Hot Carrier cells: an example of Third Generation Photovoltaics

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ABSTRACT

Third generation photovoltaic approaches aim to use multiple energy level approaches to circumvent the Schockley-Queisser limit but to still allow use of thin film approaches. Hence they offer significant potential to reduce cost per Watt and move solar cell technologies towards the levels necessary to achieve LCOE values that give grid parity.

The Hot Carrier solar cell is a Third Generation device that aims to tackle the carrier thermalisation loss after absorption of above band-gap photons. It is theoretically capable of extremely high efficiencies, 65% under one sun, very close to the maximum thermodynamic limit. However, it relies on slowing the rate of carrier cooling in the absorber from ps to ns. This very tough challenge can perhaps be addressed through nanostructures and modulation of phonon dispersions. The mechanisms of carrier cooling are discussed and methods to interrupt this process investigated to give a list of properties required of an absorber material. Quantum well or nano-well structures and large mass difference compounds with phonon band gaps are discussed in the context of enhancing phonon bottleneck and hence slowing carrier cooling. Materials for these structures are discussed and potential combined structures to maximize phonon bottleneck and slow carrier cooling are suggested.

Keywords: Hot Carriers, phonon bottleneck, IIIA-nitrides, Phonon decay, Carrier cooling, Group IV compounds

1. INTRODUCTION

Third generation photovoltaics aims to boost the efficiency of devices above the Schockley-Queisser limit for a single junction device. In addition it aims to use only abundant low toxicity materials and low energy intensity processes. It is thus an extension of Thin Film or second generation PV technology rather than of high quality wafer based, first generation technology. Hence as with thin films, third generation approaches aim to be compatible with large scale and large throughput production.

Such an approach is possible because of the large energy losses in a single band gap device due to non-absorption of below band-gap photons and thermalisation of electron-hole pairs generated by above band gap photons. Third Generation devices tackle these losses through the use of multiple energy levels incorporated in one device.

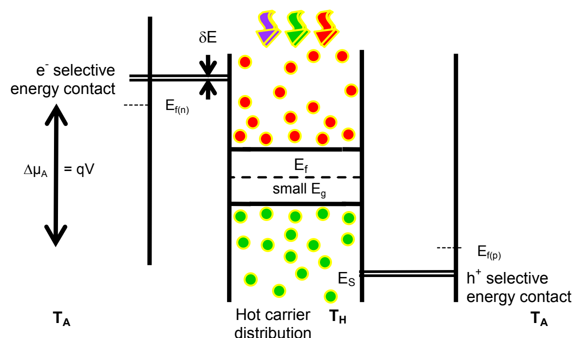


Figure 1: Band diagram of an ideal hot carrier solar cell. The absorber has a hot carrier distribution at temp T_H. Carriers cool isoentropically in the mono-energetic contacts to T_A. The difference of the Fermi levels of these two contacts is manifested as a difference in chemical potential of the carriers at each contact and hence an external voltage, V.

Physics, Simulation, and Photonic Engineering of Photovoltaic Devices,
Edited by Alexandre Freundlich, Jean-Francois F. Guillemoles, Proc. of SPIE Vol. 8256, 82560Z
© 2012 SPIE · CCC code: 0277-786X/12/$18 · doi: 10.1117/12.916520

Examples of such third generation technologies include thin film tandem cells for which quantum confinement can be used to tune band gaps; modification of the incident solar spectrum to create a narrower band width through up or down-conversion processes; and thermal approaches in which absorbed sunlight creates a thermal population of some sort, the energy from which is then extracted using secondary structures.

The Hot Carrier solar cell is an implementation of this third category. The concept is to do this by absorbing a wide range of photon energies as 'hot' electron hole-pairs and, before these "hot" carriers can thermalise with the lattice (typically a few picoseconds in bulk semiconductors), separate and collect the carriers in the external circuit. The limiting efficiency for an ideal Hot Carrier cell is 65% under 1 sun or 85% under maximal concentration [1,2].

Figure 1 is the band diagram of the Hot Carrier cell. The device has two stringent requirements: (i) Slowing of thermalization of photogenerated electrons (and holes) in the absorber material; (ii) 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.

Hot carrier cells have the advantage of consisting of only a few layers of semiconducting material and therefore can conceptually be made relatively simply compared to say a multi-junction multi-layer tandem PV cell. For similar reasons they are more likely to be amenable to thin film deposition processes with the attendant advantages of low material and energy usage.

Nonetheless the task of separating carriers in the timescales required is very difficult. Two structures are required: energy selective contacts (ESCs) to extract carriers within a narrow, well defined, range of energies, minimizing the heating of the external contacts; and an absorber in which carrier cooling is slowed to allow time for these high energy carriers to be extracted. This paper focuses on materials and structures for slowed carrier cooling in the absorber and does not discuss the selective contacts further.

