IBPOWER: INTERMEDIATE BAND MATERIALS AND SOLAR CELLS FOR PHOTOVOLTAICS WITH HIGH EFFICIENCY AND REDUCED COST

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ABSTRACT

IBPOWER is a Project awarded under the 7th European Framework Programme that aims to advance research on intermediate band solar cells (IBSCs). These are solar cells conceived to absorb below bandgap energy photons by means of an electronic energy band that is located within the semiconductor bandgap, whilst producing photocurrent with output voltage still limited by the total semiconductor bandgap. IBPOWER employs two basic strategies for implementing the IBSC concept. The first is based on the use of quantum dots, the IB arising from the confined energy levels of the electrons in the dots. Quantum dots have led to devices that demonstrate the physical operation principles of the IB concept and have allowed identification of the problems to be solved to achieve actual high efficiencies. The second approach is based on the creation of bulk intermediate band materials by the insertion of an appropriate impurity into a bulk semiconductor. Under this approach it is expected that, when inserted at high densities, these impurities will find it difficult to capture electrons by producing a breathing mode and will cease behaving as non-radiative recombination centres. Towards this end the following systems are being investigated: a) Mn: $In_{1-x}Ga_xN$; b) transition metals in GaAs and c) thin films.

INTRODUCTION

Fig. 1 shows the basic structure of an intermediate band solar cell (IBSC). It consists of an intermediate band (IB) material sandwiched between two conventional semiconductors of *p* and *n* type. The intermediate band material is characterised by the existence of a collection of energy levels (the IB) within the semiconductor bandgap, (E_G) splitting this in two (E_L and E_H). The IB allows absorption of below bandgap energy photons through optical transitions that pump electrons from the VB to the IB and from the IB to the CB. The absorption of two below bandgap energy photons produces one electron-hole pair increasing the cell photocurrent when compared with the same cell without an IB. It is worth mentioning that the absorption of these photons need not be a three particle collision process since the electron being pumped from the IB to the CB need not be that which is pumped from the VB to the IB.

Carrier relaxation within each band is assumed to be much faster than carrier recombination between bands so that each band has associated its own quasi-Fermi level to describe the occupation statistics of the electrons within it. Due to the emitters, which isolate the IB from the external electrodes, the output voltage of the cell is given by the split of electron and hole quasi-Fermi levels in the conduction and valence band respectively and is therefore still limited by the total bandgap of the cell.

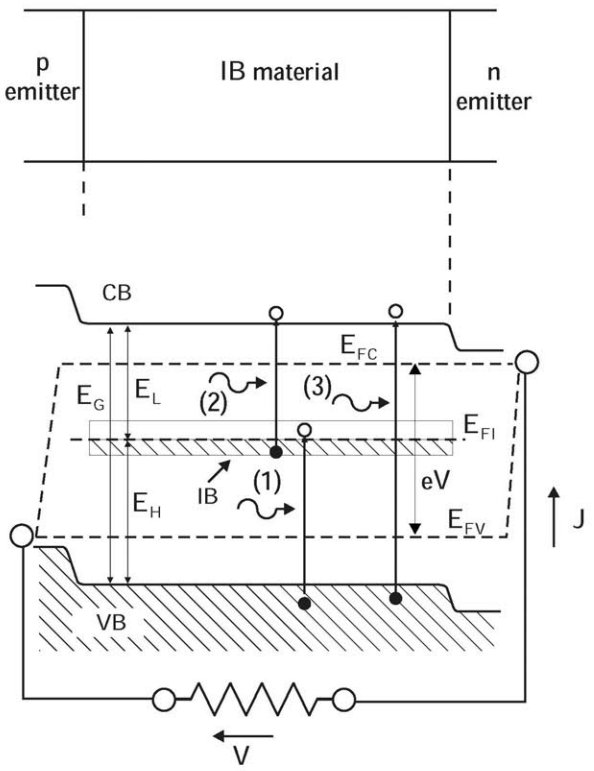

Fig. 1. Layout of an intermediate band solar cell illustrating its basic operation.

