PROGRESS IN UNDERSTANDING THE INTERMEDIATE BAND SOLAR CELL

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Abstract: High efficiency is intended by electron-hole generation with sub band gap photons while the voltage is ruled by the band gap. Most present cells have small current enhancement and some voltage loss. The reasons are described.

Napredek v razumevanju sončnih celic z vmesnim energijskim pasom

Kjučne besede: vmesni energijski nivoji, sončne celice z visoko učinkovitostjo

Izvleček: Visoko učinkovitost pretvorbe zagotavljajo pari elektron-vrzel, ki jih generirajo fotoni z energijo nižjo od energijske reže, medtem ko je napetost določena z energijsko režo. Večina celic izkazuje majhno povečanje toka, nekatere pa znižanje napetosti. Vzroki so razločeni v članku.

1 Introduction

An Intermediate Band (IB) solar cell is formed /1/ by an IB material situated between two ordinary semiconductors – n- and p-type respectively– that play the role of selective contacts to conduction band (CB) and valence band (VB) electrons. The IB material has a band of states inside the band gap between the CB and the VB. In this way, photons with less energy than the one necessary to pump an electron from the VB to the CB can be absorbed by transitions that pump an electron from the VB to the IB and from the IB to the CB. Thus a full VB→CB electron transition (or electron-hole pair generation) can be completed by means of two photons of energy below the band gap. This mechanism should increase the solar cell current.

While increasing the current the voltage has to be preserved. The voltage in the cells is the difference of the CB and VB quasi Fermi levels (QFL) splitting. In the IB solar cell a third independent QFL must appear for the IB that is isolated from the contacts through two ordinary n- and p-type ordinary semiconductors that play the role of electron and hole selective contacts.

Limiting efficiency of this concept for maximum concentration (the one providing isotropic illumination on the cell with the radiance of the sun's photosphere) is 63% to compare with the Shockley-Queisser limit of 40% for an ordinary cell in the same conditions /2/.

IB GaAs solar were fabricated first /3/ based on this concept using InAs quantum dots (QD) to form the IB by IES (UPM) and the University of Glasgow. Today several more groups have produced similar cells /4-8/. Evidence of the electron-hole formation through the described two-photon mechanism has been produced /9/. Evidence of the three QFL splitting has also been provided /10/. However, the efficiency is not higher than the one of the cells without quantum dots. Bulk ZnTe:O IB solar cells have also been presented /11/ and while the efficiency is still very low the IB behavior is crealy demosntstate and the efficiency of the IB cells is 50% higher than the one of the ZnTe ordinary cells.

2 Current enhancement

The QD IBSC show some current enhancement but it is too small. It is attributed to the small number of QD layers involved, 10 in the first IB solar cells /3/. The obvious conclusion was to fabricate solar cells with more QD layers but this resulted in the production of dislocations /12/ that spoiled the emitter photo-generated current contribution (CB→VB transitions). However the increase of sub-band-gap photon current was achieved. Strain- compensated techniques have been developed first by Hubbard and coworkers /4/ at Rochester Inst. Tech. and NASA Glenn with very good results. Other researchers have also used strain compensating techniques /4-8/. It seems that the deposition of several hundreds of layers without degrading the crystal will be possible. See in Figure 1 the best efficiency so far achieved with and IB solar cell.

However, it seems that the IB→CB photon absorption is very weak. This might be because the aspect of the QD is very flat, reminding a quantum well (QW) and it is know that this transition is forbidden in QWs for photons normal to the surface. The manufacturing of QD with another aspect ratio is desirable. But in any case diffractive methods may bent the rays so breaking the selection rule and at the same time enlarging the ray path length /13/.

But besides, the IB is in most cases not half filled or insufficiently filled because most of groups refuse to dope the IB, probably to keep the quality high. Even with a good photon capture section this will prevent the IB→CB ab-

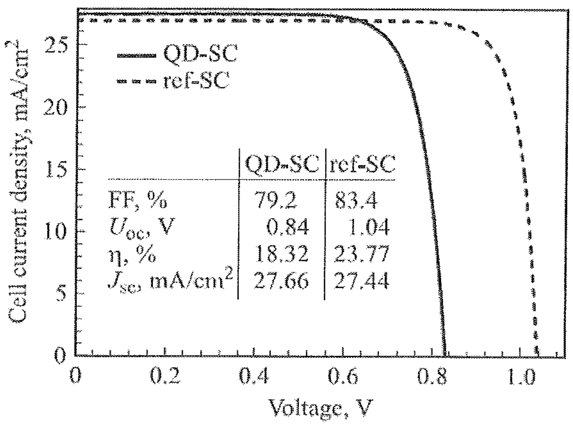

Fig. 1: IV curves of an IB-QD InAs/GaAs solar cell and the reference GaAs solar cell /8/.

sorption to be produced by lack of electrons. Maybe they observe that the quantum efficiency (QE) is better in undoped samples but again this is misleading because in most cases QE is a one-photon experiment and only tells that the IB and the CB are short-circuited, that is bad.