2. HOT CARRIER ABSORBER

The absorber consists of a semiconductor with narrow electronic band gap. This allows absorption of a wide range of photon energies and hence gives a high current for the device. For an ideal device at 1 sun the highest efficiency of 65% is given for a band gap of 0.7eV.[2] At 1 sun the number of photons absorbed below 0.7eV from the solid angle of the sun is lower than the number emitted into the whole hemisphere of the sky, and so there is no gain for absorption of photon energies less than 0.7eV. This optimum band gap decreases as concentration ratio increases, all the way to zero at maximum concentration. With concentration the solid angle for emission decreases from the hemisphere eventually down to the solid angle of the sun. Thus it is advantageous to absorb any photons at max concentration because the number emitted will be the same at open circuit and lower under generating conditions. The reduced angle of emission increases the ideal limiting efficiency at max concentration to 85%. In both cases these are very close to the ideal limiting efficiency for an infinite tandem cell, 66% and 86.8% respectively. They are slightly lower because of the slightly lower degree of freedom in thermal populations of carriers.[2]

The absorption of the wide spectral range of solar photons results in the generation of non-equilibrium populations of electrons and holes. These hot carriers would normally thermalize to their respective band edges in a very short time, of the order of ps. The hot carrier cell absorber needs to reduce this carrier cooling rate, such that carriers can be extracted whilst still hot and hence give a higher voltage for the cell.

2.1 Hot Carrier Cooling

For the majority of semiconductor materials, the 'hot' carrier population of photogenerated electron-hole pairs, contains most of the energy of the absorbed photons in the hot electrons and most of the momentum in the hot holes, because of the small effective mass of electrons as compared to holes. Hence the following discussion primarily considers electrons. Hole dynamics are qualitatively similar, but as their energy is much lower, are less important for the overall extraction of energy from the device.

The oscillating electric field of these hot electrons interacts with the valence electron shell around atoms as the hot electron passes through the lattice, causing the valence electrons to oscillate and the atom cores to oscillate out of phase. This oscillation will occur at the particular resonant frequency of the atomic lattice, i.e. the zone centre longitudinal optical (LO) phonon energy. The hot electron loses a discrete amount of energy in this process – the LO phonon energy. It cools by emission of a series of these LO phonons. The momentum change on LO phonon emission is small because

of the steep band of hot electrons, hence it is only LO phonons at zone centre which have an appreciable energy such that optical phonon emission is the most efficient electron energy loss mechanism. In polar semiconductors electrons couple to LO phonons via the Frölich mechanism. The coulombic terms of the Frölich interaction are long range and force a further compliance of zone centre emission inversely dependent on the wavevector squared ($1/q^2$) and hence very strongly focused at zone centre. For non-polar semiconductors the interaction is via the weaker deformation potential mechanism, (which depends on transitory charge coupling as electrons orbit their ion nuclei). This does not have a long range charge coupling effect and the distribution of optical phonons depends only on 1/q and so is less focused at zone centre, although low momentum phonons are still preferred. This predominant electron cooling by emission of LO phonons results in the build-up of a non-equilibrium (hot) population of optical phonons. If this population is relatively long lived, hot phonons can transfer their energy back to electrons via further reciprocal scattering events. This will effectively slow the rate of further carrier cooling and is known as the 'phonon bottleneck' effect. Hence the critical factor in determining whether a phonon bottleneck can slow the rate of carrier cooling is the rate of decay of 'hot' optical phonons.

2.2 Phonon Decay Mechanisms

An optical phonon will decay into multiple lower energy phonons. The processes require the conservation of energy and momentum. However, additionally, the principal decay path must be into two LA phonons only, which are of equal energy and opposite momenta, via an anharmonicity in the lattice,[3] as illustrated schematically in Figure 2.

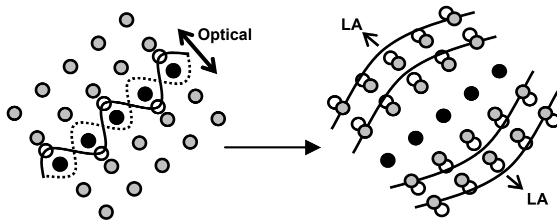


Figure 2: Schematic representation of phonon decay: Optical →LA+LA (only) via anharmonicity as suggested by Klemens. [3]

2.3 Wide Phononic Gaps in III-Vs

For some compounds in which there is a large difference in masses of the constituent elements, there exists a large gap in the phonon dispersion between acoustic and optical phonon energies, because optical phonon energies depend primarily on the high frequency vibration of the light atoms, whereas acoustic phonon energies depend on the low frequency vibration of the heavy atoms. If large enough this phonon band gap can prevent Klemens decay of optical phonons, because no allowed states at half the LO phonon energy exist. InN is an example of such a material with a very large phonon gap. The prevention of the Klemens mechanism forces optical phonon decay via the next most likely, Ridley mechanism, of emission of one TO and one low energy LA phonon. Such a mechanism only has appreciable energy loss (although still much less than Klemens decay) if there is a wide range of optical phonon energies at zone centre. This is only the case for lower symmetry structures such as hexagonal. For a high symmetry cubic structure, LO and TO modes are close to degenerate at zone centre and the Ridley mechanism is severely restricted or forbidden. [4] Unfortunately cubic InN is very difficult to fabricate precisely because of the large difference in masses which give it its interesting phononic dispersion.

