carrier Solar Cell:
Implementation of the Ultimate Photovoltaic Converter”
Institution: University of Sydney**

Annual Report April 2010

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Abstract

We have completed a comparative study of carrier cooling in GaAs and InP in order to investigate the effect of the larger phonon bandgap of InP. This was performed using the technique of time-resolved photoluminescence by upconversion in a non-linear crystal. It was found that hot carriers in InP cool substantially slower than in GaAs. This is ascribed to the closure of the Klemens mechanism in InP. The demonstration of the effect of the phononic structure on carrier cooling rates in model materials represents a crucial milestone in the development of the hot carrier solar cell. In preparation for the receipt of indirect bandgap materials (some of which will be based on silicon) and other nanostructures with low photoluminescence yield, we have built and tested a transient absorption set-up.

Introduction

The Shockley-Queisser limit applies to photovoltaic (PV) devices which allow complete thermalization of carriers with the lattice. Such PV devices are limited to an efficiency of about 33% under one sun at a band gap of 1.34 eV. However, if carriers do not completely thermalize with the 300 K lattice before they are extracted, they may be extracted at an elevated voltage and thus photovoltaic energy conversion efficiencies may be improved. The Hot Carrier Solar Cell (HCSC) is such a device. In order to implement an HCSC, two principal criteria must be met. Firstly, energy selective contacts must be engineered which allow extraction of carriers at only a subset of energies. Secondly, an absorber material must be engineered in which carriers thermalize with the lattice on a time-scale exceeding that on which they may be extracted. Carrier thermalization occurs on the picosecond time-scale. As such, observation of carrier thermalization requires the use of ultrafast spectroscopy. The role of The University of Sydney node is to characterize materials with a view to a detailed and fundamental understanding of carrier thermalization phenomena. To this end we have built two set-ups: time-resolved photoluminescence (TRPL); and transient absorption spectroscopy (TA). TRPL has been applied to investigate the differences in carrier thermalization rates in electronically similar yet phononically distinct materials: GaAs and InP. The TA set-up has just been completed and has been tested on a doped silicon sample, and Ge nanowires[†].

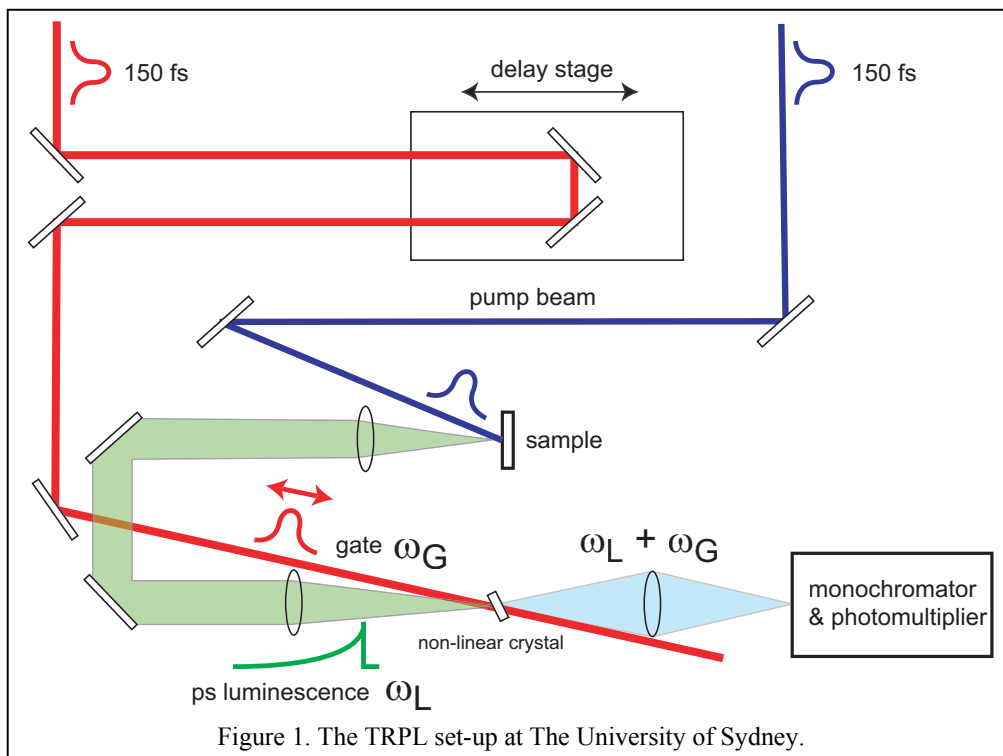
* Department of Physics and Grantham Centre for Climate Change, Imperial College, London, UK.

