A REVIEW OF THE NOVEL CONCEPTS IN PHOTOVOLTAICS THROUGH THEIR EXPERIMENTAL ACHIEVEMENTS

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ABSTRACT: The intermediate band solar cell (IBSC), the multiple exciton generation solar cell (MEGSC) and the hot carrier solar cell (HCSC) are three novel concepts in photovoltaics which aim to achieve high efficiency devices. In this paper we assess to what extent their physical principles of operation have been experimentally verified. It is found that there is experimental evidence supporting the underlying theory for all three.

Keywords: High-Efficiency, Intermediate Band, Hot Carrier, Multiple Exciton Generation

1 INTRODUCTION

Shockley and Queisser's (SQ) detailed balance calculation set a limit of 40.7% for the energy conversion of a solar cell [1]. In their work, several assumptions were made, two of which need to be reminded here: 1) the absorber material of the solar cell is a conventional single gap semiconductor; hence, photons with less energy than the bandgap of this material are not absorbed; and 2) the excess of energy, with respect to the bandgap, of the absorbed photons is lost via intraband thermalization of the photogenerated carriers. The removal of any of this constraints leads to an increase in the efficiency limit. For example, multijunction solar cells [2] can exceed the Shockely and Queisser limit (SQL) since the absorber is no longer a single gap semiconductor, but a series of semiconductors with different bandgaps.

In the last decades several photovoltaic device concepts have been proposed for achieving high conversion efficiencies. Among them, those which have not been yet commercialized are often referred to as novel concepts or next generation solar cells. In this paper we focus on three: intermediate band solar cell, multiple exciton generation solar cell and hot carrier solar cell. We examine to what extent their physical principles of operation have been experimentally demonstrated. For this, after briefly reviewing the underlying framework of theory, some expected features of the electro-optical behavior are derived for each approach and related reported results are presented as proof of experimental verification. Distinction is made between the experimental results obtained at material level and those obtained at device level.

2 INTERMEDIATE BAND SOLAR CELL

The intermediate band solar cell (IBSC) [21] consists of an intermediate band (IB) material sandwiched between two p-doped and n-doped single gap semiconductors, as sketched in Figure 1. An IB material is characterized by the presence of an electronic band within its bandgap, E_G, which is isolated from the conduction band (CB) and the valence band (VB). As illustrated in Figure 1, the presence of the IB originates two additional energies gaps: one between the VB and the IB, and the other between the IB and the CB, allowing the absorption of sub-bandgap photons. This absorption enables transitions of electrons from the VB to the IB or from the IB to the CB, indicated with arrows in the figure. Allowing the absorption of sub-bandgap photons the IBSC breaks with assumption number one of the SQ model.

Additional electron-hole pairs are created in a two-step process via the absorption of sub-bandgap photons. Therefore, extra photocurrent can be obtained, compared to a single gap solar cell made of a material with the same bandgap. However a cell made of an IB material only cannot surpass the SQL. The two single gap emitters are necessary for enabling the extraction of the photo-generated current at a high output voltage, limited only by E_G [21, 22]. These two phenomena, the production of extra two-photon photocurrent and the preservation of the output voltage, are the two operation principles of the IBSC, and lead to a limiting efficiency of 63.7%.

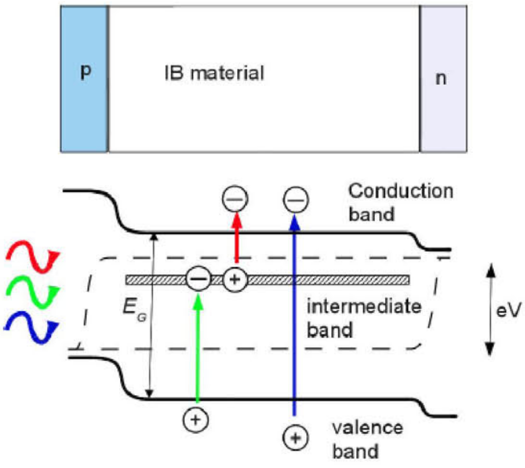

Figure 1: Illustration of: (top) the structure of an intermediate band solar cell, and (bottom) the simplified band diagram of an intermediate band solar cell under operation. The three arrows indicate the three possible interband transitions caused by absorption of solar photons. The dashed lines are the quasi-Fermi levels for electrons and holes, and their energy difference is equal to the output voltage, V, multiplied by the electron charge, e.