2.4 Slowed carrier cooling in MQWs

Low dimensional multiple quantum well (MQW) systems have also been shown to have lower carrier cooling rates. Comparison of bulk and MQW materials has shown significantly slower carrier cooling in the latter. Figure 3 shows data for bulk GaAs as compared to MQW GaAs/AlGaAs materials as measured using time resolved transient absorption by Rosenwaks [5], recalculated to show effective carrier temperature as a function of carrier lifetime by Guillemoles [6]. It clearly shows that the carriers stay hotter for significantly longer times in the MQW samples, particularly at the higher injection levels by 1½ orders of magnitude. This is due to an enhanced 'phonon bottleneck' in the MQWs allowing the threshold intensity at which a certain ratio of LO phonon re-absorption to emission is reached which allows maintenance of a hot carrier population, to be reached at a much lower illumination level. More recent work on strain balanced

InGaAs/GaAsP MQWs by Hirst [7] has also shown carrier temperatures significantly above ambient, as measured by PL. Increase in In content to make the wells deeper and to reduce the degree of confinement is seen to increase the effective carrier temperatures.

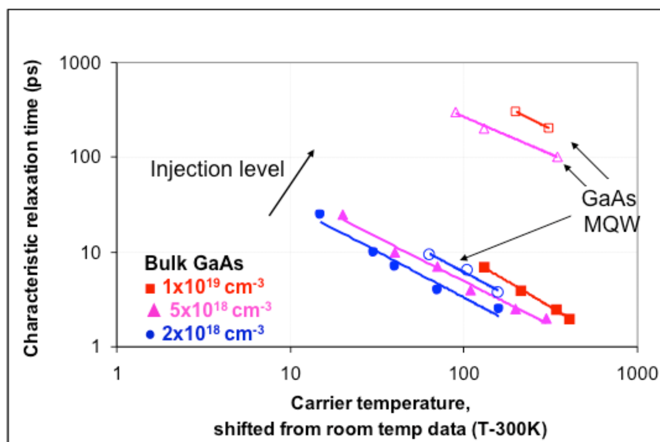


Figure 3: Effective carrier temperature as a function of carrier lifetime for bulk GaAs as compared to GaAs/AlGaAs MQWs: time resolved transient absorption data for different injection levels, from Rosenwaks [5], recalculated by Guillemoles [6].

The mechanisms for the reduced carrier cooling rate in these MQW systems are not yet clear. However there are three effects that are likely to contribute. The first is that in bulk material photogenerated hot carriers are free to diffuse deeper into the material and hence to reduce the hot carrier concentration at a give depth. This will also decrease the density of LO phonons emitted by hot carriers as they cool and make a phonon bottleneck more difficult to achieve at a given illumination intensity. Whereas in a MQW there are physical barriers to the diffusion of hot carriers generated in a well and hence a much greater local concentration of carriers and therefore also of emitted optical phonons. Thus the phonon bottleneck condition is achieved at lower intensity. [6]

The second effect is that for the materials systems which show this slowed cooling, there is very little or no overlap between the optical phonon energies of the well and barrier materials. For instance the optical phonon energy ranges for the GaAs wells and AlGaAs barriers used in [5] at 210-285meV and 280-350meV, respectively, exhibit very little overlap in energy, with zero overlap for the zone centre LO phonon energies of 285 and 350meV. [8] Consequently the predominantly zone centre LO phonons emitted by carriers cooling in the wells will be reflected from the interfaces and will remain confined in the wells, thus enhancing the phonon bottleneck at a given illumination intensity. The latter hypothesis is supported by the evidence of significantly improved thermoelectric figures of merit (ZT) for superlattices of materials with very small barrier height but significant phonon energy mismatch. Such ‘phonon glass / electron crystal’ materials allow reasonable electronic transport but significant phonon scattering. Examples include metal nitride nano-well materials with a small conduction band offset in Zebarjadi et al. [9] and Si/Ge nano-well materials in Lee et al. [10].

Thirdly, if there is a coherent spacing between the nano-wells (as there is for these MQW or superlattice systems) a coherent Bragg reflection of phonon modes can be established which blocks certain phonon energies perpendicular to the wells, opening up one dimensional phononic band gaps (analogous to photonic band gaps in modulated refractive index structures and discussed further below in section 4.5). [11] For specific ranges of nano-well and barrier thickness these forbidden energies can be at just those energies required for phonon decay. This coherent Bragg reflection should have an even stronger effect than the incoherent scattering of the second mechanism at preventing emission of phonons and phonon decay in the direction perpendicular to the nano-wells. Whilst this does depend on a specific and coherent nano-well array it does not require the nano-wells to be thin enough to be electronically quantized as such phonon dispersion folding occurs for any size of superstructure as long as it is coherent, (anechoic chambers and bridge bearings are macroscopic examples).

It is likely that all three of these effects will reduce carrier cooling rates. None depend on electronic quantum confinement and hence should be exhibited in wells that are not thin enough to be quantized but are still quite thin

(perhaps termed 'nano-wells'). In fact it may well be that the effects are enhanced in such nano-wells as compared to full QWs due to the former's greater density of states and in particular their greater ratio of density of electronic to phonon states which will enhance the phonon bottleneck for emitted phonons. The fact that the deeper and hence less confined wells in [7] show higher carrier temperatures is tentative evidence to support the hypothesis that nano-wells without quantum confinement are all that are required. Whist several other effects might well be present in these MQW systems, further work on variation of nano-well and barrier width and comparison between material systems, should be able to distinguish which of these reduced carrier diffusion, phonon confinement or phonon folding mechanisms might be dominant.