† In collaboration with Professor Paul McIntyre, Stanford.

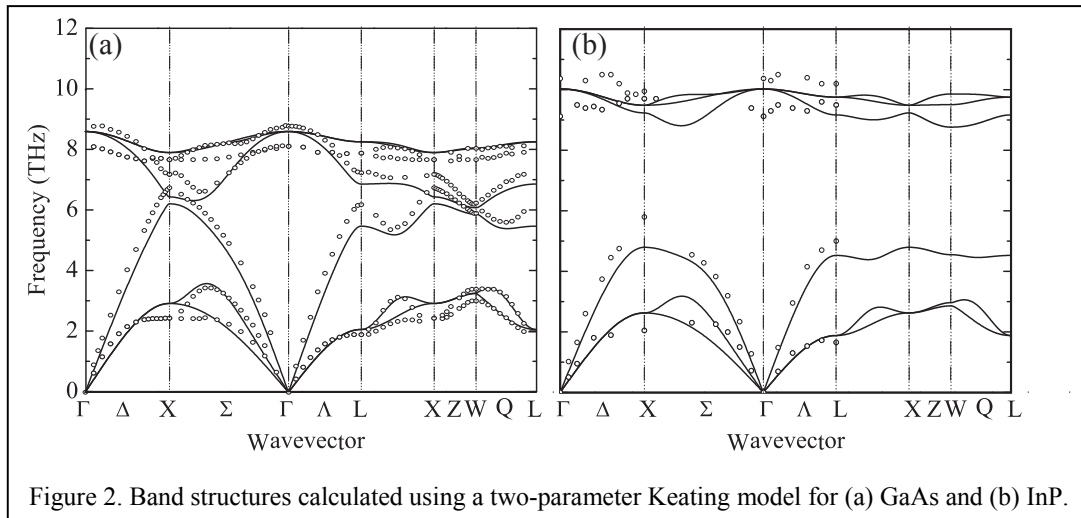
Time-Resolved Photoluminescence of GaAs and InP

We have studied the ultrafast time-evolution of the emission spectra of GaAs and InP under identical experimental conditions. Since both are direct band gap materials, the emission spectra may be directly related to the temperatures of the carriers. Briefly, a 150 fs pump pulse excites bulk GaAs or InP and creates an ensemble of carriers at energies exceeding the band gap. On the hundred femtosecond timescale (shorter than our resolution), the carriers thermalize with one another. Because the carriers are at a temperature exceeding that of the lattice, they are termed “hot carriers”. The lifetime of the hot carriers is a crucial parameter governing the efficiency of an HCSC.

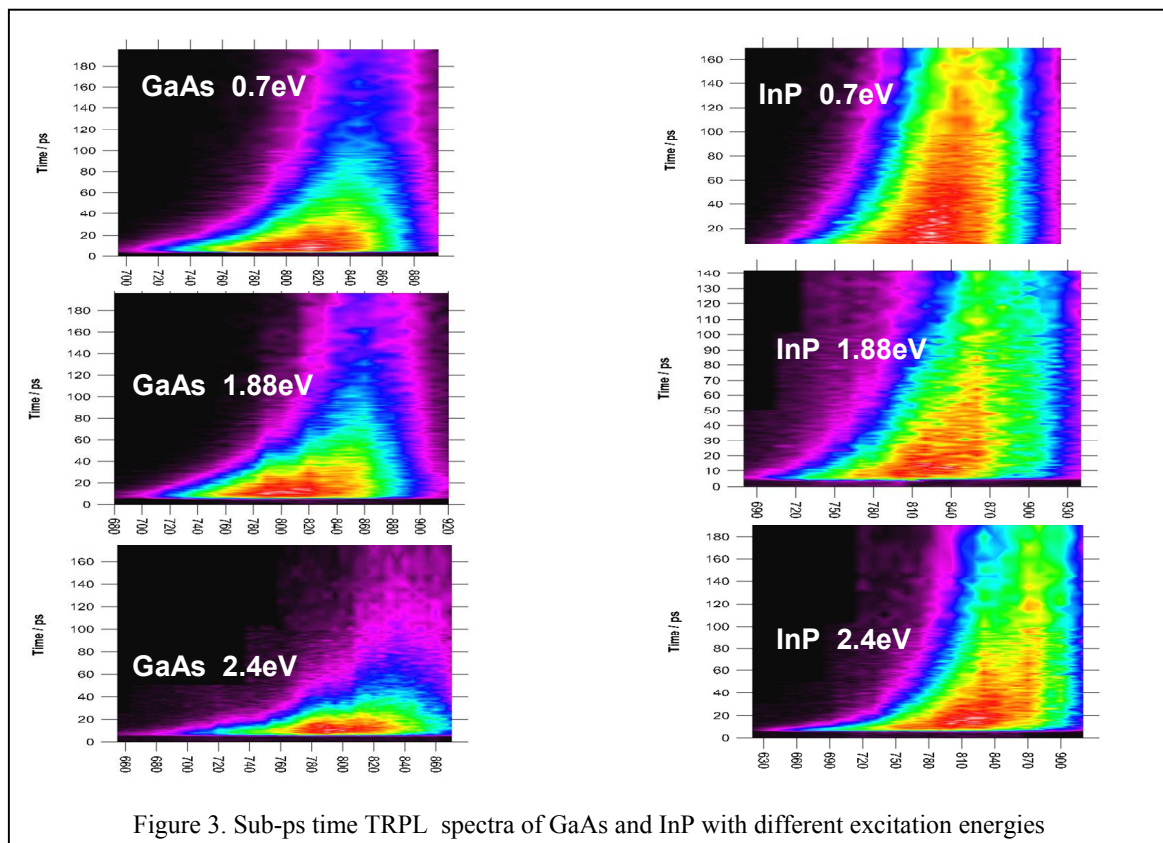
Immediately, the carriers begin to radiatively combine, emitting a spectrum which reveals the temperature of the ensemble. This photoluminescence is focused into a non-linear crystal, spatio-temporally overlapped with a 150 fs gate pulse. The upconverted luminescence is detected as a function of the pump-gate delay to reveal the time-dependence of the photoluminescence spectrum. The experimental set-up is illustrated in Figure 1.



