Intermediate band solar cells and paths towards their implementation by micro and nanotechnologies

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Abstract. A new type of solar cell of potentially higher efficiency is presented. It is based in a intermediate band that acts as a relay to allow two energy photons with less energy than the bandgap to pump one electron from the valence band to the conduction band. Alloys for obtaining the intermediate band material using a compound semiconductor in which an additional element is introduced are the object of a research based on advanced band theory calculations. Alternatively, arrays of quantum dots may also form an intermediate band. If produced by MBE they seem a simpler way of fabricating prototypes to prove the principle of operation. Experimental work along this line is in progress.

Summarium. Quiddam novum genus cellularum solarium potentialiter efficientiorum proponitur quibus fultura est aliqua fascis energiarum in medio hiatu posita quo electron photone e valentiae fasce excuditur undeque photone altero ad conductionem fascem eripitur. Hujusmodo electron binorum minoris energíae quam hiatus photonum ope hiatum trasilit. Ad temperationem intra hiatum fasciatam conficiendam semiconductoriorum mixtuarae compositorum, aliquo elemento introducto, per rationem simulacri fascium perspiciuntur. Ordinibus enim guttarum quanticarum fasces in medio hiato etiam conficiuntur. Fabricatio autem MFE exemplorum ad principium cellulae illius demonstradum simplius esse videtur. Experimenta per iter hoc incepta sunt.

Introduction

Solar cells can have an inherently moderate efficiency because photons below the bandgap cannot produce transitions from the valence (VB) to the conduction band (CB) and therefore they cannot provide electrons to the current delivered by the cell. If, attempting to overcome this drawback we use very low bandgap semiconductors then the electric current is delivered to the external circuit at a very low voltage, that do not exceed the bandgap. Therefore a trade-off is to be established leading to an optimum bandgap of about 1.1 eV, the one of silicon.

The introduction of a band of intermediate energy levels in the bandgap between the conduction and valence bands could perhaps improve the cell efficiency. As shown in Figure 1, photon absorption by transition from the valence band to the intermediate band (IB) and from the intermediate band to the valence band are possible with energy below the one of the valence to conduction band bandgap. The absorption of two sub-bandgap photons of this type may allow for consecutive transitions from the valence band to the intermediate band and from there to the conduction band. If properly designed, the cell fabricated according to this principle may supply electrons to the electric circuit at a potential energy (voltage) higher than the one of the photons absorbed.

The fabrication of a material with IB is an object of our research. Two paths are being followed: the formation of an alloy that has naturally this structure and the formation of quantum dots arrays.

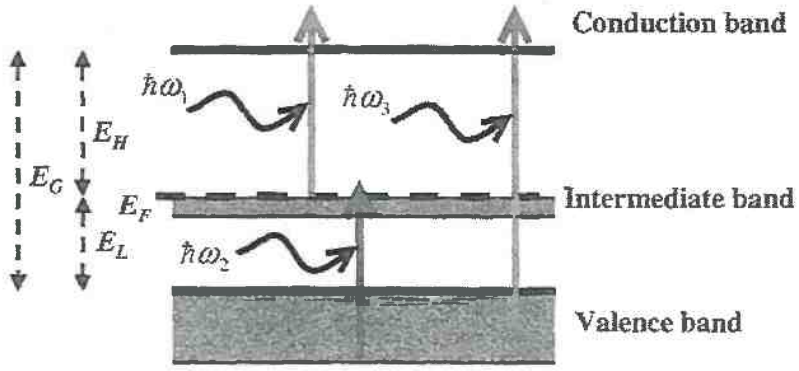

Figure 1. Intermediate band material showing sub-bandgap photon absorption mechanisms.

We present in this paper the structure and principle of operation of this intermediate band solar cells and the paths we are following to attempt realising it.

IB solar cell description

As shown in Figure 2, the MIB solar cell consists in a material showing an intermediate band together with a valence and a conduction band [1]. Density of state gaps exists therefore between the valence and the conduction bands. This material is sandwiched between two layers of an ordinary semiconductor [2] with bandgap similar or higher to the main bandgap (from VB to CB) of the IB material. Notice that in the IB material the Fermi level passes trough the IB rendering it metallic or half-full of electrons. This is necessary for efficient absorption of photons producing electron transitions from the VB to the empty states of the IB and also transitions from the full states of the IB to the CB.