3. HOT CARRIER CELL ABSORBER REQUISITE PROPERTIES

The discussion in the previous section allows us to suggest a series of properties that would be required of a good hot carrier absorber material. These are listed below in approximate order of priority.

1. Small electronic band gap E_g – to allow a wide range of photon absorption. This should preferably be less than 1eV. For 1 sun concentration the optimum is 0.7eV - as a band gap below this energy gives no advantage in the balance between absorption and emission. As the concentration ratio increases this optimum E_g decreases to zero at maximum concentration. [2]
2. Strong scattering of phonon modes from interfaces in the material. In nano-well, nanowire or nano-dot materials this means a large mismatch between optical phonon energies between nanostructure and matrix.
3. Large phononic band gap ($E_{O(min)}$ - E_{LA}) - in order to suppress Klemens' decay of optical phonons this must be at least as large as the maximum acoustic phonon energy. Hence a large mass difference (or large force constant difference) between constituent elements is required. [4]
4. Narrow optical phonon energy dispersion (E_{LO} - $E_{O(min)}$) – in order to minimise the loss of energy to TO phonons by Ridley decay. This requires a high symmetry atomic or nano-structure, preferably cubic with degenerate optical phonon energies at zone centre.
5. A continuous (or nearly continuous) DOS for energies above E_g . This is necessary to allow absorption of the full range of solar photons above the band gap energy.
6. A small LO optical phonon energy (E_{LO}). This reduces the amount of energy lost per LO phonon emission, requiring a greater number to be emitted for a given energy loss. [12] However, it is difficult to have both a small E_{LO} and the large phononic gap required in 1. Furthermore a small Frölich constant is needed for small E_{LO} , which implies less polar materials. In turn this means a phonon population will be generated which is less focussed at zone centre. The greater number of phonon states populated would thus make the back reaction of phonon absorption and achievement of a phonon bottleneck more difficult. This condition requires further investigation, but does still argue for a small E_{LO}.
7. An absolute small maximum acoustic phonon energy (E_{LA}). This maximises the phononic gap if E_{LO} is also small. A small E_{LA} requires a large mass for the heavy atom and/or small force constant for its bonds.
8. Very fast (sub ps) renormalisation rates in the material, i.e. good e-e and h-h scattering (e=electron, h=hole). This requires a reasonable DOS at all energies above E_g, or at least only very narrow gaps between energy levels, $\leq kT_{300K}$. (Also required for criterion 5.) This in turn requires a good overlap of wavefunction for carriers through the material, i.e. poor electronic confinement or a reasonable conductor. This condition is met in all inorganic semiconductors quite easily, with e-e scattering rates of less than 100fs. It may not be met in organic semiconductors or in nanostructures with large barrier heights.
9. Good carrier transport in order to allow transport of hot carriers to the contacts. This is similar to 7, except that it only need be in the direction of the contacts, probably the z growth direction. A reasonably low resistance is probably good.
10. Earth abundant and readily available and processable constituent elements and processes and non or low toxicity of the elements, compounds and processes.

NB. E_{LO} , $E_{O(min)}$ & E_{LA} are the maximum optical, minimum optical and maximum acoustic phonon energies respectively.

InN has most of these properties, and is therefore a good model material for a hot carrier cell absorber. Calculations of the potential efficiency of a HC cell with InN absorber give values of around 43% for an assumed thermalisation time (τ_{th}) of 100ps, and to be very dependent on τ_{th}.[13] Transient absorption spectroscopy has shown carrier cooling rates in

InN of about 20ps, an order of magnitude greater than most III-Vs [14]. This efficiency would be significantly enhanced by even longer τ_{th} .

InP also has several of the required properties of an absorber. Although its E_g at 1.54eV is larger than would be ideal, it can be made as good quality single crystal material. Time resolved photoluminescence has demonstrated slowed carrier cooling compared to GaAs, attributed to suppression of the Klemens mechanism. [15] This ties in well with the long LO phonon lifetime of 200 ps calculated for InP by other authors. [16] However In has a low abundance in the earth's crust, about the same as Ag, at about $5x10^{-8}$ that of Si. [17] Hence, these In compounds do not meet criterion 10 for an absorber material and are unsuitable for large scale implementation. Hence analogues of InN that retain the large phononic and small electronic band gaps, but which use more abundant elements, are of interest as potential appropriate absorber materials.

4. ANALOGUE ABSORBER MATERIALS

As InN is a model material, but has the problems of abundance and bad material quality, another approach is to use analogues of InN to attempt to emulate its near ideal properties. These analogues can be II-IV-nitride compounds, large mass anion III-Vs, group IIIA or IVA nitrides, group IV compounds/alloys or nanostructures.

