BAND STRUCTURE CALCULATION FOR QUANTUM DOT SOLAR CELLS USING K.P METHOD

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ABSTRAT

Quantum dot hetero structures are possible candidate materials for high efficiency solar cells using advanced approaches such as intermediate bands. Lattice mismatch in the epitaxial growth of quantum dot (QD) causes strain in the structure. Here we report the use of the k.p method to calculate the band structure including the effects of strain, and light and heavy holes. With the modified band gaps due to strain, a material search is performed among III-V binaries and ternaries for a high efficiency QD solar cell material with negligible valence band offsets. It is found that the condition of negligible valence band offsets severely limits the choice of materials. The closest to ideal barrier/dot material system found is $Al_{0.57}In_{0.43}As/InP_{0.87}Sb_{0.13}$ corresponding to an efficiency of 58% under x1000 solar concentration for AM 1.5 spectrum.

1. INTRODUCTION

Intermediate band solar cells (IBSCs) have been proposed as one of the approaches to overcome the single junction limit and achieve efficiencies as high as 63% [1]. Intermediate band solar cells absorb photons of energy less than the band gap of the barrier material mediated through the confined states in the dot material as schematically shown in Figure 1. Closely spaced array of quantum wells/dots has a potential to form Intermediate band solar cells. These solar cells absorb photons of energy less than the band gap of the barrier material mediated through the confined states in the dot material as schematically shown in Figure 1. The theoretical efficiency of IBSCs depends on the band gaps of the materials (barrier/dot or well) from which it is made. Detailed balance efficiency calculations have referred to certain range of band gaps for the high efficiencies (>50%). Previous attempts to search material combinations for high efficiency quantum dot intermediate band solar cells (QDIBSCs) were simply focused on the band gaps of bulk materials and did not include the effect of strain in the band gaps and valence band offset (VBO). We use the correct band gaps of barrier and dot materials with the effect of strain.

In a pseudomorphic growth of quantum dots (QD) using the techniques like MOCVD or MBE, the lattice mismatch between the substrate/barrier/dot materials causes strain in the system which causes a significant change in the band gap of the materials. Previously Identified material systems such as AlGaAs/InGaAs [2] and GaAsSb/InAs [3] for nanostructured absorbers were proposed without including the effect of strain. Here we report the effect of strain in the band gap and search material systems among direct band gap III-V semiconductors binaries and ternaries for multiple transition solar cell with negligible valence band offset.

Optimum band gaps for intermediate band solar cell (IBSC) as calculated by detailed balance modeling, at maximum solar concentration for blackbody radiation are E_G=1.95eV, E_{CI}=0.71eV and E_{IV}= 1.24eV [1]. Calculation of limiting efficiency of IBSC under terrestrial AM 1.5 spectrum has been reported with broader range in the band gaps for efficiency higher than 50% for moderate (~100 suns) as well as high concentration [4]. We have calculated the theoretical efficiency of III-V substrate/barrier/QD combinations under terrestrial AM1.5 spectrum. The exact theoretical efficiency depends on the position of the middle energy level (E_{CI}) in the structure which in turn depends on the size and shape of the quantum dots and their uniformity.

In order to search material combinations for QD solar cells we have calculated the strain profile in and around the QD due to lattice mismatch between the barrier and dot material, and its effect on the band diagram (Γ-point).

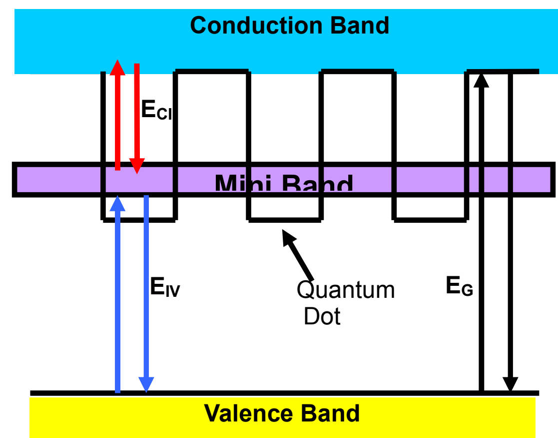

Figure 1: Schematic diagram of Intermediate band material

The remainder of the paper is organized as follows. In section two the authors review the calculation of strain and

the band structure for quantum dots. In section three the authors describe the constraints used for the material combination for QD solar cell including the effect of strain. Section four gives the result of the material search obtained by using k·p calculation including the strain to calculate band structure. Section five concludes the paper.

