The effect of band offsets in quantum dots

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ABSTRACT

The insertion of quantum dots in a host material produces band offsets which are greatly dependent on the field of strains brought about by this insertion. Based on the Empiric KP Hamiltonian model, the energy spectrum of the quantum dot/host system is easily calculated and a relationship between the conduction and valence band offsets is determined by the energy at which the lowest peak of the sub-bandgap quantum efficiency of an intermediate band solar cell is situated; therefore knowledge of the valence band offset leads to knowledge of both offsets. The calculated sub-bandgap quantum efficiency due to the quantum dot is rather insensitive to the value of the valence band offset. However, the calculated quantum efficiency of the wetting layer, modeled as a quantum well, is sensitive to the valence band offset and a fitting with the measured value is possible resulting in a determination of both offsets in the finished solar cell with its final field of strains. The method is applied to an intermediate-band solar cell prototype made with InAs quantum dots in GaAs.

1. Introduction

The intermediate-band (IB) solar cell [1] (SC) contains several levels or bands permitted to the electrons in the forbidden bandgap of a semiconductor. These permitted values may be used for the transfer of electrons from the valence band to the conduction band by absorbing low-energy photons. The triple-level system arising in this case, may emulate a triple-junction solar cell. Shockley and Queisser, in an elegant paper, calculated the detailed efficiency limit of a single-junction solar cell to be 41% [2]. For an IBSC, the efficiency value determined in a similar manner is 63% [1]. There are several different ways of manufacturing IBSCs [3], whose operation is described further in [4].

In semiconductor materials, the intermediate band may be formed by quantum dots [5] (QDs). A type I QD produces offsets in the host material bands leading to a well in the conduction band (CB), and a pedestal in the valence band (VB). They both produce confined states (the pedestal is attractive for the negative-mass holes) with energy levels which are within the band gap of the host material; those derived from the CB offset form the IB. Unfortunately, efficiency higher than a control cell without QDs has seldom been produced, and when so, only marginally [6]. The main reason is that the absorption of low energy (sub-bandgap) photons by the QDs is too

weak. This stresses the importance of a good characterization and modeling of the photon absorption process.

A very important aspect in QD characterization in a semiconductor device is the determination of the potential offsets in the CB and in the VB, which is the depth of the CB well and the height of the VB pedestal. In this paper we will present a method to determine these offsets. The method will be applied to the determination of the offsets produced by InAs QDs in a GaAs host.

InAs QDs can be obtained by growing an InAs layer on the GaAs substrate. Because of the large mismatch in the lattice constant, the structure will grow according to the Stransky–Krastanov mechanism, which means the formation of a thin film first, and after that, islands grow thus forming the QDs. However, a fine continuous layer remains which is referred to as the wetting layer (WL). This InAs thin film, in this case, can be regarded as a quantum well. It produces a photo-generation, stronger to that of the QDs, close to the bandgap.

1.1. The energy spectrum

After the formation of the QDs, their characterization through experiments is a very important task. Photoluminescence (PL) is perhaps the most commonly used technique. It can be performed on a finished device or in samples *ad hoc*. An interesting PL signature of the confined states is presented in reference [7], the PL plots are reproduced in Fig. 1. According to the authors the peaks represent the position of the confined electron levels below the

Fig. 1. Tuning of the intersublevel energy spacing with the substrate temperature during the growth of InAs/GaAs QD's. Larger QD's with smaller intersublevel energy spacings are obtained at higher temperatures: (a) Shows $T_{\text{growth}}=535^\circ\text{C}$, (b) $T_{\text{growth}}=515^\circ\text{C}$, (c) $T_{\text{growth}}=500^\circ\text{C}$, and (d) $T_{\text{growth}}\sim 480^\circ\text{C}$, giving an adjustable intersublevel energy spacing of between 57 and 90 meV. The state-filling spectroscopy is obtained with photoluminescence at 77 K, with the highest excitation of a few kW/cm^2 above the barrier energy.

host CB edge. In each panel the different curves reflect a variation in the laser excitation that pumps electrons from the VB to the CB. The PL is produced by luminescent emission from the levels of the electrons confined by CB offset potential to the VB states. More levels (the excited states) are revealed by increasing the excitation. In panel (b) the levels are labeled. The different panels refer to different samples that have been built according to the description in the caption. For more details see reference [7].