Using energy levels inside the bandgap to increase the efficiency of solar cells was first analysed by Wolf [1] in 1960 (before Shockley and Queisser published [2] their detailed balance analysis of the efficiency of solar cells). After his analysis, the possibility of using these levels to increase the efficiency of solar cells was rejected. It is perhaps worthwhile pointing out that the possibility of using tandem solar cells (proposed by Jackson [3]) was also rejected at that time since the use of tunnel junctions for connecting the cells was not yet realised. Luque and Marti revisited the topic in 1997 [4] using detailed balance arguments to analyse the efficiency. They concluded that the efficiency limit of the concept was 63.2 % at maximum light concentration. This maximum was achieved for E_G=1.95 eV, E_L=0.71 eV and E_H=1.24 eV. They also pointed out the need for an intermediate "band" rather than a collection of intermediate "levels" to suppress the non-radiative recombination generally introduced by energy levels located inside the gap, and the need for the emitters to isolate the IB so as to split the quasi-Fermi levels and hence produce an output voltage [5] not limited by E_L nor E_H. To achieve the maximum efficiency, the absorption coefficient associated to each of the transitions should not overlap (Fig. 2a) or, if they do, the absorption coefficient associated to the transition across the total bandgap (E_G) must be dominant over that of the transition from the VB to the IB (E_H) which in turn must be dominant over that of the transition from the IB to the CB (E_L) (Fig. 2b). In order to enable the IB to accommodate electrons from the VB as well as supply electrons to the CB, the IB should be partially filled with electrons.

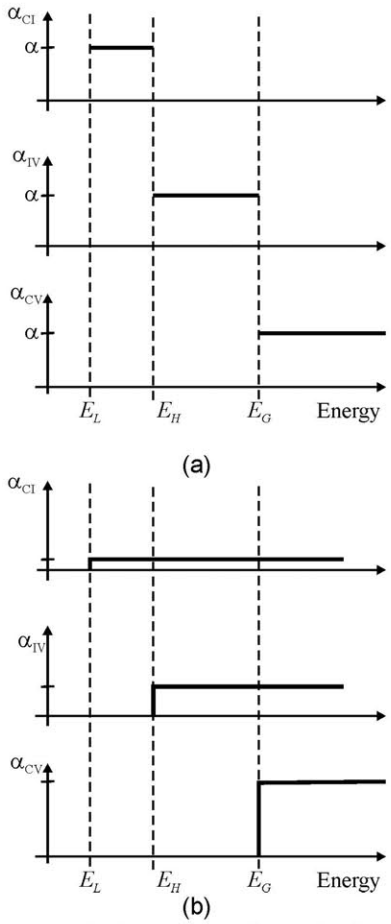

Fig. 2. Two equivalent ideal conditions for the absorption coefficients in order for the IBSC to achieve maximum efficiency. In (a) the absorption coefficients do not overlap. In (b) they overlap but the absorption coefficient associated to E_G is greater than that associated to E_H which is greater than that associated to E_L. In the plot, α_{XY} is the absorption coefficient associated to transitions from band X to band Y [6].

INTERMEDIATE BAND SYSTEMS

For implementing the IBSC we require an intermediate band material. At the beginning of the research on IBSCs, it was uncertain that such materials could exist. Today, many have been theoretically predicted using ab-initio calculations (such as those based on the insertion of Ti and Cr in GaAs, GaP and $CuGaS_2$ [7, 8], Ti and V in $MgIn_2S_4$ and In_2S_3 [9]) and some have been synthesised (V in In_2S_3 [10], diluted II-VI oxides [11] and GaNAsP alloys [12]). However, no report of an actual cell has been published yet based on these materials to our knowledge.

The first IB material with which a solar cell has been manufactured [13] was proposed in this same Conference

on the basis of quantum dots [14]. When using quantum dots, the IB arises typically from the confined energy states of the electrons in the conduction band. It is also conceivable creating an IB from the confinement of the holes in the valence band although perhaps this will be more difficult given the higher effective mass of the holes with respect to the electrons, which reduces the energy spacing of the confined energy levels in the valence band. Research on quantum dot intermediate band solar cells (QD-IBSCs) is one axis of IBPOWER. These cells will be the topic of discussion of the following section.