3 Voltage preservation

A voltage reduction of 100 to 200 mV is usually observed between the QD solar cell and the reference GaAs solar cell. It is mainly due to the reduction of the barrier material band gap caused by:

- The formation of a wetting layer when the QD are grown in the Stranski Krastanov mode. The wetting layer is in reality a quantum well and as such it has not a zero density of states between IB and CB and as such its width has to be considered as a reduction of the barrier material band gap.
- The existence of high quantum number confined states differing in energy less than the optical phonon energy and therefore behaving very much as a continuous band.
- The appearance of a VB offset due to the confined hole states whose excited states also form a continuous in the same terms as above.

Photoreflectance measurements /14/ made in our group show several confined layers that deped on the size and shape of the QDs. This is also confirmed by quantum calculations (by Zunger and coworkers) for the InAs/GaAs case show a reduction of the band gap that at 0°K is of about 300 meV. The reduction observed in the voltage is smaller but is to be expected that it mirrors at least qualitatively the theoretically expected band gap reduction.

But this effect is not negative in itself. It only tells that the bandgap of the barrier material is modified by the addition of QD and thus it is unfair to compare InAs/GaAs cells with GaAs cells. To compare cells of the same badgap it woud be necessary to make the IB cell ain a larger bandgap material like AlGaAs.

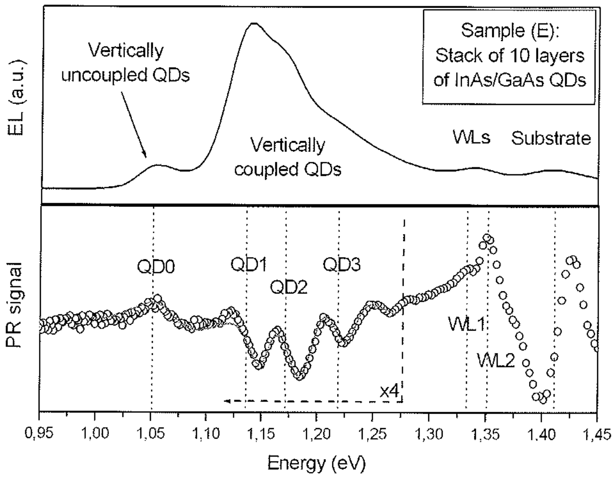

Fig. 2: Electroluminescence and Photoreflectance spectrum of an IB QD solar cell. The first seed layer has one wetting layer and a confined states. The rest of the layers have their wetting layer and three confined levels, each one vertically coupled /14/.

But besides this it looks that the IB in this system is strongly connected to the CB. This means that the capture section of CB electrons by the IB is very high /15/. This makes the separation of the three QFL difficult. The main reason for it is the multitude of levels populating the IB-CV interval as seen in Figure 2. But in addition to it the high electric fields present in the cells favor the tunneling of the confined electrons into the CB. We have experimental evidence (in preparation for publication) that the later mechanism has been avoided in recent cells but the fact remains that even the ideal detailed balance calculations tell that the InAs/GaAs QD cell cannot give more efficiency than the GaAs cell at one sun illumination. Thus we believe that a practical QD device has to be made with a larger bandgap barrier material.

4 Bulk material ib cells

IB materials have been found along several paths. The first to be followed that was based on *ab initio* quantum calculations /16/ has recently led to the solvothermal synthesis of $Va_{0.25}In_{1.75}S_3$ /17/ in which the theoretically predicted /18/ three absorption bands have been found. No cell has been done because the synthesis method is not compatible with solar cell manufacturing.

The band anticrossing mechanism /19/ in highly mismatched alloys has led to the discovery of several IB materials as detected by photoreflectance spectroscopy /20, 21/. Recently the first bulk IB solar cell has been produced /11/, of ZnTe:O, where the IB cell is clearly better than the corresponding ZnTe ordinary cell, as shown in Figure 3.

But in reality any deep level impurity might be the precursor of an IB cell. Several new ideas are now in development along this line /22, 23/.