Modeling is another of the tasks which are necessary for understanding the behavior of the QD structures. IBSCs have been modeled frequently. Modeling can be derived from *ab initio* calculations [8] or from *k*·*p* methods among others. This analysis is based on a model of the QD based on the Empiric KP Hamiltonian [9,10] (EKPH). In contrast to the *ab initio* calculations this model, although less accurate, can be used with modest calculation equipment (a laptop) and is relatively fast; details may be found in reference [11], a method summary is described in reference [12].

The method requires us to solve four effective-mass Schrödinger equations: for the conduction band (*cb*) states and the heavy hole (*hh*), light hole (*lh*) and split-off (*so*) bands in the valence band (VB). One of the reasons for the rapidity of the method is that it assumes that the QDs are squat parallelepipeds with well/pedestals (the band offsets) of constant depth/height. This allows the states to be written as *lhh121* for instance, the three digits being the quantum numbers – n_x, n_y, n_z – corresponding to three very simple one-dimensional Schrödinger equations if the potential is considered separable [13]; the quantum numbers may be conserved even if this approximation is

Fig. 2. Energy levels in InAs QD in GaAs calculated with the parameters of Table 1.

Table 1

Parameters used for the calculation of the energy spectrum of the QD of Fig. 2

Parameter	Value	Source
Host bandgap, E_g (eV)	1.42	[14]
InAs relative <i>cb</i> effective mass relative to mass in <i>vacuo</i> , m_{cb}	0.0294	[15]
InAs relative <i>lh</i> effective mass relative to mass in <i>vacuo</i> , m_{lh}	0.027	[15]
InAs relative <i>hh</i> effective mass relative to mass in <i>vacuo</i> , m_{hh}	0.333	[15]
InAs/GaAs CB well offset (eV)	0.58	[16] and this paper
InAs/GaAs VB pedestal offset (eV)	0.22	[16] and this paper
QD height (nm)	6	TEM
QD base side (nm)	14.9	[16]

refined, as we have done. The conduction band (CB, with capital letters) and the VB include not only states bound to the QD, such as *lhh121* or *lcb111*, but also extended states characterized by (slightly modified) Bloch functions. In the EKPH method the calculation of the energy spectrum is almost instantaneous. It is presented in Fig. 2 for the set of parameters enlisted in Table 1.

The energy levels are calculated with an upgraded [13] separable approximation (to the first order, very close to the exact value). The labeling is simplified, omitting the band, because the position reflects the band they belong to (and also for reasons of space).

The IB, in this plot, is formed of the states near the host CB which are within the host bandgap. They are *cb* states, detached

from the CB. It is also worth noticing that there are bound states within the host CB (as well as within the host VB), therefore they are degenerate with some extended states. These are called virtual bound states and have an important role in photon absorption.

Due to the high effective mass of the hh their levels are closely packed, thus forming a quasi-continuum, forming, in practice, a faint queue extending the VB within the host bandgap. Degenerate with them we find the lh states.

It must be taken into account that in these structures the offsets affect the number of levels in the CB and the VB of a quantum dot. By increasing the depth of the quantum well in the conduction band, more IB levels with bounded wavefunctions appear. In Fig. 2 we can see five IB levels; two of which are double degenerated, besides the double spin degeneracy that affects all the states.

In Fig. 1, case (b) we can observe the five levels found in our calculation. The position the authors attribute (at 77 K) to the IB levels (-125 , -175 , -235 , -305 , -370 eV) is also close to those we have obtained (at 300 K) by calculation (-49 , -82 , -142 , -251 , -361 eV), at least for the lowest level (called the fundamental level). This position can also be compared with the more exact calculations in [8] (at 4 K) with only four levels calculated (-125 , -205 , -255 , -330 eV). It is difficult to say whether our cell prototype is the same as that used for this case (b) of reference [7] because the data provided do not allow us to determine how different those for our growth are. As for the data calculated in reference [8], they differ from ours in size and symmetry (it is a lens shaped QD of 20 nm in diameter and 4 nm of height) so that differences are to be expected.

Despite the possible inaccuracies to be expected from our oversimplified offset potentials and the QD shape, the model is rather useful for understanding many details of QD physics.

The selection of parameters is indeed very important for describing the QD properties. As said before, the parameters selected are listed in Table 1. Only eight parameters need to be chosen.