An IB material should, as stated before, absorb sub-bandgap photons. More precisely, the absorption coefficient of such a material should present three singularities at the energy threshold of the three existing gaps. Absorption measurements are therefore very useful for evaluating the potential of a candidate IB material for being used as absorber in an IBSC. Sub-bandgap absorption has been reported for candidate QD- materials such as InAs/GaAs [23, 24] and InAs/AlGaAs [25]; in the highly mismatched alloy (HMA) [26] ZnTe doped with O [27, 28]; and in bulk materials doped with deep level impurities (BMDLIs) [29] such as $CuGaS_2$ doped with Sn/Fe [30, 31] and $CuInS_2$ doped with Sn[30].

At device level the production of two-photon photocurrent can be verified [32] by measuring an increase in the generated photocurrent when adding illumination with photons with energy greater than the smallest of the three gaps (IB-CB in Figure 1) but smaller than the other two, to previous illumination with energy smaller than E_G but higher than the two other gaps. Two-photon photocurrent was first verified in IBSC devices made of InAs/GaAs QDs [33], but only at low temperature. Later it was also measured at room temperature [34], but differences in the employed experimental set-ups do not allow for direct comparison of the results. It has also been verified in GaAs/AlGaAs QDs [35] and in the HMAs GaAs doped with N [36] and ZnTe doped with O [37]. Voltage preservation can be experimentally verified by measuring a photogenerated voltage higher than any of the two gaps related to the IB (divided by the electron charge). This would imply that the output voltage of the cell is limited solely by E_G, as predicted by the theory. Voltage preservation has been measured in IBSC prototypes made of InAs/GaAs QDs [38] and in BMDLI GaAs doped with Ti [39].

The most employed technology so far to implement IBSC prototypes are QDs [40], and, in particular, the InAs/GaAs system. In addition to serve as demonstration of the two operation principles of the IBSC, other IB-related behavior was experimentally verified. For example, the production of sub-band photocurrent [41-43] and the radiative interaction between the IB and the valence and conduction bands [44, 45]. In recent years, other IB-related experimental results have been also obtained for some HMA-based and BMDLI-based IBSCs.

3 MULTIPLE EXCITON GENERATION SOLAR CELL

The multiple exciton generation (MEG) solar cell (MEGSC) was proposed by Nozik in 2002 [3] as a particular case of carrier multiplication solar cell [4] in which the absorber material is not a bulk semiconductor but semiconductor quantum dots (QDs). Both devices are intended to generate multiple electron-hole pairs via the absorption of a photon with energy at least twice the semiconductor bandgap. As illustrated in Figure 2 for the MEG case, the absorption of a photon with energy twice as high as the absorption threshold of the QD, E_g, generates an excited exciton in the QD (process labeled 1 in the figure). Then, the excited electron hands over part of its kinetic energy to an electron in the valence band of the QD, creating a bi-exciton. Analogously, the absorption of a photon with energy three times E_g could give raise to three excitons, and so on. The carrier multiplication process breaks with assumption number two of the SQ model, and now the resulting limiting efficiency results in85.4% [5].

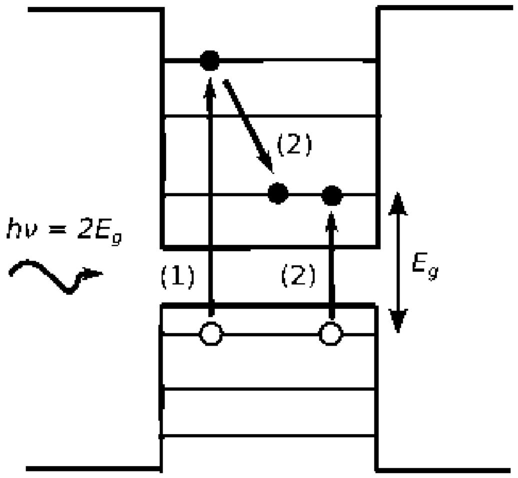

Figure 2: Illustration of the multiple exciton generation process in a QD material. (1) corresponds to the photogeneration of a hot exciton, (2) indicates the carrier multiplication process due to impact ionization. Note that E_g stands for the energetic difference between the confined ground states for electrons and holes of the QD, and not for the bandgap of the bulk semiconductor material.

Using a experimental technique called transient absorption, that takes advantage from the fact that the carrier multiplication is a faster process that electron relaxation, the first experimental result of the MEG mechanism was obtained for PbSe colloidal QDs, reporting the generation of two excitons from a single photon with energy three times E_g [6]. Other results demonstrating MEG in PbSe QDs followed [7-9]. Discrepancies among the reported results have been explained by the chemical treatment of the QDs [10] or the effect of photocharging of the QDs [11, 12]. MEG has been also confirmed for other colloidal QD materials such as PbS [7], PbTe [13], Si [14], InAs [15], InP [16], CdTe [17] and CdSe [18]. Time-resolved photoluminesce was used for obtaining some of the previous results. MEG has also been demonstrated in single-walled carbon nanotubes [19].