2. STRAIN AND BAND STRUCTURE

When a material is epitaxially grown on a substrate with significant lattice mismatch (e.g.InP/InAs, 3.2%), initial growth occurs layer by layer but the accumulation of strain energy causes the formation of isolated quantum dots [5]. The shape and size of epitaxially grown self assembled QD's depend on growth conditions and materials parameters. The shape of these QD's is not known exactly and it is reported to be as that of a lens, pyramid or truncated pyramid [6,7].

For our calculations the shape is considered to be that of truncated pyramid as schematically shown in Figure 2, with base width 20 nm and height 5nm. The initial misfit strain is defined as:

$$\varepsilon_0 = \frac{(a_s - a_l)}{a_l}$$

where, a_s and a_l are the lattice constants of substrate or barrier and quantum dot materials, respectively. The misfit strain is taken to be negative for material under compression.

We use an analytical method [8] based on continuum theory of elasticity to calculate the strain distribution in and around a QD and incorporate this strain induced elastic potential to calculate the band parameters of the structure using eight band **k·p** method [9,10].

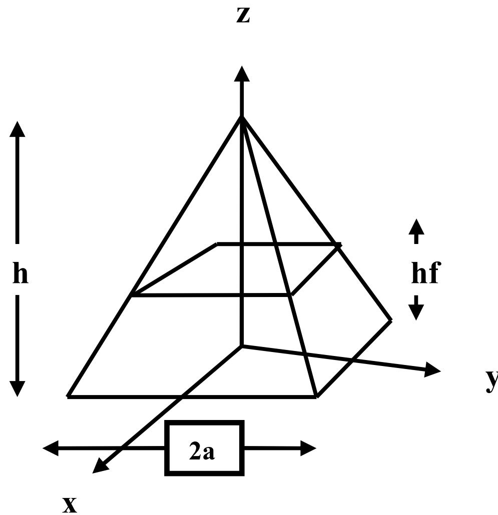

Figure 2: Schematic diagram for the shape of a quantum dot under consideration, square based truncated pyramid with base width 2a and height 'hf' with f as truncation factor.

The hydrostatic and biaxial strains which have the effect in band structure are given by;

$$\varepsilon_h = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \quad \textbf{[1]}$$

$$\varepsilon_b = \varepsilon_{zz} - \frac{1}{2}\left(\varepsilon_{xx} + \varepsilon_{yy}\right) \quad \textbf{[2]}$$

Where $\varepsilon_{xx}, \varepsilon_{yy}$ and ε_{zz} are diagonal strain components of strain tensor. The hydrostatic strain is almost constant inside the dot where as the biaxial strain has strong spatial variation.

The k·p method has had considerable success in band structure calculations for bulk and heterostructures. In direct band gap semiconductors the optoelectronic transition mostly happens at the band edge (Γ-point) and the method finds out the band structure by expanding the wave function in terms of band edge Bloch functions $u_{n0}(r)$. In k.p method strain is included via deformation potential theory. The conduction band edge energy at k=0 (Γ-point) is given by:

$$Ec = E_c^0 + \delta Ec \quad \textbf{[3]}$$

Where E_c^0, is the band edge energy of the conduction band in unstrained case and δEc is the shift in it due to strain which is expressed as;

$$\delta Ec = ac(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$$

The heavy and light hole energies of the strained material at Γ-point are no longer degenerate and their energies at that point is given by,

$$Ehh = \left(Ev, av + \frac{\Delta_0}{3}\right) + a_v\varepsilon_h - b\varepsilon_b \quad \textbf{[4]}$$

$$Elh = Ev, av - \frac{\Delta_0}{6} + a_v\varepsilon_h + \frac{1}{4}b\varepsilon_b + \frac{1}{2}\sqrt{\Delta_0^2 + \Delta_0 b\varepsilon_b + \frac{9}{4}b\varepsilon_b} \quad \textbf{[5]}$$

In these expressions $\mathbf{a_c}$ is the conduction band deformation potential, $\mathbf{a_v}$ and **b** are the valence bands hydrostatic and shear deformation potentials, Ev,av and Δo are average valence band energy and spin orbit split off energy respectively. The material parameters for the calculation of band gap, VBO and strain are taken from references [11,12].

