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Hot carrier solar cell absorber prerequisites and candidate material systems

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ABSTRACT

The hot carrier cell aims to extract the electrical energy from photo-generated carriers before they thermalise to the band edges. Hence it can potentially achieve a high current and a high voltage and hence very high efficiencies up to 66% for unconcentrated sunlight and 85% under maximum concentration. To slow the rate of carrier thermalisation is very challenging, but modification of the phonon energies and the use of nanostructures are both promising ways to achieve some of the required slowing of carrier cooling. Required absorber material properties have been identified, relating to phononic and electronic properties as well as to practical considerations. Candidate materials evaluated in terms of these prerequisites include large mass anion, transition metal nitrides, Group IV compounds and nanostructures. Promising candidate materials include InN, HfN and SnSi. Initial measurements indicate slowed carrier cooling in III–Vs with large phonon band gaps in multiple quantum wells. It is expected that soon proof of concept of hot carrier devices will pave the way for their development to fully functioning high efficiency solar cells.

1. Introduction

The hot carrier solar cell is a solar energy converter that utilises the excess thermal energy of photo-excited carriers to generate DC electric power. Unlike conventional solar cells, the hot carrier cell maintains the hot carrier population by inhibiting ultrafast cooling processes. The excess carrier energies above the respective band edges thus contribute to a higher conversion efficiency than that of a conventional cell, which is restricted by the detailed-balance (Shockley–Queisser) limit for a single junction cell to 33%. The hot carrier cell has a limiting efficiency of 66% for unconcentrated sunlight rising to 85% at maximum concentration (46,200 suns), assuming ideal operation [1]. The model of Ross and Nozik [2] assumes a conservation of the numbers of electrons and holes in the material, whilst that of Würfel [3] allows for fast Auger processes so that particle number is not conserved although energy is still with the assumption that there is no energy loss to phonons. This avoids the problem that particle number conservation can lead to the unphysical prediction of temperatures higher than that of the sun's surface [4].

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 to be 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 that 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 minimised [5,6]. In principle these can be iso-entropic [3], but in practice would involve some entropy increase probably with a minimum determined by 3 kT. Fig. 1 is a schematic band diagram of a hot carrier cell illustrating these requirements [7].

The optimum electronic band gap at maximum concentration is zero [1], but for anything less than maximum a non-zero band gap reduces emitted photons to a greater extent than it limits absorption at long wavelengths. The optimum at 1 sun is about 0.7 eV [1] although limiting efficiency falls off fairly slowly for higher values.

2. Slowing of carrier cooling

The energy dissipation of photo-generated carriers is a multi-step process. The inelastic scattering of carriers takes place in the

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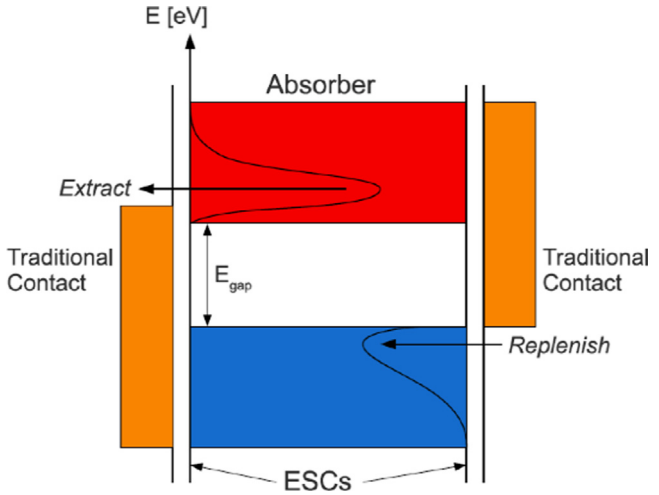

Fig. 1. Band diagram of the hot carrier cell carriers remain at elevated temperature in the absorber and are extracted through narrow band energy selective contacts at high voltage [6]. The device has the four following stringent requirements: (a) to absorb a wide range of photon energies; (b) to slow the rate of photogenerated carrier cooling in the absorber; (c) to extract these "hot carriers" over a narrow range of energies, such that excess carrier energy is not lost to the cold contacts; and (d) to allow efficient renormalisation of carrier energy in the absorber via scattering of energy between electrons and separately between holes to achieve and maintain elevated thermal populations.