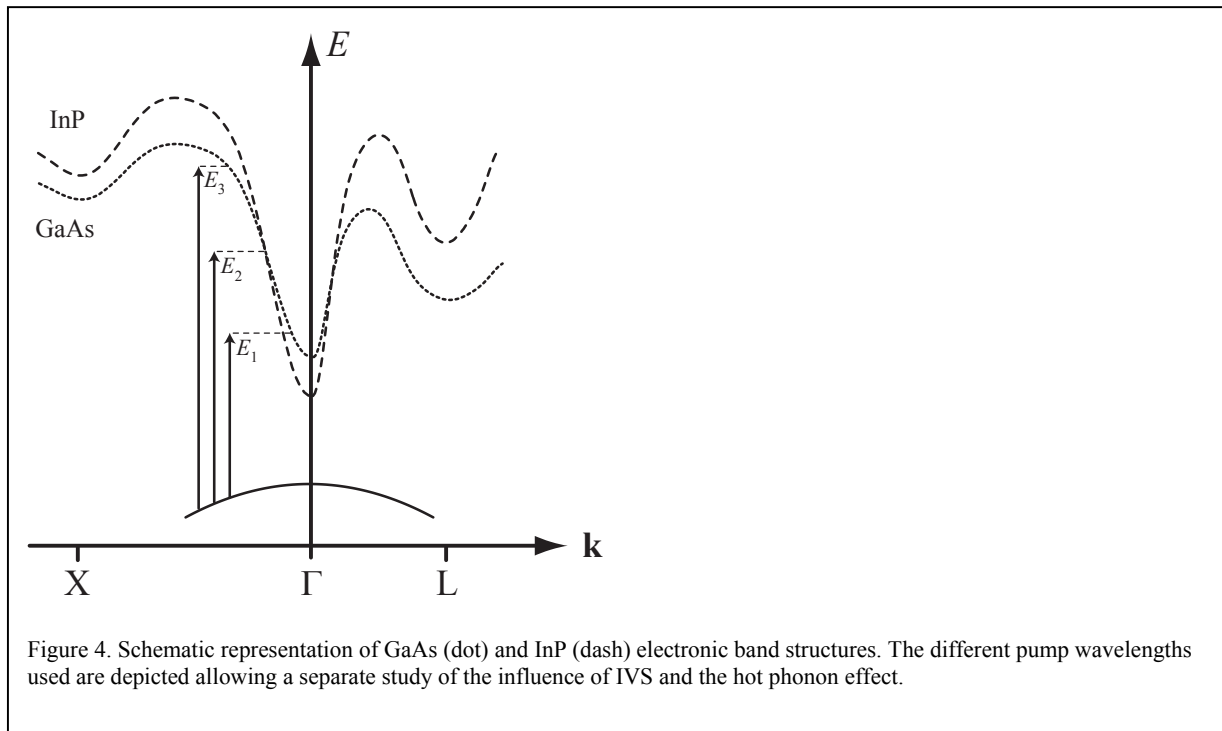
GaAs and InP were chosen as model absorbers due to their well characterized electronic structures, and differing phononic band structure. The phononic structures of these materials are quite different due to the large mass-mismatch in InP which induces a large phononic band gap. It is postulated that the phononic band gap in InP hinders carrier cooling by the Klemens mechanism. Fits to experimental data using the Keating model reveal phenomenological bending and stretching force constants for GaAs and InP. The band structures are illustrated in Figure 2.