Another body of theory that can lead to intermediate band materials has arisen from a better understanding of deep centres in semiconductors. Deep centres introduce energy levels inside the semiconductor bandgap but, as mentioned before, this alone is not sufficient since these levels still have to form a band. In the IBSC context, the meaning of "forming a band" is that non-radiative recombination to and from these centres to the conduction and valence band is minimized. A band is formed when the wavefunction of the electrons associated to the deep levels becomes delocalized. As explained in Ref. [15], delocalization can be achieved for example by increasing the impurity density beyond Mott's transition (typically 6×10^{19} cm^{-3}). When delocalization is achieved, the wavefunction, and therefore the charge, of an electron being captured by the deep centre will extend over many atoms preventing a strong perturbation (breathing mode) of the impurity or defect responsible for the deep centre. Since the creation of the breathing mode is the mechanism that allows that the large energy that separates the deep centre from the CB and VB be interchanged in a single step, its inhibition is believed to minimize non-radiative recombination. Experimental evidence of this has been obtained recently: silicon samples doped with titanium at concentrations in the range of 10^{20} at/cm^3 have shown an increase of their average lifetime with increased Ti implanted doses [16]. We think, in fact, that it is because electrons are delocalized in both bands in conventional semiconductors that radiative recombination can become dominant. In order to achieve the partial filling of the emerging IB with electrons, co-doping might be necessary when using this approach. Along this line of research IBPOWER will investigate the insertion of Mn in InGaN and the insertion of transition metals in thin films and GaAs as explained in the next sections.

It must be said, however, that the use of the term "band" in the case of QDs, could be misleading since it might suggest that dots should be coupled. As was pointed out before, the term "band" was introduced originally for implying that just "a collection of energy levels" within the semiconductor bandgap was not sufficient to produce an intermediate "band" solar cell. The wavefunction of an electron in a confined state of a quantum dot is already quite delocalised (the envelope wavefunction extends along many atoms) and, in fact, laser devices exploiting the radiative recombination between the confined state and the valence band, for example, have become commercially available. We think this is another indication that producing extended states is fundamental to the inhibition of non-radiative recombination. On the other hand, this does not mean that having the dots coupled cannot provide additional advantages to the QD-IBSC. For example, although carrier transport through the IB is not required in the ideal IBSC model (since the IB is isolated from the external contacts) in practice it can assist the internal redistribution of carriers in the device when one of the absorption coefficients involving the IB is higher than the other [17]. Coupling can also increase the overlap between the wavefunctions of the electrons in the IB and the CB and therefore taylor the absorption of photons related to these two bands [18]. Finally, coupling also decreases the volume in which electron-hole pairs can recombine from the CB to the VB but cannot be generated with assistance of the IB [19]. Fitting to photoreflectance measurements has been proposed as one of the means for determining whether this coupling exists [20]. Along this same line of argument, impurities in which the wavefunction of the captured electron is in itself extended (such as Cr in ZnS) could also serve the purpose of manufacturing an IBSC without actually forming a "band".[21].

QUANTUM DOT INTERMEDIATE BAND SOLAR CELLS

Quantum dots, as opposed to other low dimensional structures such as quantum wells or wires, were proposed to implement the IBSC since QDs are the low dimensional structures with the highest potential for creating a true zero density of states between the IB and the CB. As of today, QDs have been the only IB system with which it has been possible to implement complete solar cells [13, 22-25]. These experimental devices have allowed successful testing of some of the operation principles of the IBSC, such as the two-photon absorption process [26] and the existence of three distinct quasi-Fermi levels [27]. They also have allowed identification of the practical problems to be solved in order to manufacture actual high efficiency devices. These problems, in general, are:

a) Although, to our knowledge, no systematic study of the absorption coefficient associated to the quantum dots currently exists for the whole spectrum, it seems that this absorption coefficient follows the scheme illustrated in Fig. 2b (perhaps it is even possible that the absorption related to the IB to CB transition do not overlap with the VB to IB transition). Although this scheme is one that can lead to maximum efficiency it also makes high absorption of photons related to the IB to CB transition difficult. In this framework, IBPOWER is studying the use of light management structures such as the use of diffraction structures [28] and surface plasmon polaritons [29] to increase this absorption. Nevertheless it must also be remembered that in the case that the operation of the cell is based on an impact ionization process, the absorption of

photons creating transitions from the IB to the CB would not be required [30].