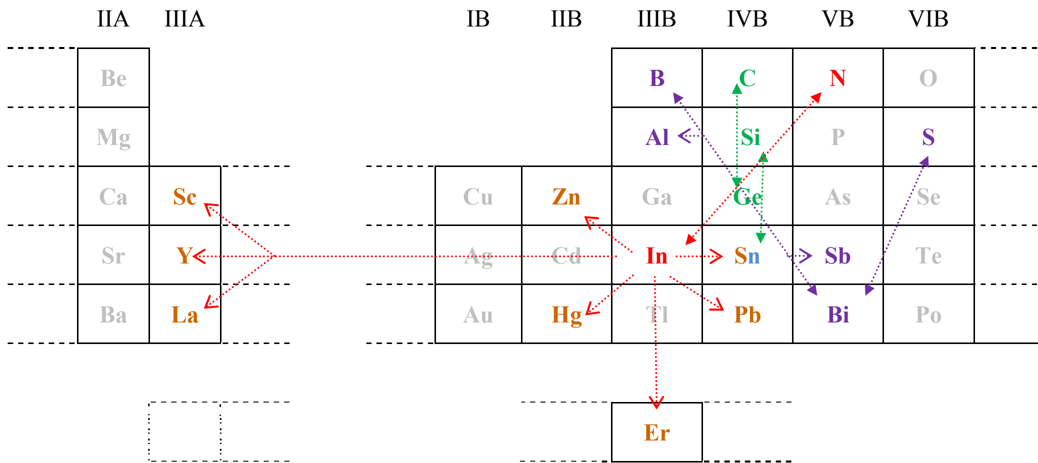


Figure 4: Section of the periodic table. Potential analogues of InN are indicated which have the saem properties of large mass difference between constituent elements.

4.1 II-IV-Vs: ZnSnN; ZnPbN; HgSnN; HgPbN of InN

Replacement of In on the III sub-lattice with II-IV compounds is analogous and is now quite widely being investigated in the Cu_2ZnSnS_4 analogue to $CuInS_2$.[18] ZnGeN can be fabricated [19] and is most directly analogous with Si and GaAs. However, its E_g is large at 1.9eV. It also has a small calculated phononic band gap.[20] ZnSnN has a smaller electronic gap (1 eV) and larger calculated phononic gap,[20] as shown in Figure 5. It is however difficult to fabricate, and also its phononic gap is not as large as the acoustic phonon energy making it difficult to block Klemens decay completely. HgSnN or HgPbN should both have smaller E_g and larger phononic gaps. These materials have not yet been fabricated [21] and have the problem that Hg is around the same abundance as In.[17]

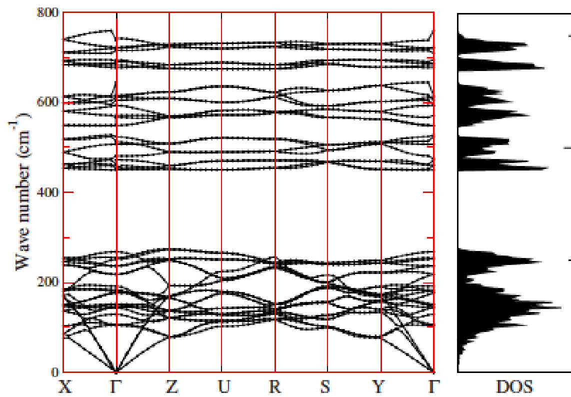


Figure 5: The phonon dispersion for $ZnSnN_2$ (redrawn from Paudel et al [20]). Showing a significant gap, although not as large as the acoustic energy and thus too small to completely block Klemens decay.

4.2 Large mass anion:

Bi and Sb are heavy elements and hence their compounds with B and Al have large predicted phononic gaps. BiB has the largest phononic gap but AlBi, Bi_2S_5, Bi_2O_3 (bismuthine) are also attractive.[12]

AlSb has a calculated and measured phononic gap the same size as its acoustic phonon energy,[22] with an E_g of 1.5eV. It also has a very high calculated phonon lifetime probably because of its large phononic gap.[23] This, and the fact that it is of reasonably widespread use and can be made of reasonable quality, makes AlSb marginal in suitability as an absorber material and similar to InP. BSb has electronic band gap of 0.59eV and a large elemental mass difference giving it a very large phonon band gap more than twice the acoustic phonon energy, as calculated for a 1D force constant model [28], sufficient to block Klemens' decay completely if the material quality is high enough. It also can be fabricated by co-evaporation and has a measured E_g of 0.59eV.[24] This band gap is indirect and hence not ideal, but the absorption coefficient remains high even out to 1700nm.

However, Bi is a rare element with an earth abundance similar to In and Sb is only about 5x more abundant.[17] Nonetheless their large phonon gaps make particularly BsB and AlSb interesting to pursue further for proof of concept.

4.3 Group IIIA and IVA nitrides:

LaN and YN both have large predicted phononic gaps, both bigger than the acoustic phonon energy, whilst that for ScN is rather smaller. These elements have good to reasonable abundance, Sc, La and Y being around the same abundance as Pb and slightly higher than Sn at about 10^{-5} that of Si.[17] Thus these materials look attractive as absorbers. They can be sputtered as thin films and formed into quantum well nanostructures for use in thermoelectrics. This could be important for the combination of nano-well structures with phononic band gap materials.

The Lanthanides can also form III-Vs. ErN can be grown by MBE and ErAs can be fabricated, particularly as ordered nanocrystals in a GaAs matrix. Er has about a tenth the abundance of Pb and so is not very rare.[17] The phononic band gaps of the Er compounds are predicted to be large, because of the heavy Er cation, but its discrete energy levels make it not useful as an absorber, although the combination of properties in a nanostructure could be advantageous.