The TRPL spectra of GaAs and InP at a range of pump pulse energies are shown in Figure 3.



Several excitation wavelengths were used to investigate the effects of satellite valley scattering on the relaxation. Figure 4 represent a schematic view of the electronic band structure, with the three pump wavelength used to investigate the influence of the satellite valleys: 1.7 eV allow the excited electron to stay in the main Γ valley, while 1.88eV and 2.4 eV allow study of the influence of the L and X valley of both materials.



In both materials, a broad photoluminescence signal which extends from the bandgap energy to values larger than the pump pulse energy has been observed during the first few picoseconds after photoexcitation. This demonstrates fast carrier- carrier interactions (< 100 fs) for each pump energy at carrier densities of $\sim 10^{19} \text{ cm}^{-3}$.

The TRPL spectra in Figure 3 may be interpreted in terms of a carrier temperature. Plots of time-resolved carrier temperature are shown in Figure 5. At all excitation energies, InP is seen to cool more slowly than GaAs, which is ascribed to the differing phononic band structures of these materials.

Summary of GaAs/InP comparison

The cooling of hot carriers has been investigated in bulk GaAs and InP using femtosecond luminescence spectroscopy with different pump energies. For a typical carrier concentration in a solar cell under highly concentrated solar irradiation, a longer hot carrier cooling transient has been observed in InP as compared to GaAs, proving the influence of the ‘hot phonon effect’ on the carrier relaxation. A clear indication of the wide phonon band gap of InP slowing carrier cooling by minimizing the decay of zone center optical phonons by the Klemens mechanism was observed, corroborated by a stronger Frohlich interaction for InP as compared to GaAs. This shows that the Frohlich interaction is not the limiting factor for electron cooling in the Γ valley.

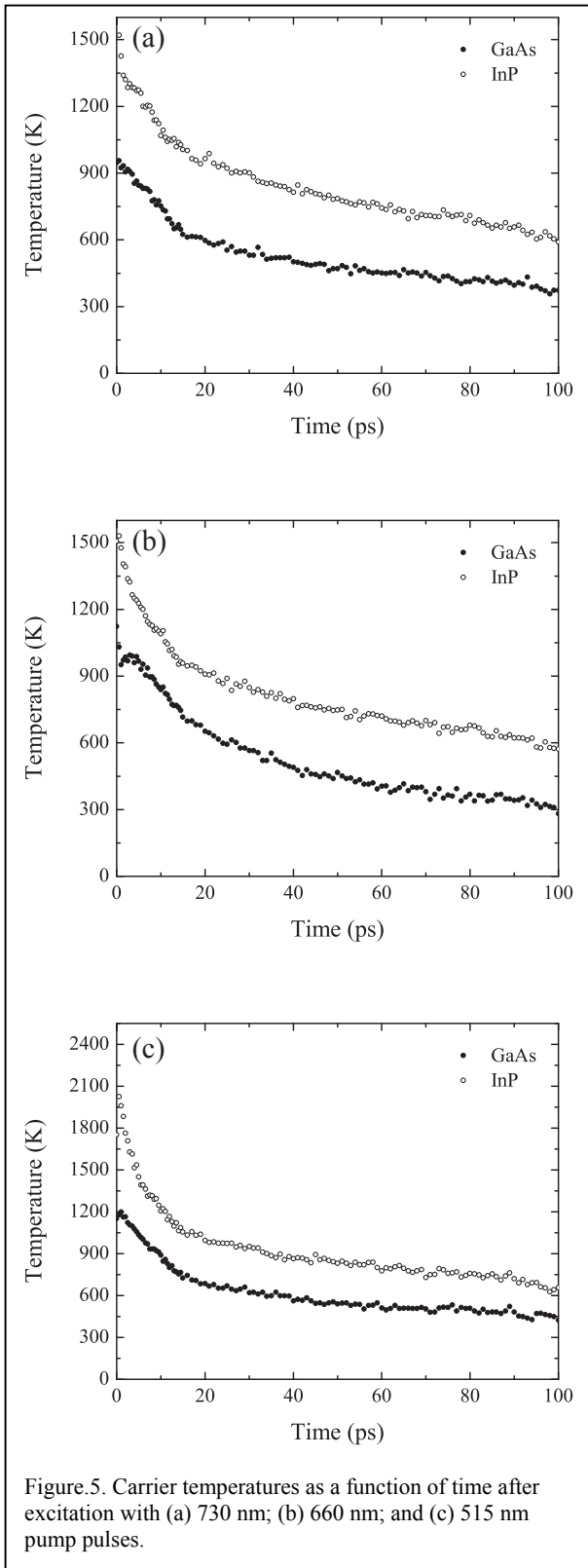


Figure.5. Carrier temperatures as a function of time after excitation with (a) 730 nm; (b) 660 nm; and (c) 515 nm pump pulses.