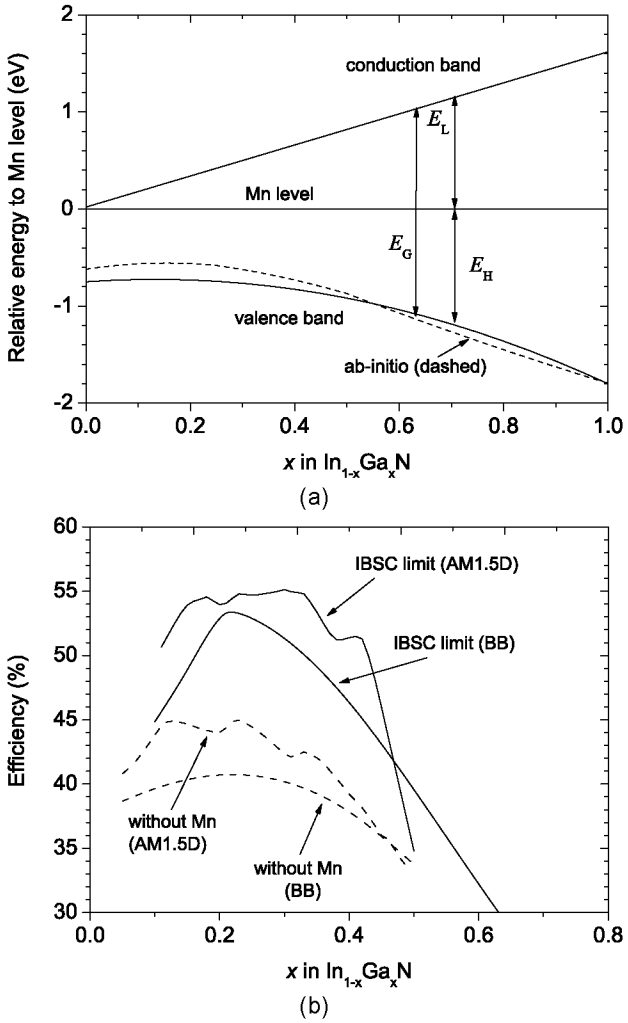

Fig. 3. (a) Expected position of the energy level introduced by Mn into $In_{1-x}Ga_xN$ as a function of x. (b) comparison of the limiting efficiency of the system with and withouth Mn (no IB) for two different spectrums: BB (black body at 6000 K, 1595.88Wm-2) and AM1.5 D (ASTM G173-03, 900Wm-2). In both cases, maximum concentration (46050 suns) have been assumed (after [31], reproduced with permission).

b) From an experimental point of view, most of the solar cells that have been manufactured are based, with some variations, on InAs/GaAs QDs. This system is not the optimum to provide maximum efficiency since, for example, the total bandgap is limited to the GaAs gap (1.42 eV) while the optimum should approach 1.94 eV. This is not of principle concern as this system can also lead to high efficiencies [32]. The major problem arises from implementing a practical system in which the bandgap E_L can be in the range of 0.4 eV or higher. This requires systems with large conduction band offsets and small dots [33].

Mn: $In_{1-x}Ga_xN$

The approach described above of implementing the IBSC concept through deep centres requires impurities that, besides introducing energy levels inside the semiconductor bandgap, have high solubility in the semiconductor. We expect Mn inserted into $In_{1-x}Ga_xN$ to fulfil these conditions. It is therefore one of the systems investigated in IBPOWER. In this respect, Fig. 3 shows the predicted energy band gap diagram as well as the limiting efficiency as a function of the composition x [31, 34]. The optimum composition is predicted to be in the range x=0.2-0.3.

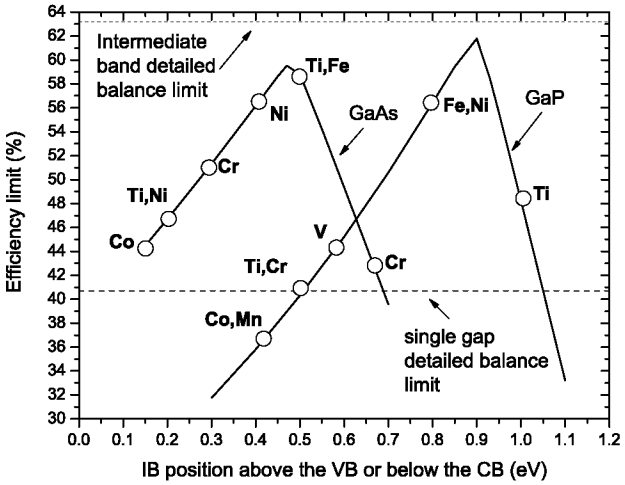

Fig. 4. Efficiency limit (black body spectrum at 6000 K and maximum light concentration) of and IBSC based on GaAs and GaP. Hollow dots indicate the values that would correspond to an intermediate band arising from the deep centres introduced by the indicated transition elements. The energy levels have been taken from [35] .