In a photovoltaic MEG device excitons generated in a MEG absorber must dissociate into electron and holes that, in turn, need to be extracted through selective contacts. If this dissociation and the subsequent carrier collection are efficient, quantum efficiencies (i. e., the ratio between extracted electrons and incident photons) higher than 100% are expected in such a device. Recently carrier multiplication was proven at device level in a PbSe QD-based solar cell [20]. In this device, an array of PbSe forms a heterojunction with a ZnO layer to extract electrons through an ITO electrode. Holes are collected by an Au electrode. External QE higher than 100% was reported for photon energies greater than three times E_g, exhibiting a peak of 114% at around 3.4 E_g. The internal QE peak was calculated to be 130%.

4 HOT CARRIER SOLAR CELL

The hot carrier (HC) solar cell (HC-SC) was first proposed by Ross and Nozik in 1982 [46]. The main idea of this concept is that if photo-excited carriers are extracted before they reach thermal equilibrium with the semiconductor lattice (which is, in turn, in equilibrium with the ambient); that is, whilst they are still *hot*, higher voltages than in a conventional single gap solar cell can be achieved. Hence, this concept removes the limitation introduced by assumption number two of the SQ model. Special contacts are needed, capable of isoentropically cooling the hot carriers and increasing their electro-chemical potential, rising the efficiency limit of this device to 85%, as calculated by Würfel [47]. These contacts should be selective in carrier energy –which is why they are referred to as energy selective contacts (ESCs)–, accepting only a narrow range of energies. Figure 3 shows an illustration of the HCSC concept.

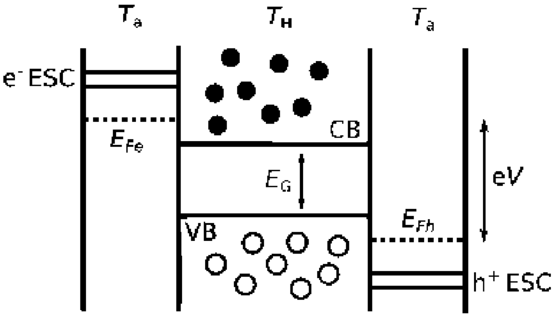

Figure 3: Illustration of the hot carrier solar cell concept. T_A and T_H stand for ambient temperature and temperature of the hot carriers, respectively. The dashed lines are the quasi-Fermi levels for electrons and holes, and their energy difference is equal to the output voltage, V, multiplied by the electron charge, e.

A suitable material for implementing a HCSC should account for a reduced electron-phonon interaction, slowing down the cooling rate of the carriers from the ps timescale to the radiative recombination timescale of ns under realistic light illumination [48]. Slow cooling of carriers was reported in QW superlattices [49], but only a very high illumination intensities. Recently the thermalization rate of carriers in InN films has been measured [50], finding a slower time constant than the theoretical value but still insufficient for achieving a high efficient device.

It has been proposed that QDs materials in which resonant tunneling mechanism take place could serve as selective contacts [51, 52]. Such materials should exhibit negative differential resistance (NDR) at room temperature. In [52] NDR was reported for Si QDs, indicating its potential to be used as ESC.

Resulting for the difficulty of achieving both an appropriate absorber and the ESCs, the HCSC has not yet stepped into the device level phase.

5 SUMMARY

Novel concepts in photovoltaics have the potential of surpassing the SQL for single gap solar cells. We have the examined the experimental progress achieved in three among them: the IBSC, the MEGSC and the HCSC. We have assessed the issues of the demonstration of their principles of operation and the consecution of a photovoltaic device. It has been found that:

IBSC: this concept is well established in the device level phase. IB behavior has been verified in different technological approaches (QDs, HMAs and BMDLIs). The principles of operation of the IBSC have been demonstrated in InAs/GaAs QD-IBSCs prototypes.

MEGSC: carrier multiplication has been demonstrated for various QD materials by transient absorption or time resolved photoluminescence. A solar cell based on PbSe QDs has exhibited an external QE exceeding 100%.

HCSC: There is experimental evidence of slow carrier cooling in quatum well superlatices and in InN films. NDR, a possible way of implementing ESCs, has been verified in Si QDs. No HCSC complete device has been yet reported.

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