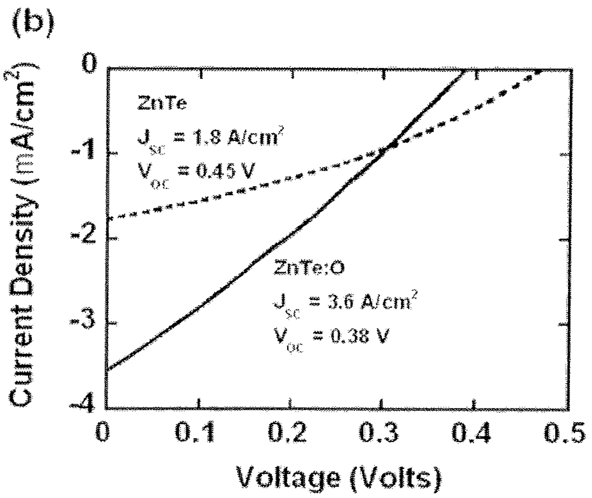

Fig. 3: IV curves of a ZnTe:O IB solar cell and an ordinary ZnTe solar cell. Effciencies are below 1% but 50% higher in the IB solar cell.

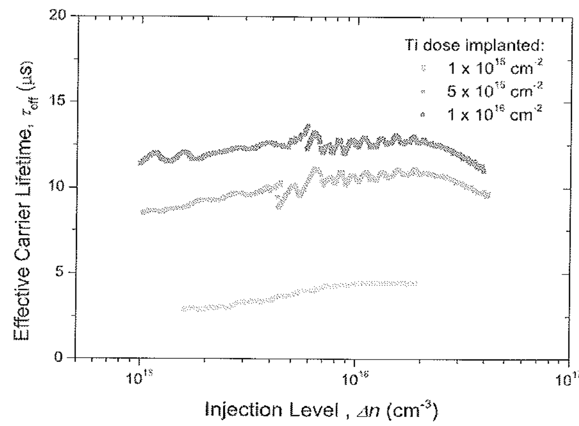

Fig. 4: Lifetime vs. injection level as measured by conductivity decay /27/ in heavily Ti-implanted Si wafers /26/.

4.1 Suppression of the non-radiative recombination

It is well known that deep levels are the origin of SRH non radiative recombination. In bulk materials we believe that the main cause of it is the so called multiphonon emission mechanism /24/ that is associated to the disequilibrium caused when the electric charge an extended electron in the CB or in the VB makes a transition to a localized state with the charge localized around the impurity in the deep level. The lattice start vibrating heavily and this vibration is subsequently damped by the emission of several phonons. We have anticipated /25/ that if the semiconductor is heavily doped so that the impurity states become extended states in an impurity band thie mechanism cannot be produced and the non radiative recombination mush result suppressed. By ion implantation and pulsed laser melting we have doped heavily wafer of Si with Ti that is known to be a strong lifetime killer. We have found that the lifetime is increased when the implanted dose increases /26/. The experiment result is presented in Figure 4.

It is to be noted that this result is just opposite to the common belief of device physicists: the more the Ti the longer the lifetime. We believe this is an important result and explains why IB behavior is to be different form deep level behavior.

5 Conclusions

Stress production during the QD growth seems to be the main cause for reduction of the cell photo generated current. Indeed this also affect drastically to the voltage. When the stress is controlled the voltage is still reduced due to the shrinkage of the main band gap. This is not to be considered as a drawback in itself. The comparison with GaAs cells is inappropriate. The band gap can be restored by using alloys such as GaAlAs as barrier material.

The multiple confined lavels seems to provide an easy path to have the IB and the CB thermally connected. This makes difficult the appearance of three quasi Fermi levels and therefore the conservation of the voltage

Doping the IB is essential for the IB→CB photon absorption. Without it the high voltage operation is also impossible. But maybe the shape of the QDs, very close to that of the QWs makes this absorption difficult as it is known that it is forbidden in QWs.

In general, revisiting the optimal materials proposed by us at the beginning /28/ seems now pertinent. QD's should be smaller and their levels more separated from the CB. For it the main bandgap must be higher.

Several bulk IB materials have been found experimentally and many more have been anticipated theoretically. This contrasts to the first predictions of some scientists that considered impossible to find IB materials. IB solar cells have been manufactured although their efficiency is still small.

The different behavior of deep levels and IB in the sense that no SRH recombination is to be expected in the seconds has been anticipated and experimental evidence has been provided.

Over two dozen of groups have published so far in ISI-recorded journals on IB solar cells. Most If the publications are of the last three years and results start to appear copious. We think that soon we shall practical IB solar cells, either in tandem /29/ for operation in concentration, to explore the range of 50% efficiency, or as thin film solar cells more efficient than the present ones and therefore able to compete better in market.

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