XMetal: GaAs IBSC

In order to investigate the implementation of the IBSC concept following the deep centre approach, the insertion of different transition metals at high densities into GaAs will also be investigated. One of the reasons for choosing this system is similar to that which led to the choice of InAs/GaAs for implementing the IBSC under the quantum dot approach: the energy levels introduced by transition metals into GaAs are relatively well known (see for example the review by Hennel [35]) and GaAs is a material of mature technology that allows manufacturing good reference solar cells to compare the results with. In this framework it is expected that research can be more easily focused on aspects related to the IBSC theory by taking advantage of pre-existing knowledge related to deep centres and GaAs material parameters and processing. On the other hand, this does not imply that the

potential efficiency improvements are negligible, as illustrated by means of Fig. 4. In this figure we plot the efficiency limit of an IBSC solar cell based on GaAs and GaP (a more optimum material from the point of view of the total bandgap) as a function of the transition element introduced assuming that an intermediate band could be formed from the energy level these elements introduce as deep centres.

THIN FILM-IBSC

The examples illustrated above are based on the use of III-V semiconductors. This implies that, in order to make their use cost competitive, they will have to be used under concentrated sunlight.

The implementation of the IBSC concept on thin films has the goal of finding a low cost cell option for the intermediate band solar cell concept. It is worth remembering that the thin film approach does not (usually) contemplate the use of concentrated sunlight. Therefore, the results reviewed here are intended for operation at one sun. In this sense, it must be noted that introducing an intermediate band material on a host of bandgap lower than 1.2 eV does not provide any advantage for operation at one sun because the current gain does not compensate the voltage loss due to the extra recombination (even if this is radiative) introduced by the intermediate band [36].

Following the deep level approach, we have made a first approximation to the position introduced by different transition elements in $CuGaS_2$. The results of these calculations are plotted in Fig. 5 [37]. They suggest that titanium and iron are the best candidates in order to implement an IBSC in $CuGaS_2$.

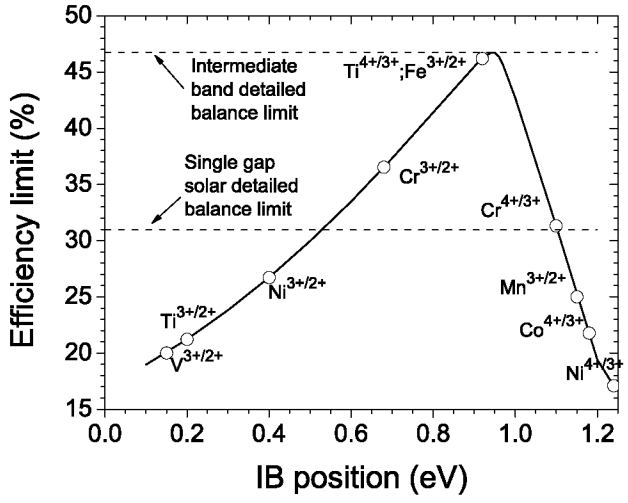

Fig. 5. Limiting efficiency at one sun (black body 6000K) of a solar cell with the bandgap of $CuGaS_2$. The impurities that could lead to the intermediate band located at the indicated position are shown as hollow dots (adapted from [37], reproduced with permission).

SUMMARY

IBPOWER is a Project funded by the European Commission researching different approaches for developing the IBSC concept. These approaches can be grouped into two categories: quantum dots and bulk IBSCs. The first will investigate ways to increase the absorption of light provided by the dots as well as how to enlarge the bandgap that separates the IB from the CB. The starting point for the second approach is the study of impurities that introduce deep centres into the semiconductor and that can be incorporated into it at high concentrations. The material systems investigated under the second approach are, in general, transition metals inserted into III-V compounds and thin films, for example Mn: $In_{1-x}Ga_xAs$, Ti:GaAs and Ti:$CuGaS_2$.

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