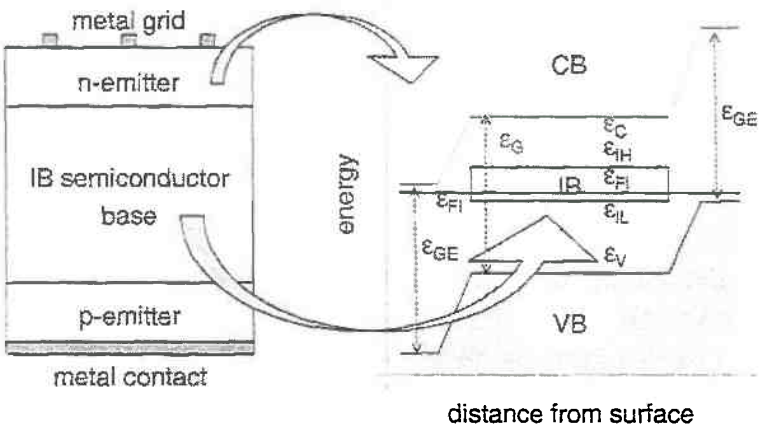

Figure 2. Schematic and band diagram of a IB solar cell.

The IB material is sandwiched between two ordinary semiconductors and this is because of several reasons. First, the IB becomes isolated from the metallic contacts that would otherwise short-circuit the solar cell, operating like just a metal. Second, these semiconductors respectively *n*- and *p*-doped constitute selective contacts to the CB and the VB respectively. This is the way electrons are taken from the CV at a higher

potential energy, are used for useful work in the load and are returned back to the cell at its VB with lower potential energy.

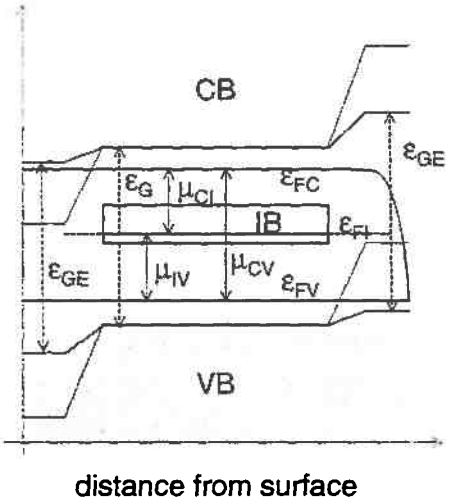

Figure 3. Band diagram of the MIB solar cell under illumination.

Under illumination the population of the electrons and holes in the valence band and in the conduction band increases causing the Fermi level to split into three quasi-Fermi levels, one almost invariable for IB the metallic band and other two for the valence and the conduction band that in this material both behave as minority-carrier bands. The band diagram under illumination is therefore presented in Figure 3. The operation voltage is determined by the separation of quasi-Fermi levels. The difference of the free energies (quasi-Fermi levels) at which electrons are withdrawn from the conduction band at the *n*-emitter side and rendered to the valence band at the *p*-emitter side, in electrons volts, is the device voltage in volts.

But we have not talked of recombination so far. Electron transitions downwards are a counterpart of the upward transitions photon-driven described so far. The cell current is thus the difference between electron income to the CB due upward transitions driven by photon absorptions and the downward transitions. In the later the energy delivered may be transferred to vibration states in the lattice or can be delivered to emitted photons. In principle, only the radiative transitions — radiative recombination — is physically unavoidable as the 2nd law of thermodynamics imposes. When only this recombination is left and the carrier mobilities are infinite, the efficiency reachable with the MIB solar cell is represented in Figure 4.

The achievement of the efficiencies presented requires isotropic illumination on the cell at the sun temperature. This is what we often call full concentration. It also requires that the absorption spectra in the IB material is such that photons are absorbed only in a single transition type. In other words the possibility that a low energy photon can be absorbed in both VB→IB and IB→CB transitions is excluded. Only one of such processes is permitted for a given photon.

In this case, the efficiency is represented as a function of the lower energy photon. The main bandgap energy (VB→CB) appears in the figure. The other bandgap can be obtained in this case as difference between the main bandgap and the smaller bandgap in the abscissas. The results reaching the 63.2% are compared to the results of a single bandgap cell, as studied by Shockley and Queisser [3], of 40.7%. It is also compared to

double junction tandem cell. In all cases our cell, in the ideal analysis, shows a better efficiency.