The host (GaAs) bandgap at 300 K is a very well known value, found everywhere. The relative effective masses are calculated in reference [15] using the widely accepted model in [17], which considers the strain caused in the quantum wells, but that we have also estimated it as valid for QDs after observing the InAs bandgap in the QW of the same thickness, of 0.72 eV (notice that for the unstrained InAs this value is 0.418 eV), which is not very different from the value established in this paper, as described later (0.62 eV), nor from the effective masses in the InAs bulk material ($m_{cb}=0.023$, $m_{lh}=0.026$ and $m_{hh}=0.41$).

In quantum efficiency (QE) plots, the two lowest energy peaks are usually very visible. The lowest peak allows the energy difference between the states $lcb111$ and $lhh121$ to be determined (the transition $lhh111 \rightarrow lcb111$ is forbidden). Thanks to the model, this provides a relationship between the CB and the VB offsets [16]. If the VB offset is known, the CB offset may be calculated. The determination of the VB offset will be the main object of this paper.

As regards the QD dimensions, its height is easily seen in cross-section pictures from the transmission electron microscopes (TEM). The base side of the QD parallelepiped representing the QD in the EKPH is provided by the distance of the first two peaks that we have alluded to, thanks to the model, with the procedure described in [16]. The size obtained is similar to that obtained by TEM, but in our opinion more accurate (the measurement of sizes in TEM are related to the contrast mechanism, which is often based on the lattice strain) and better adapted to reproduce experiments with the EKPH.

In summary, leaving aside the effective masses, whose uncertainty has been explained, the parameters used are dependent on experimental data; this dependence is still to be explained concerning the VB offset.

2. Quantum efficiency analysis

The calculation of the photon absorption coefficients is more involved. It is described in detail in reference [11]. We discuss here the additional parameters necessary for this calculation but, to do so, we need to describe the EKPH very briefly. It is based on the development of the one-electron Hamiltonian on a basis made up of the Bloch functions in the Γ -point of the reciprocal space ($\mathbf{k}=0$) multiplied by the exponential of $i\mathbf{k}\mathbf{r}$ with $\mathbf{k}$, an arbitrary vector in the reciprocal space, usually in the first Brillouin zone. If the spin-orbit interaction is ignored the Hamiltonian matrix, which we call (H_0), is rather easy and takes the form of a matrix whose elements are functions of $\mathbf{k}$. The matrix dimension is the number of bands considered, four (cb , lh , hh and so) in our case. The eigenvalues of this matrix form the dispersion functions $E(\mathbf{k})$ of each of the four bands. However this approximation is totally unacceptable. Among other flaws, it does not produce any bandgap. The EKPH, which we call (H_{EKP}), adopts the parabolic dispersion functions deduced from the effective masses measured in the different bands as the (H_{EKP}) eigenvalues. In the EKPH approximation, the eigenvectors of (H_0) are also considered valid for (H_{EKP}).

However in (H_0) the hh and so dispersion functions are the same, these degenerate eigenvalues lead to a two-dimensional subspace of eigenvectors of which any orthogonal couple may be chosen as eigenvectors of the non-degenerate experimental dispersion functions for (H_{EKP}). An angle $\arcsin(\alpha)$ defines the eigenvectors of (H_{EKP}) univocally. The photon absorption coefficients depend on the parameter α . For values of 0 and 0.2 they give in [10] exactly the same sub-bandgap current which is measured in the prototype cell studied here; up to 0.3 the values are very similar. In this paper we use $\alpha=0.2$. Unfortunately, the calculated IQE is spikier than the measured IQE.

Further parameters to determine the absorption coefficients are the fraction of area covered by the QDs in each layer (0.1), the separation between layers (80 nm). Both parameters are obtained using an atomic force microscope (AFM) observation and sample design data (or TEM observation) and the Si doping of the GaAs. The Si acts as a donor in GaAs; the electrons provided fall in the $lcb111$ level of the QDs where the energy of these electrons is smaller. The filling of the $lcb111$ with electrons prevents further transitions to the filled states.

In Fig. 3 we present the internal QE of a prototype IBSC published in reference [18] and called SM in this reference. It is made of InAs QD embedded in a GaAs matrix. The thick line represents the curve resulting from the measurements. The curves calculated with different values of the VB offset appear as thinner lines with different dot-dash patterns. The offsets (U_{cb} and U_{vb}) for each case are given in Table 2.