Related to the IIIA compounds are the group IVAs – Hf, Zr and Ta nitrides and oxides. Hf and Ta are about the same abundance as Er, with Zr 100x more abundant and a widely used metal. Again because of their large mass cations these oxides and nitrides all have large phonon gaps. That for Hf_3N_4 is shown in Figure 6, showing a large gap (although still too small to block Klemens decay completely).[25] But also a narrow optical phonon dispersion – important to block secondary Ridley decay (criterion 4 in section 3). They can also readily be fabricated and have existing applications.

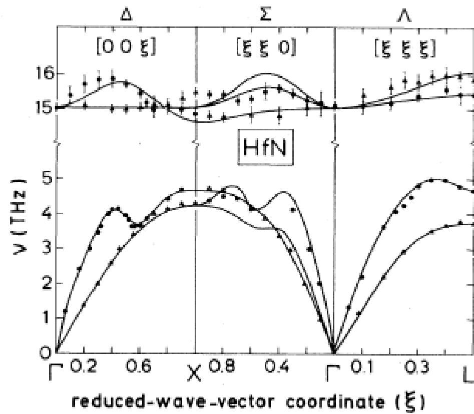


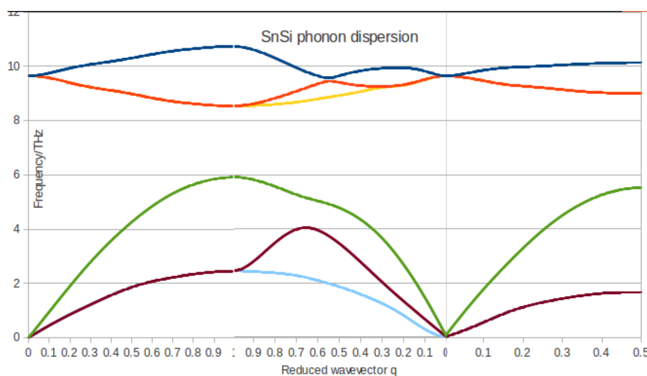
Figure 6: The phonon dispersion for Hf_3N_4 (redrawn from Norlund-Christensen et al [25]). Again a reasonable gap, although still too small to block Klemens' decay.

4.4 Group IV alloy/compounds:

All of the combinations Si/Sn, Ge/C or Sn/C look attractive with large gaps predicted in 1D models. [26] However being all group IVs they only form weak largely covalent bonds. Unfortunately SiC, whether 3C, 4H or 6H, has too narrow a phononic gap. Nonetheless GeC does form a compound and is of significant interest. [27]

The IV-VI PbS also has a large mass ratio and is interesting, but its measured phonon dispersion shows an additional TO branch which fills the phonon gap,[22] thus likely making it unsuitable for an absorber, although phonon folding in a nanostructure (see below) could reflect these modes and make PbS nano-crystals suitable.

The calculated phonon dispersions for GeC, SnSi and SnC are shown in Figure 7. [28] These are calculated using an adiabatic bond charge model. Force constants are input from bulk elemental values. There is not currently any allowance for Coulomb interactions and hence the splitting one would expect from polar effects in the optical phonons at zone centre is not present. However as these are largely covalent compounds this is not expected to be a big effect. Nonetheless it will be rectified in future work. The large gaps in the large mass ratios of GeC and SnC are larger than the respective acoustic phonon energies and hence should completely block Klemens' decay. The narrow optical phonon dispersions (albeit slightly under-represented because of the lack of polarity mentioned above) should further limit secondary Ridley decay.



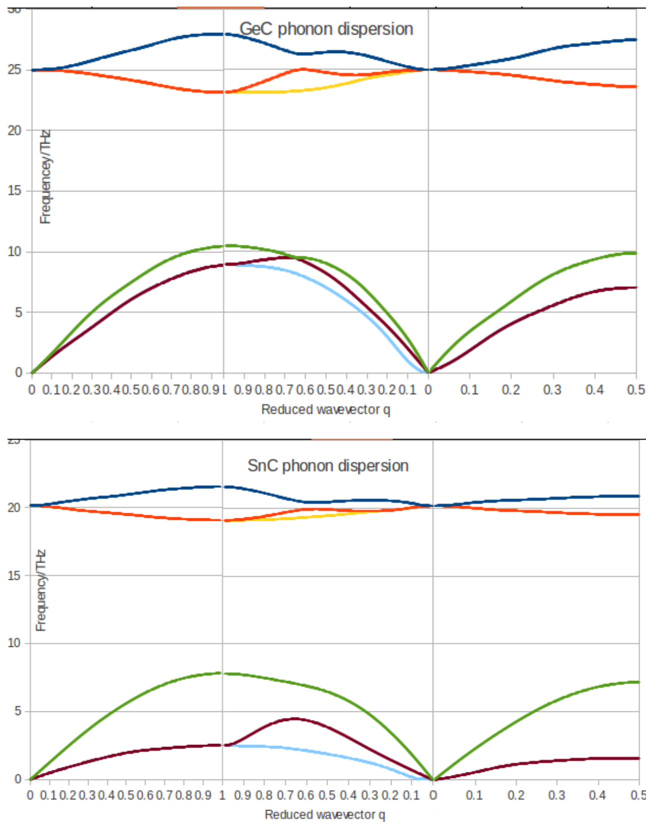


Figure 7: Adiabatic bond charge calculations of phonon dispersions for group IV compounds. Phonon gaps increase as the mass ratio increases with those for GeC and SnC large enough to block Klemens' decay.