first few 10 s of femtoseconds after their generation. This process normalises momentum and leads to a distribution of electron energies which can be described by a Boltzman distribution and a single high temperature, i.e. a thermal population, and a separate (generally lower temperature) thermal population of holes. [8] Then on a longer timescale (typically several picoseconds) carriers scatter inelastically with phonons, predominantly emitting optical phonons in a series of discrete hops in each of which energy and momentum are conserved in the combination of electron and emitted phonon. For polar semiconductors the major scattering process is with longitudinal optical phonon modes. These optical phonons emitted by the excited carriers then interact with other phonons due to the anharmonic nature of the crystal potential. Through various routes these over-populated optical phonons decay into low-energy acoustic phonons. The final step is the transport of these acoustic phonons, which macroscopically manifest as the heat dissipation to the environment. The carrier cooling process can be slowed by blocking any of these three processes. Other processes, such as direct emission of acoustic phonons and diffusion of optical phonons, are not significant for polar semiconductors.

The cooling of carriers by emission of optical phonons leads to the build-up of 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 [9]. The build up of emitted optical phonons is strongly peaked at zone centre both for compound semiconductors due to the Fröhlich interaction (strong quadratic dependence on momentum) and for elemental semiconductors due to the deformation potential interaction (less strong linear dependence on momentum). The strong coupling of the Fröhlich 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 as is the case for high energy carriers well above the band minima [10]. This zone centre optical phonon population determines that the dominant optical phonon decay mechanism is this pure Klemens decay.

2.1. Wide phononic gaps in III–Vs and analogues

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 high-lying optical phonon energies and low-lying acoustic phonon energies. If large enough this "phononic band gap" can prevent Klemens decay of optical phonons, because no allowed states at half the LO phonon energy exist. Indium nitride (InN) is an example of such a material with a very large phonon gap.

This 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 with a very flat dispersion and the Ridley mechanism is severely restricted or forbidden. Unfortunately cubic InN is very difficult to fabricate precisely because of the large difference in masses that give it its interesting phononic dispersion. In addition to the small dispersion in cubic structures dispersionless structures can be achieved by engineering nanostructures.

Slowed cooling has been observed in some III–V compounds in which there is a large difference in atomic mass. Slower carrier cooling has been observed in InP as compared to the small mass ratio GaAs [11]. Fitting of effective carrier temperature to time resolved photoluminescence data indicates approximately 300 °C higher carrier temperatures for InP at all times up 200 ps as compared to GaAs. This supports the theory of suppression of Klemens' decay in the wide phononic gap InP as compared to the zero phonon band gap of GaAs [11]. Slowed carrier cooling has also been shown in InN with its even larger phonon band gap [12], as plotted below in Fig. 3. Analogues of InN not only with abundant elements, but also with narrow E_g are discussed below in Section 4.1.

3. Hot carrier cell absorber requisite properties

The above discussion allows us to estimate the major properties required for a good hot carrier absorber material. These are listed below in approximate order of priority, although their relative importance may well change in light of future research:

1. Large phononic band gap ($E_{LO}(_{min})-E_{LA}$) – to suppress Klemens' decay, requires large mass difference between elements.
2. Narrow optical phonon energy dispersion ($E_{LO}-E_{LO}(_{min})$) – to minimise the loss by Ridley decay, requires a high symmetry.
3. Small $E_g < 1$ eV – to allow a broad range of strong photon absorption.
4. A small LO optical phonon energy (E_{LO}) – to reduce the amount of energy lost per LO phonon emission but not so small as to increase the occupancy of LO modes unduly. $E_{LO}\exp(-E_{LO}/kT)$.
5. A small maximum acoustic phonon energy ($E_{LA}(_{max})$). This maximises ($E_{LO}(_{min})-E_{LA}$) and is important if E_{LO} is also small.
6. Good renormalisation rates in the material, i.e. fast *e–e* and *h–h* scattering. This condition is met in most semiconductors quite easily, with *e–e* scattering rates of less than 100 fs. But it may be compromised in nanostructures.
7. Good carrier transport in order to allow transport of hot carriers to the contacts.
8. Ability to make good quality, ordered, low defect material.
9. Earth abundant and readily processable materials.
10. No, or low, toxicity of elements, compounds and processes.

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