The density of Si atoms is adjusted to fit the height of the first peak. It corresponds to 0.4 of electron filling factor, factor 0.6 for empty states, and this is similar to the doping determined from capacity-voltage curves. The calculated internal QE due to the QDs is rather accurate overall but its spectral distribution is less so, but there is a small difference for the different VB offsets. This has already been discussed in reference [19]. Therefore, the variation in the VB offset does not allow us to select one offset rather than another.

In our calculations we have also included, for the first time, the absorption by the wetting layer. As already mentioned, the wetting layer is actually a quantum well appearing in each layer of QDs. The calculation of the absorption of photons in quantum wells using the EKPH is presented in [20]. The offsets for the quantum well are assumed to be the same as for the QDs, both made of InAs. The introduction of the wetting layer in the quantum efficiency is rather sensitive to the value selected for the VB offset. A very good fitting is achieved by the joint selection of the VB offset, which mainly affects the height of the QE; and the wetting layer

Fig. 3. The internal quantum efficiency vs. the energy of the incident radiation for different VB offset potentials. The value of the band gap of the host material and the value of the transition $|hh121\rangle \rightarrow |cb111\rangle$ in the quantum dots remain constant. The dot/dashing patterns are found in Table 2.

Table 2
Offset potentials for IQE curves from Fig. 3.

Line	Black, Dotted	Black (best fit)	Gray	Gray, dashed	Black, dashed
(U_{ch}, U_{vb}) , eV	(0.59, 0.21)	(0.58, 0.22)	(0.54, 0.27)	(0.49, 0.21)	(0.44, 0.26)

thickness, which affects the onset energy of the strong absorption. This thickness of 0.36 nm is the result of this fitting. As regards the VB, the best fitting is 0.22 eV. Remember that once the VB fitting is determined, the CB offset is based on the energy position of the first peak, as presented in [16]. The values in Table 2 summarize the offsets to be selected. These have already been used in the spectrum in Fig. 2. The QD material (InAs) bandgap, which is 0.62 eV, is obtained by subtracting these offsets from the host material (GaAs) bandgap. The calculation for the bandgap with InAs quantum wells in GaAs is, as already said, 0.72 eV for quantum wells of the same thickness. It is normal for the bandgap with the QDs to be smaller, that is, closer to the bulk material (0.418 eV). This reflects that the strain is smaller. This also supports the frequent claim that the QD systems may be structurally perfect, free from dislocations, and therefore may lead to very effective semiconductor devices.

The use of the EKP model in this paper contains some refinements described in [19]. In particular, although the transitions from bound and virtual bound states are the main components of the sub-bandgap photon absorption, transitions from states extended in one dimension (filamentary states) [21] are dominant at the absorption of photons close to 1.2 eV, which is taken into account. Furthermore, a solar cell contains many QDs of different sizes, whose distribution is obtained using TEM. This variability has been used to determine the

Table 3

Parameters used for the calculation of the IQE of the quantum dots of Fig. 3.

Parameter	Value	Source
Fraction of area covered by QDs in each layer	0.1	AFM
Separation between QD layers (nm)	80	Design, TEM
Donor concentration (fraction of QD states)	0.4	1st QE peak value
Wetting layer thickness, (nm)	0.36	QE WL position

variance in the Gaussians representing the transition lines. These improvements reduce the spiky aspect of cruder models. However, the most important improvement for our purpose here is the introduction, as described, of the modeling of the wetting layer.

In summary, the four parameters used for calculating the IQE, in addition to those in Table 1, are detailed in Table 3.

3. Conclusions

In this paper we offer an experimental method for determining the VB QD offset and the CB offset associated to it. This provides an experimental description of the QDs in a finished device (in this case an IBSC) which is difficult to obtain otherwise.

This allows us to calculate the full spectrum of the QDs within the bandgap of the host material, which is shown in Fig. 2. It is similar to the PL signature obtained in prototype samples. Again the potential square shape of our model is too crude to be able to allow to much quantitative confidence to our found values, but it surely allows them to be accorded a qualitative description, and even a semi-quantitative value.

We want to emphasize that our offsets are based on the assumption that the QDs and the WL have the same composition. This might be not totally true (and this is a general weakness of all the modeling attempts, even those which are deemed to be very accurate). Nevertheless, we think it is the best we can obtain at the present state of the research. We firmly believe that combining modeling with experimental results is the best way to progress in a sounder interpretation of the experiments and a more accurate characterization of the QDs.

We hope the results of this paper are of interest for the experimental characterization of the QDs embedded in a solar cell and may also be useful for other semiconductor devices using QDs or even other nanostructures [22].

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