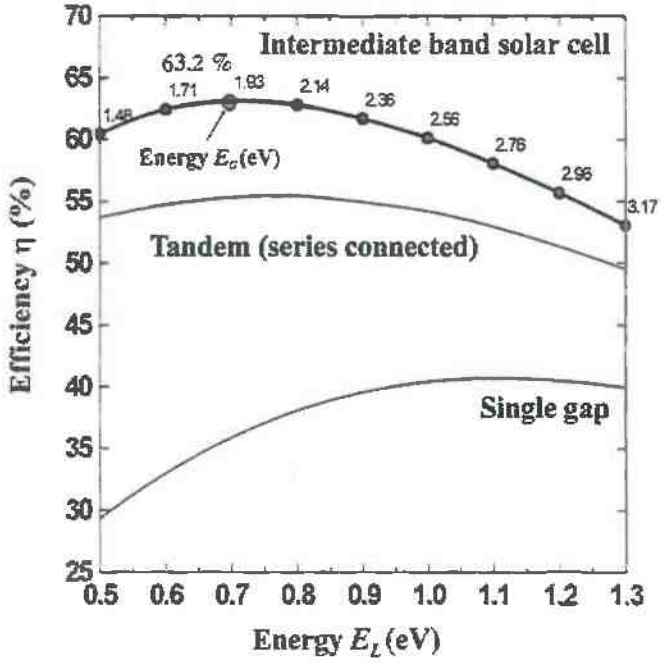

Figure 4 Efficiency vs. lower bandgap energy for an IB solar cell, a double junction tandem and a single gap solar cell

At one sun, the efficiency is reduced to 46.2% and at 2000 suns a concentration not yet usual but in development today, the efficiency is still 57.6%, When some overlap is produced in the sense that the upper limit of an optical band of absorption invades the lower limit of the following one, or, on the contrary, leaves a gap where no photon is absorbed, then, the efficiency is somewhat reduced but the effect is very dependant on the specific absorptions conditions.

Reduction of recombination

Good cell behaviour is usually associated to the reduction of any avoidable source of recombination. Suppression is to be understood as reduction well below of the unavoidable radiative recombination. Recombination in solar cells is associated to imperfections and it is difficult to know what will be the behaviour of imperfections in the still non-existent IB material. However some statements may be ventured.

It is well known that certain elements dissolved in the lattice of an ordinary semiconductor may affect strongly the semiconductor properties. In particular impurities located in the mid-gap provide strong source of SRH recombination and therefore, they tend to be avoided if long minority-carrier lifetimes are sought. In consequence, intermediate bands may be the origin of strong non radiative recombination, and therefore to have deleterious rather than beneficial effects.

However, interband transitions, and therefore recombinations, are not produced in a one-electron approximation in a perfect crystal. Coupling with the field of photons may produce recombination, and this is the radiative recombination taken already into account. Coupling with a second electron can do the same, and this is the Auger recombination on which we must keep one eye (it can have positive and negative effects

[4]). In any case transitions in a perfect crystal must conserve the energy and also the crystal momentum. This prevents the appearance of non-radiative recombinations with the emission (or absorption) of phonons because the phonon energy, of less than 50 meV, is insufficient to collect the energy of an interband transition. Only multiphonon processes, extremely improbable, could do it.

In contrast, impurities situated at random in the network are to be treated as single impurities. By doing so electronic states associated to the impurity become extremely localised, more so when the impurity level is deep in the mid-gap [5] and the matrix element for radiative recombination becomes very weak.

At the same time, the impurity itself stimulates local states for vibration in the network that can be considered as composed of many phonons. The multiphonon processes required for non-radiative recombination become facilitated. In summary, impurities present reduced radiative recombination and therefore reduced absorption of phonons, which is its detailed balance counterpart, and facilitates the non-radiative recombination. In contrast, bands formed by regular arrays of impurities, so closely spaced that lead in practice to an alloy, are likely to present reasonable radiative recombination and are free of local modes of vibration so that reduce the multiphonon process probability and therefore the non-radiative recombination probability.