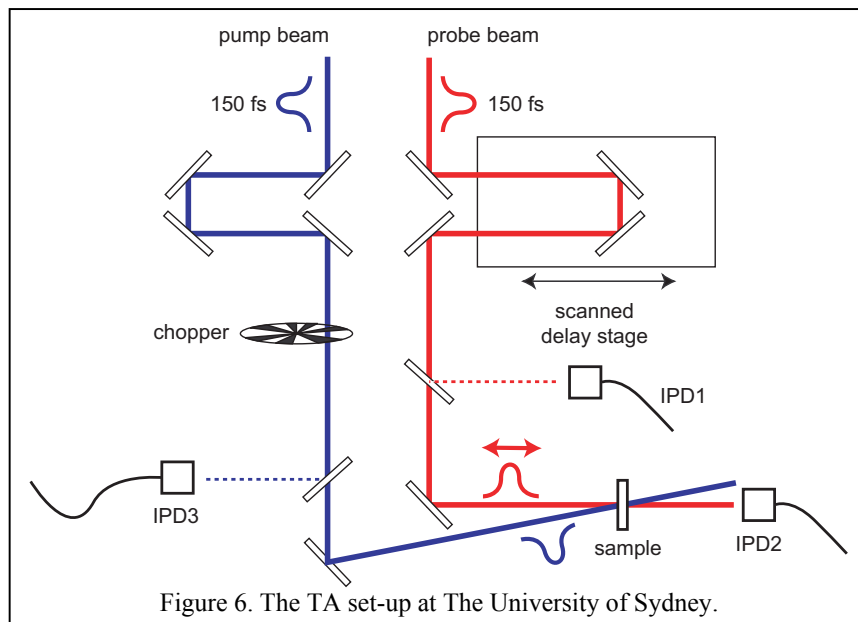
This suppression of optical phonon decay in InP is shown to depend on a concentration of emitted optical phonons of low wavevector very close to zone center. Further, that low wavevector concentration is necessary to explain the detail of the decay, because otherwise the efficient single step Klemens decay of near zone edge phonons would proceed very quickly, whereas in fact decay via this route requires a slow two step Ridley and Klemens multi-phonon decay.

Photoluminescence at wavelengths shorter than the excitation of the ground valley has also been presented, demonstrating spectral broadening occurring during initial thermalization. Intervalley scattering has also been proven to decrease the hot carrier cooling rate into the main valley. The Frohlich interaction appears to dominate intervalley scattering, resulting in slowing of carrier cooling in GaAs by storing hot electrons in side valleys due to its lower Frohlich constant as compared to InP. While the intervalley scattering time scale is too short to delay hot electron cooling efficiently, anisotropic hot carrier extraction convoluted with the momentum vectors of the side valleys may be able to be exploited.

Future similar experiments will be performed on an InN sample, since its small electronic band gap and even bigger phononic band gap makes it a serious candidate as hot carrier solar cell absorber.

Transient absorption spectroscopy

In order to characterize indirect band gap materials such as silicon, which have very weak photoluminescence, The University of Sydney group has built a transient absorption set-up to investigate the time-evolution of electronic excitation.



The set-up is illustrated in Figure 6. The pump is chopped at half the frequency of the laser system (1 kHz) to obtain a “pump on - pump off” succession for each probe pulse. The probe is detected by reflection off or transmission through the sample. A beam splitter and some home-built integrating photodiodes (IPD) allow recording of the intensity of the probe pulse before and after the sample. The optical density at the probe wavelength is obtained from the logarithm of the ratio of these two measurements. The change in optical density is obtained from the difference between successive measurements, respectively “pump on” and “pump off”, normalized by the intensity of the pump pulse.

An initial study of the carrier relaxation processes in a Si sample with implemented O^- ions has been performed and is presented in Figure 7.