There are also several other inherent advantages of group IV compounds/ alloys all of which are associated with the four valence electrons of the group IVs which result in predominantly covalent bonding:

a) The elements form completely covalently bonded crystals primarily in a diamond structure (tetragonal is also possible as in βSn). However for group IV compounds the decreasing electronegativity down the group results in partially ionic bonding. This is not strong in SiC and whilst it tends to give co-ordination numbers of 4, can nonetheless result in several allotropes of decreasing symmetry: 4C, 4H, 6H. However, as the difference in period increases for the as yet theoretical group IV compounds, so too does the difference in electronegativity and hence also the bond ionicity and the degree of order. For a hot carrier absorber this is ideal because it is just such a large difference in the period that is needed to give the large mass difference and hence large phononic gaps. All of GeC, SnSi, SnC (and the Pb compounds) have computed phononic gaps large enough to block Klemens decay, and should also tend to form ordered diamond structure compounds.

b) Because of their covalent bonding, the group IV elements have relatively small electronic band gaps as compared to their more ionic III-V and much more ionic II-VI analogues in the same period: e.g. Sn 0.15eV, InSb 0.4eV, CdTe 1.5eV. In fact to achieve approximately the same electronic band gap one must go down one period down from group IV to III-V and down another period from III-V to II-VI: e.g. Si 1.1eV, GaAs 1.45eV, CdTe 1.5eV. This means that for group IV compounds there is greater scope for large mass difference compounds whilst still maintaining small electronic band gaps. A small band gap of course being important for broadband absorption in an absorber – criterion 1 in the desirable properties for hot carrier absorbers listed above in section 3.

c) The smaller E_g would tend to be for the larger mass compounds of Pb or Sn, which, to give large mass difference, would be compounded with Si or Ge. This trend towards the lower periods of group IV also means that the maximum optical phonon and maximum acoustic phonon energies will be smaller for a given mass ratio - the desirable properties 4 and 5 in section 3.

d) Furthermore, unlike most groups, the group IV elements remain abundant for the higher mass number elements – desirable criterion 10 in section 3. (Ge is the rarest at 10^{-6} x Si, but is still moderately abundant.) [17] The low toxicity requirement of criterion 10 is also satisfied by the group IVs.

These features and their large phononic band gaps make the Group IV alloys/compounds highly attractive as hot carrier absorber materials.

4.5 Nanostructure analogues:

III-V compounds or indeed most of the cubic and hexagonal compounds can be considered as very fine nanostructures consisting of 'quantum dots' of only one atom (say In) in a matrix (say N) with only one atom separating each 'QD' and arranged in two interpenetrating 'fcc' lattices. Modelling of the 1D phonon dispersion in this way gives a close agreement with the phonon dispersion for zinc-blende InN extracted from real measured data for wurtzite material. [4]

Similar 'phonon band gaps' should appear in good quality nanostructure superlattices, through coherent Bragg reflection of modes such that gaps in the superlattice dispersion open up. [4] There is a close analogy with *photonic* structures in which modulation of the *refractive index* in a periodic system opens up gaps of disallowed *photon* energies. Here modulation of the ease with which phonons are transmitted (the *acoustic impedance*) opens up gaps of disallowed *phonon* energies.

3D force constant modelling, using the reasonable assumption of simple harmonic motion of atoms in a matrix around their rest or lowest energy position, reveals such phononic gaps. [29] The model calculates longitudinal and transverse modes and can be used to calculate dispersions in a variety of symmetry directions and for different combinations of QD sub-lattice structure and super-lattice structure.

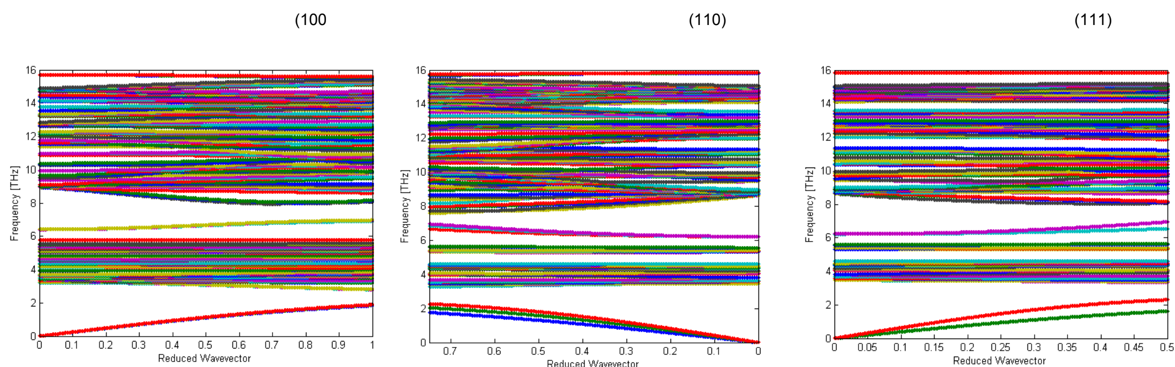


Figure 8: Phonon dispersion in 3 main symmetry directions for 1nm QDs embedded in matrix with mass difference ration of 1:7. [29]

The phononic gaps shown in the fcc nanostructure of Figure 8 are small. Nonetheless in combination with large mass difference materials, quite possibly also with anisotropic properties, structures should be possible which block Klemens decay.