In conclusion, while we think that isolated impurities must be avoided, arrays of atoms regularly spaced, forming an alloy able to produce an IB should be promoted. This will be illustrated in the next section.

Direct synthesis of the IB material

Alloys might be found that lead to the desired IB material. if certain elements are introduced substitutionally in the semiconductor lattices of the GaAs and GaP band calculations show the existence of such a band [6]. We present in Figure 5 the crystal lattice used for the calculations. Several combinations of atoms in this lattice have been studied. Some of them form a separate IB bands and some do not.

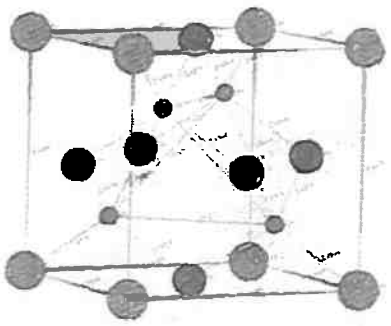

Figure 5. IB material lattice used in band calculations: Ti blue, Ga red, As brown. The composition is Ga_4TiAs_3 .

We present in Figure 6 [7, 8] a set of band diagrams showing the $E(k)$ function in the reciprocal space, in a wide series of symmetry directions so that we can get a rather complete picture of $E(k)$ for any k. Actually the band diagram as it is usually presented in device physics can be considered as the projection of the energy curves in the energy axis. It is easy to see that this projection gives three separate bands in the cases of Ga_4P_3Sc, Ga_4P_3Ti and Ga_4P_3V, but not in the case of Ga_4P_3Cr where all the bands intermix. The Fermi level (at 0 K) corresponds to the 0-energy. It is easy to see that only in the Ga_4P_3Sc and in the Ga_4P_3Ti, the IB is half empty, that is, metallic. Many other materials have been studied. In particular Ga_4As_3Ti and Ga_3As_4Ti both present a metallic IB.

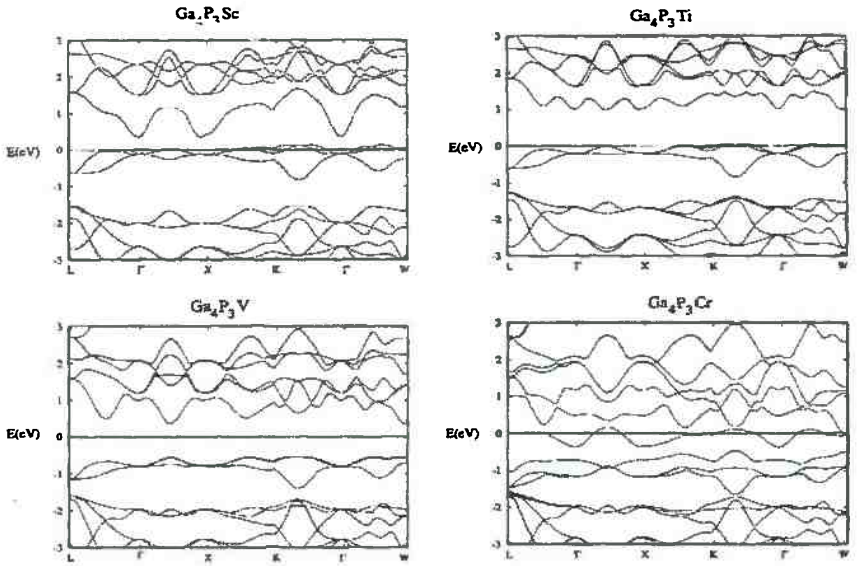

Figure 6. Band diagram calculations for a variety of alloys.

The calculations used, which are state of the art, are very complex and the results are believed to lead to correct predictions concerning band separation. But, indeed, we do not know yet if the crystal structure assumed is chemically stable. Only experiments will be able of determining the appearance of an IB. Nevertheless such calculations constitute an extremely powerful guide in the difficult task of determining the novel materials.

Light absorption in such materials is direct and indirect. They can be calculated taking into account two aspects, on one side the matrix elements of the transition involving a photon and, in indirect transitions, one phonon as well. Such calculations are now under way. On the other hand the joint density of states, or number of permitted transitions between full and empty states in all the bands affect to the absorption coefficient. Both calculations require the knowledge of the band structure and the wave functions.