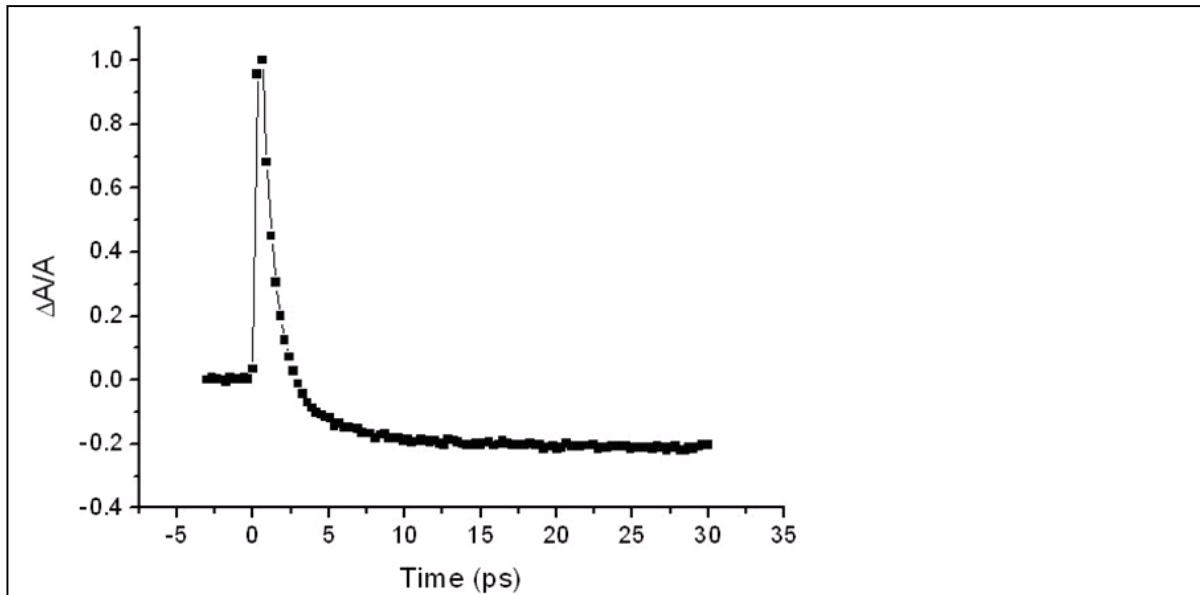


Figure 7. Degenerate transient absorption of a O- doped Si sample. The pump and the probe are 625nm (2 eV).

This result demonstrates the influence of incorporated dopant atoms which creates recombination sites, and therefore induce a faster carrier relaxation rate.

Some future TA experiments are planned on Ge nanowires and also on bulk Bi_2S_3 . The complex electronic band structure of the latter makes the TRPL results hard to analyse. Therefore, TA experiments are a tool particularly adapted to study the hot carrier lifetime in such a material.

Conclusions

The University of Sydney node of the HSCS project has completed a comparative study of GaAs and InP, and has demonstrated that the phononic structure of InP is responsible for attenuating carrier cooling in that material, as compared to the electronically similar GaAs. This represents a critical milestone in the evolution of the hot carrier solar cell. In preparation for receiving materials with indirect band gaps and low photoluminescence yields, we have prepared and tested a new ultrafast transient absorption set-up.

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**Project: “Hot Carrier Solar Cell:
Implementation of the Ultimate Photovoltaic Converter”
Institution: Instituto de Energia Solar-UPM, Madrid (IES-UPM)**

Subcontract Final Report April 2010

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Abstract

The absorber of a hot carrier solar cell (HCSC) relies on a material that absorbs photons above a given threshold (namely the semiconductor bandgap E_G) creating high energy electrons (or hot electrons). In addition, in this material, the electron relaxation within the electronic band is inhibited (by blocking the interaction of the electrons with phonons) so that the electrons remain hot until they reach the contacts. These contacts have to be special in the sense that they have to preserve the entropy of the electron flux when these finally cool down at the contacts to reach the lattice temperature. Effective research on this novel cell requires the development of suitable characterization techniques, which has been the main motivation of this subcontract. Along this period, current-voltage characterization, quantum efficiency, capacitive and noise techniques have been developed with the possibility of being performed at low temperatures. In addition, the importance of researching in novel concepts for photovoltaics characterized by a fast learning curve has been reviewed [1]. The potential of silicon, gallium arsenide and germanium solar cells when operated in hot carrier solar cell mode has also been studied [2].