5. COMBINED PHONONIC/MNW ABSORBER DESIGN

The multiple nano-well structures have demonstrated reduced carrier cooling by enhancing the phonon bottleneck, probably at a stage prior to optical phonon decay. Large phononic band gap materials would seem to have strong potential to block Klemens' decay of optical phonons. A structure combining both structures should give even greater reduction in carrier cooling rates as the mechanisms should not interfere directly with each other and hence their effects should be additive. A combined absorber for a hot carrier cell should look similar to Figure 9.

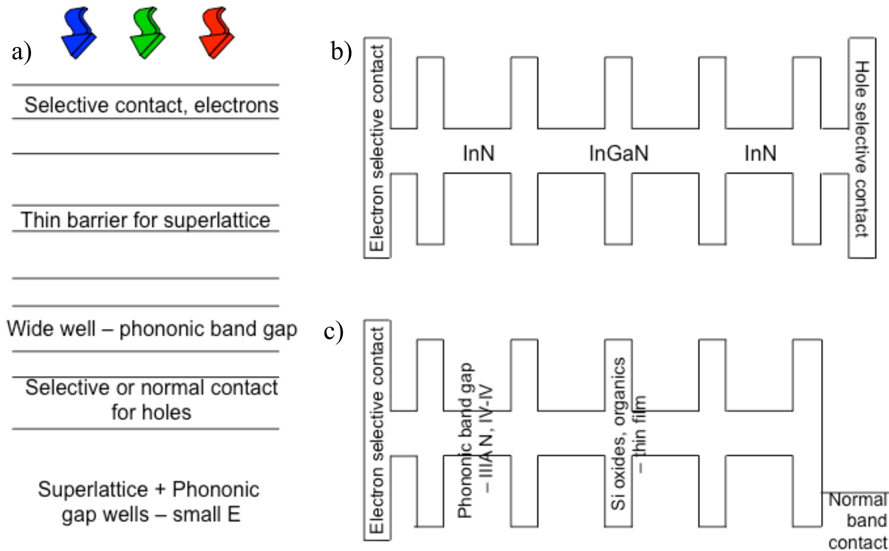


Figure 9: Hot Carrier cell design combining Multiple Nano-Well with phononic band gap materials: (a) schematic and (b) band structure for InN/InGaN epitaxial multiple nanowell with phononic band nano-wells; (c) band structure with nano-wels of analogues of InN with large phononic band gap with thin film barriers.

This has narrow nano-wells of phononic band gap material, not thin enough to give quantum confinement, separated by thin barriers. The barriers would either have an electronic band offset to block hot carrier diffusion or an optical phonon energy offset with the nano-wells and probably a coherent nano-well structure, or all three, depending which of the multiple nano-well (MNW) mechanisms, discussed in section 2.4, is dominant. This will enhance the phonon bottleneck either by preventing hot carrier diffusion, by reflecting and confining optical phonons or by blocking certain folded phonon modes, respectively, or all three. The phononic nano-wells themselves will further enhance phonon bottleneck by preventing Klemens' decay of optical to acoustic phonons. This should maximise the phonon bottleneck and minimise carrier cooling for a given illumination intensity. A lattice matched pair of large phononic band gap nano-well and barrier materials (InN/InGaN) is suggested in Figure 9 (b), whereas in (c) a wider range of possible InN analogue phononic band gap materials could be used in a thin film structure with thin probably oxide barriers. The thin barriers (a few nm) should facilitate tunnelling between wells and hence transport of the carriers to the contacts.

6. CONCLUSION

Materials exhibiting mechanisms that can slow carrier cooling are challenging. Hot carriers cool by emission of optical phonons which subsequently decay into acoustic phonons, i.e. heat in the lattice. The lifetime of these optical phonons can be extended by establishing a phonon bottleneck whereby phonons scatter their energy back to hot carriers, keeping them hot long enough to be extracted.

The properties required of a hot carrier absorber are identified. The most important of these are one or more mechanisms to maximise the phonon bottleneck and hence prevent further cooling and a small electronic band gap with continuous DOS above the band gap so as to allow absorption of a wide range of solar photons.

Multiple nano-well materials exhibit slower carrier cooling, probably through localisation of carriers and emitted phonons leading to a phonon bottleneck. Compounds with a large mass difference between constituent atoms exhibit large phonon band gaps which should block the decay of optical phonons and also promote phonon bottleneck.

The indium compounds, particularly InN and InP, are found to have these required properties, but are difficult to fabricate and contain the very rare In. Analogues of InN with abundant elements, but also with narrow E_g include II-IV-VI compounds such as $ZnSnN_2$, IIIA nitrides such as LaN and YN which should have large phonon gaps, and IVA nitrides such as Zr_3N_4 and Hf_3N_4 which are readily available. Bi and Sb compounds should also have large phonon gaps but are not abundant. Group IV compounds have large calculated gaps and small E_gs, as well as several other advantages.

A combined multiple nano-well (MNW) structure utilising wells with large phononic band gaps is suggested as a structure which can maximise the phonon bottleneck caused by all these mechanisms to slow carrier cooling, and hence give hot carrier lifetimes long enough to be extracted to the external circuit at high voltage.

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