What we say now is a bit involved because we use the term band with three different meanings: absorption bands or range of photons absorbed in transitions between VB→IB, IB→CB and VB→CB; the semiconductor bands as understood in device physics, VB, IB and CB, comprising all the quantum states with energies in a non disjoint range; and finally electronic bands as understood by solid state physicists as the electronic states whose only differing quantum number is the reciprocal lattice vector, leading to the bunches of tangled lines with energies forming connected segments in the vertical axes, as found in Figure 6. An important characteristic for high efficiency is to

obtain an optical absorption structure such that absorption or bands for transition between VB→IB, IB→CB and VB→CB, do not overlap (see Figure 2). If this cannot be achieved it seems that structures with very different absorption coefficients for the three absorption bands indicated (VB→IB, IB→CB and VB→CB) might achieve rather high efficiencies based on improving the absorption of the less absorptive band by light confinement (see Figure 5).

Nanoelectronic synthesis of the IB material

An alternative way of producing intermediate bands is the use of nanotechnological structures [9]. Such structures produce localized states with energy within the gap. However, the structure dimensionality rules the shape of the density of states within the bandgap. Quantum wells with dimensionality 2 present a continuous density of states linking the deepest confined states and the band edges. This continuous is due to the unconfined character of the wave function in the direction parallel to the growth direction. Quantum wires, with dimensionality 1, also present such a continuous due to the unconfined character of the wave function along the wire. Only quantum dots (QD) or artificial atoms of dimensionality 0, present a gap of density of states between the confined states and the barrier material bands. Arrays of QDs may, in principle, provide the desired IB as represented in Figure 7.

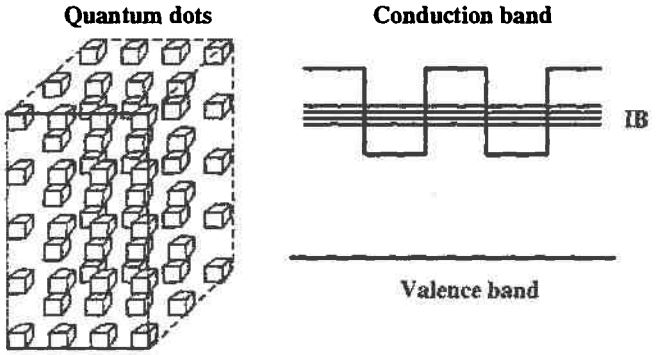

Figure 7 Array of quantum dots to form an IB material.

The basic cell structure based on this concept is presented in Figure 8. The IB material is formed of dots of a low bandgap semiconductor such as the $In_{0.45}Ga_{0.55}As$ are embedded in a higher bandgap semiconductor such as $Al_{0.44}Ga_{0.56}As$. This IB material is located between two regions (one being the substrate) of the same $Al_{0.44}Ga_{0.56}As$, *p* and *n* doped respectively. These semiconductors are called dot and barrier materials respectively.

The difference of electron affinities (barrier height) between the dot and barrier material, adjusted by Al-Ga and Al-In proportions, as well as the dot size determine the IB position. The values indicated in the figure are believed to lead to the optimum efficiency [10]. Practical considerations associated to strain between gaps and VB offset (causing a reduction of the bandgap of the barrier semiconductor due to the quasi continuous of many dot levels at the VB associated to the higher effective mass of the holes) recommend to use InAs with no Ga as the best dot material. Limiting efficiencies for this material at one sun is 39.8% as compared to 31.0% for a conventional junction material [11]. However this conclusion is very dependent on the strain model used and experimental work must be used for cell trimming.

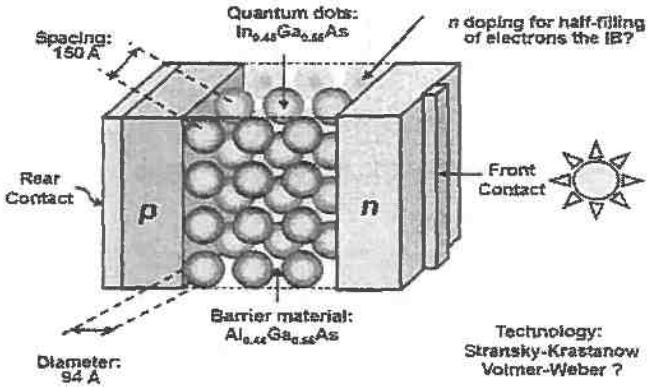

Figure 8. MIB **solar based in QD technology**

The separation among dots must be as small as possible for two purposes, to enhance light absorption by the IB —weak absorption may be a limitation for effective operation— and to provide a IB conductivity able to produce an homogenisation of the IB population without large electric fields that would be deleterious. Density of dots in the range of almost 10^{18} are to be achieved. We are not yet able to assess on the real importance of such effects