Introduction

This subcontract aims to support theoretically and experimentally the research in hot carrier solar cells (HCSC). Figure 1 briefly illustrates the operation of this cell for the purpose of completeness of this report. The photon absorber of the cell relies on a material that absorbs photons above a given threshold, E_G , creating a high energy electron (or hot electron). In this absorber, the electron relaxation is inhibited (by blocking the interaction of the electrons with phonons) so that they remain hot until they reach the contacts. Ways of achieving this blockade have already been investigated by researchers in this consortium [3, 4]. These contacts have to be special [5, 6] in the sense that they have to preserve the entropy of the electron flux when these finally cool down at the contacts to reach the lattice temperature. It can be demonstrated that this can be achieved by manufacturing narrow energy bandpass contacts, possibly in the form of quantum resonant tunnel structures or intermediate band materials [7, 8]. Electrons at these contacts decrease their temperature but increase their electrochemical energy, which is seen at the external circuit as an output voltage. Further details can be found in Refs. [3, 5, 7, 9, 10].

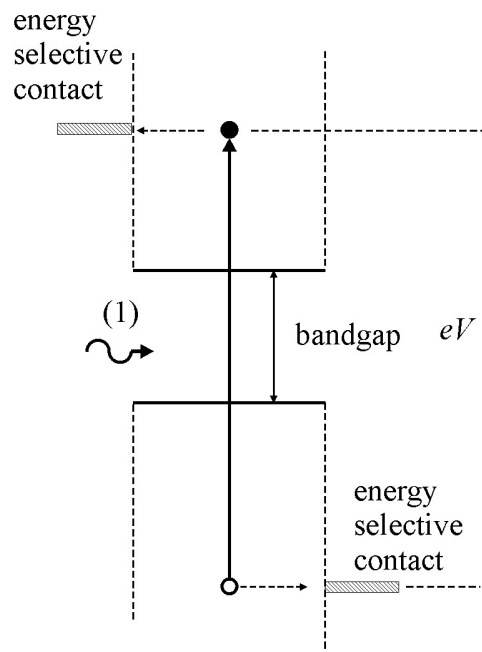


Figure 1. Schematics describing the fundamental operation of a hot carrier solar cell. Photons (1) are absorbed creating hot electrons. Electrons do not (ideally) interact with phonons so that they do not thermalize. Special energetic contacts are required so that excited carriers can be extracted with non-zero electrochemical energy (eV) when, at these contacts, they reach the lattice temperature.

From the experimental point of view, this subcontract has aimed to investigate and develop suitable characterization techniques for hot carrier solar cells. Along this line, work towards the implementation of experimental set-ups has been carried out in order to:

- a) Measure the current-voltage characteristic of hot carrier related devices at low temperature

- b) Measure the quantum efficiency in the ultraviolet region, also as a function of the temperature
- c) Formulating the theory for characterizing HCSC selective contacts through photorefectance techniques.

From the theoretical point of view, the following topics have been investigated:

- d) Connections with the intermediate band solar cell (IBSC) concept [11] have been explored. This was motivated by the expertise of the IES-UPM group in the IBSC concept and, for example, because both approaches use “quantum dots” is some or part of their implementation.
- e) The importance of the hot carrier solar cell as a novel concept has been reviewed [1].
- f) The potential of silicon, gallium arsenide and germanium solar cells as hot carrier solar cells has been investigated [2].

Background

Soon after the Project started, this contractor was aware of the fact that Sponsors were particularly interested in the Background in which the Project was being developed. The contractor realized that this background itself was worthwhile disseminating in periodic journals and publish the work *A. Luque and A. Marti, "Ultra-high efficiency solar cells: the path for mass penetration of solar electricity," Electronics Letters, vol. 44, pp. 943-945, 2008.* The interested reader is referred to it. In particular, in this work it has been defended that for achieving a photovoltaic penetration above 1/3 of the world demand of electricity in the first half of this century, it is important to develop novel concepts with a fast manufacturing learning curve. The HCSC, together with the IBSC [11], the multiple exciton generation (MEG) solar cell [12] and multijunction solar cells [13] could be one of these concepts.

Results

Our introduction enumerated several experimental and theoretical research lines. We now summarize the results obtained in each of them in the framework of our subcontract.

- a) An experimental set-up for measuring the current-voltage characteristics of hot carrier solar cell related devices has been developed and is available. This set up will allow the characterization of devices manufactured in the range of temperatures from 5 to 300 K. It has two implementations, one for measuring at high currents (from 1 μ A to 50 mA) and another for measuring at low currents (from 100 pA to 1 μ A). Characterization at low temperatures is important for HCSC since by decreasing the temperature the phonon population is decreased which allows study of the phonon blockade phenomena at the research stage. The set-up will also allow characterizing the energetic selective contacts implemented, for example, through quantum dot resonant tunneling structures [7].
- b) An experimental set-up for measuring quantum efficiency in the ultraviolet has been developed. Investigating quantum efficiency in the ultraviolet region is considered important in the context of HCSC because, once interaction with phonons is minimized, it is expected that impact ionization processes are detected as an evidence of this suppression.