Another important requirement for ideal operation of the MIB cell is how to render metallic or half filled the IB. This can be done by n-doping the barrier material [12]. One electron per QD is to be provided. This electron will fall into one of the two localized levels in the QD, with different spins, leaving one level filled and one empty.

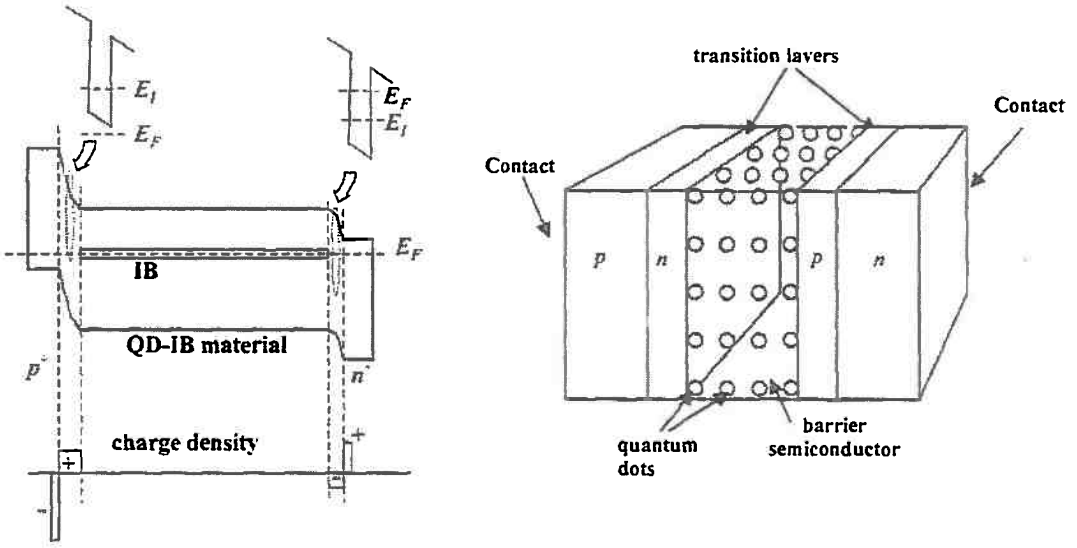

Figure 9. Forming dipole layer in the emiitters

The MIB cell structure, as represented in Figure 3, requires an electric field in the interfaces of the ordinary semiconductors of the emitters and the IB material. This electric field requires a dipole layer that in the case of the IB material will be supplied by QD layers totally filled of electrons (two per QD) or totally empty of them. This will render such QD idle for the cell operation as such parts become unsuitable for IB photon absorption as schematically depicted in Figure 9.

Since the fabrication many layers of QDs may be a difficult task, providing the whole dipole layer in the emitter can cave some few QD layers. In this way the proposed device will have a pnIBpn structure instead of the simpler pIBn one [11].

Construction of an MIB solar cell prototype based on QDs.

With the cooperation of the University of Glasgow and Compound Semiconductors Technologies, we are attempting to fabricate a prototype able to prove the principle of operation involved in this device, namely the ability of supplying electric current at a certain potential energy (voltage) higher that the energy of the photons impinging on it.