The two techniques above were presented at the GCEP meeting in 2009 [14]. The poster can be downloaded from:

http://gcep.stanford.edu/pdfs/Y0NOS1cDbWD509Q0m5Reyw/Symposium2009Poster_Garcia-Linares.pdf

- c) We presented at the GCEP meeting in 2008 [15] how photoreflectance techniques could be used to characterize these contacts. The poster is available for downloading from:

http://gcep.stanford.edu/pdfs/ZRAPIUdyiefFt3uYicaVFQ/Enrique_Canovas_GCEP_Poster2008.pdf

In this work it was shown that the photoreflectance technique is a powerful spectroscopy method in order to characterize the hot carrier solar cell selective contacts in particular when implemented with quantum dots. In this case the dots should show a third derivative signature (a sort of oscillatory peak).

A copy of these posters is also annexed to this report for completeness of this report.

- d) The following similarities and differences between the intermediate band solar cell (IBSC) and the hot carrier solar cell (HCSC) were identified:
- Both cells are ultra high efficiency concepts proposed to make a better use of the solar spectrum. The IBSC, with a single intermediate band has a limiting efficiency of 63.2 % while an ideal HCSC has a limiting efficiency of 85.4 %.
 - The performance of a conventional single gap solar cell is limited by two facts. On one side, it cannot absorb photons with energy below the bandgap. On the other hand, although it can absorb photons with energy higher than the bandgap, only a fraction of the energy of these photons (approximately the energy of the semiconductor bandgap) is recovered. Then, globally considered, it could be said that the IBSC aims to use below band gap energy photons and the HCSC aims to make a better use of the high energy photons.
 - HCSCs requires special contacts. It has been proposed that intermediate band materials could take to practice these special contacts [7, 8]. This is a strong point of connection between research carried out under both approaches.
 - Quantum dots have been proposed to engineer the IBSC [16]. Under this approach, the IB arises (normally) from the confined states of the electrons in the conduction band (for example). Quantum dots have also been proposed by scientists at UNSW to engineer the selective energy contacts in the form of quantum dot resonant tunnelling structures [7].
 - When engineering the IBSC by means of quantum dots, the “phonon bottleneck” effect is desired as the means to make difficult carrier relaxation between the conduction band and the valence band [17]. Quantum dots can also provide a “phonon bottleneck” effect for the HCSC although, this time, due to a poor transmission of lattice vibrations across the interface between the QD and its matrix [3].
- e) The importance of the HCSC as a new concept was reviewed (see “background section) and produced a paper [1] with acknowledgments to the Project.
- f) The results of our study related to the potential of silicon, gallium arsenide and germanium solar cells as hot carrier solar cells has been actually published [2] in the framework of the development of this project and the reader is referred to this publication

for a complete information. It is found that Si and Ge solar cells, mainly under concentrated sun light, might lead to better efficiencies than conventional cells.

Conclusions

The World is facing the big challenge of sustainability. Perhaps, more than a billion of inhabitants will incorporate to the consumption patterns of the First World in the next decades. This will place stresses in many resources and, in particular, the need of a sustainable energy supply is not an exception. Besides, the CO₂ emission of our present energy transformation processes, based mainly in burning fossil fuels, is possibly the main cause of the Global Climatic Change. The photovoltaic conversion of the solar energy is a clean way of producing electricity with high land-occupation efficiency (e.g. as compared to biomass) that for sustainability should (and most probably will) become a major source of electricity.

As other novel high efficiency photovoltaic devices, with a limiting efficiency of 85.4 %, the HCSCs aims to introduce a radical change in present solar cell technology in order photovoltaics can generate 1/3 of the world energy demand by this century.

In this sub-contract, we have contributed to develop characterization techniques for the HCSCs and, in this way, assist in the development of its technology. The techniques aim, in particular, at the characterization at low temperatures of the current-voltage characteristics of the HCSCs and selective energetic contacts as well as to the detection of impact ionization phenomena in the quantum efficiency. We have also, with theoretical works extended our knowledge of the fundamental operation of this new type of devices.

Publications

1. A. Luque and A. Martí, "Ultra-high efficiency solar cells: the path for mass penetration of solar electricity," *Electronics Letters*, vol. 44, pp. 943-945, 2008.
2. A. Luque and A. Martí, "Electron-phonon energy transfer in hot-carrier solar cells " *Solar Energy Materials and Solar cells*, vol. 94, pp. 287-296, 2010.

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