For it, the QD technology has been selected. Several procedures to form QD seem possible but among them, the one fitting more to our purposes seem to be the realisation of an array of QD formed by a field of strains. The principle, as depicted in Figure 10, is the following [13]. If on a given semiconductor we deposit another one without lattice mismatch a continuous layer may indefinitely growth. However, if some lattice mismatch exists, then, the deposit shrinks in droplets after a few monoatomic layers have been deposited. Under certain conditions of lattice mismatch and number of monoatomic layers, the droplets produced show a regular pattern. With lattice mismatch in the range of 10% we are in the Stransky-Krastanov growth mode where the deposited

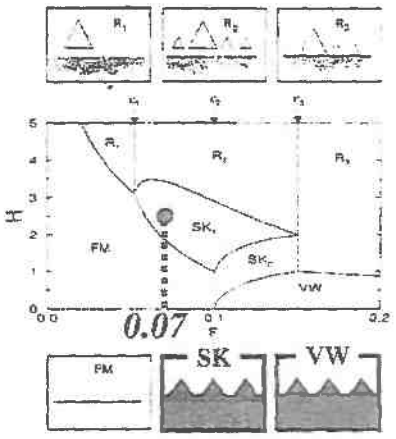

Figure 10. Modes of epitaxial growth of hetherolayers

material forms a regular structure up to some 3-4 monolayers separated from the substrate material by one very thin layer called wetting layer. Thicker layers rearrange in a similar structure but not any more regular. Most probably the thin size of the wetting layer does not break the 0-dimensionality of the desired structure. Higher mismatch produce the Volmer-Weber growth mode without wetting layer. However, in this case, the layer ceases to be regular after the first monolayer becoming irregular very soon. The regular feature and close spacing is a desired feature because otherwise, due to the so-called Anderson localization, the IB electrons cease to exhibit metallic mobility.

Thus, in spite of the wetting layer it seems that the optimal growth regime is the Stransky-Krastanov one. This would produce QD's of the size and separation required by us although with pyramidal instead of spherical shape on which we based our calculations.

Once the first layer of QDs has been formed additional layers of barrier material are to be grown in order to embed the QDs in the barrier material and a second layer of QDs is

to be realized subsequently. The number of QD layers seems not to have a theoretical limit but probably in practice the more layers the more difficult maintain good material properties.

In addition, the self-organized arrays of QDs present no interface recombination and no defects in general so no introducing non-radiativerecombination. The surface density of dots is very high ($\cong 10^{11} cm^{-2}$). In the Glasgow University this structure will be grown by MBE.

Practical use of MIB cells

Present fabrication of the MIB cell prototype is by using MBE self-organized arrays of QDs. This is certainly an expensive device based in the expensive technology used for it. However the same QD arrays have been achieved by MOCVD, a common technology in optoelectronics. This would probably render the cells cheaper although still expensive as compared to Si cells. Big efforts are being paid to develop a very high concentration device that would render cheap the complex multijunction cells. MIB cells can be used to substitute multijunction stacks or to combine with them to cover the whole energy spectrum. In principle, one MIB cell may substitute with efficiency advantage two junctions.

There is another possible way of utilisation of the MIB principle: it is the formation of QDs in porous materials. With the Hahn Meitner Institute we are exploring this principle. A highly porous absorbing layer is sandwiched between two layers of transparent *p* and *n* semiconductors. The absorber porosity separates it into QDs that so result embedded in the transparent semiconductor surrounding it. This could a very cheap way of forming MIB cells, so allowing for not a full exploitation of the MIB cells potential.

Conclusions

The MIB solar cell, a new type of solar cells has been proposed with a high theoretical potential.

Such cells have been modelled so to be able to understand the cell behaviour under less ideal conditions.

Three ways for obtaining the IB material are under investigation. One, which seems rather promising, is the direct synthesis of an alloy presenting the desired IB. No experimental work is under way yet along this line.

A less attractive one in the long term but easier to implement is the uses of arrays of quantum dots. Studies of this structure are under way.

A third way based in intercalating a high porous absorbing material between two high bandgap semiconductors seems to provide a very low cost fabrication method. Less theoretical studies have been developed on this path.

The experimental work immediately under way aims at proving the basic principle of the MIB solar cell. We shall try to prove that low energy photons can produce electron current at higher potential energy.

We consider that MIB cells will produce either thin film cell of low cost able to exceeding the efficiency of present thin film cells or will be used under high concentration for very high efficiency converters, either in operation alone or in tandem with additional solar cells. In theory the MIB solar cell can favourably substitute a double junction solar cell.

Acknowledgement

This work is developed under partial support of contract ENK6CT2000 00310 MIB-CELL with the Energy Programme of the 5th EC Framework RTD Programme.

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