3. CONSTRAINTS FOR MATERIAL SELECTION FOR QD SOLAR CELL

The main factors limiting the material search are the strain and the band gaps. The choice of substrates is limited to commercial availability of III-V binaries. For this paper the substrates considered are GaAs, InP, InAs and InSb. For strain, two cases are considered to broaden the criteria of material search.

1. Barrier fully relaxed and

2. barrier fully strained.

Both of these cases are viable from experimental point of view. The first case mentioned above gives more flexibility on the choice of barrier.

Three main criteria are considered for material identification for high efficiency QD solar cells. The first criterion is the negligible valence band offset (VBO) between the barrier and dot materials. Due to the higher effective mass of holes in valence band, even a small confinement potential gives rise to many bound states very close to each other so that the holes simply thermalize through these states and consequently reduce the open circuit voltage (V_{OC}). The other reason for negligible VBO is that the lifetime of the carriers is reduced as they can easily recombine between the bound states rather than bound to valence band continuum or from valence band continuum to conduction band continuum. We have taken the VBO to be ~3/2kT where k is the Boltzmann constant and T is room temperature. The second criterion is the requirement of materials to form quantum dot in an epitaxial growth like metal-organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE) when grown on a barrier material. For the first case mentioned above we have taken the lattice constant of dot material to be greater than 2% to that of barrier and for the second case the lattice constant of dot material was taken to be greater than 2% to that of substrate. The third criterion is regarding the band gaps. Barrier band gap is taken to be greater than 1 eV and conduction band offset (CBO) greater than 0.4 eV. The values of band gaps expressed in this paper are the ones at room temperature after the including the effect of strain.

4. RESULTS AND DISCUSSION

An extensive calculation was done with the constraints mentioned in previous section for both fully relaxed and fully strained barrier. A code was written to include all the III-V binaries and their alloys with direct band gap. The strain profile, as mentioned earlier, was calculated by analytical method and was incorporated in the k·p hamiltonian to find out the band gaps and the valence band offsets. The target VBO between the barrier and the dot materials was taken to be within ±0.06 eV. Valence band edge energies are no longer degenerate at the strained case, and the VBO taken in our case is for the heavy hole band edge energies.

Table 1 contains the material combination (substrate/barrier/dot) nearest the target parameters for case of fully relaxed barrier. The $InP_{1-y}Sb_y$ dot in $Al_{1-x}In_xAs$ has negligible valence band offset. The conduction band offset of the materials in this case is about 0.5 eV. Specifically, for a the $InP_{0.87}Sb_{0.13}$ dot in $Al_{0.57}In_{0.43}As$ matrix, the band gap(E_G) of barrier is 1.707 eV, and the band gap of dot 1.183 eV as shown in figure 3. The theoretical efficiency for this material triad is 58% under 1000 solar concentrations for AM 1.5G spectrum which is very close to the maximum efficiency (61%) at this concentration.

Material combinations for case of fully strained barrier are presented in table 2 and 3 for GaAs and InP substrates respectively. The band diagram of one of the material combination: InP QD in $Al_{0.63}In_{0.37}As$ matrix on GaAs substrate is shown in figure 4. This material combination has the band gap of barrier material 2.079 eV and the band gap of dot material 1.62 eV. The band diagram of $InAs_{0.41}Sb_{0.59}$ QD in $Al_{0.21}Ga_{0.79}Sb$ matrix on InP substrate is shown in figure 5. This material combination has the band gap of barrier material 1.218 eV and the band gap of dot material is 0.52 eV.

Barrier	x	Dot	y
$Al_{1-x}In_xAs$	[0.43→0.54]	$InP_{1-y}Sb_y$	[0.13→0.21]

Table 1: Barrier/QD materials combination for fully relaxed barrier.

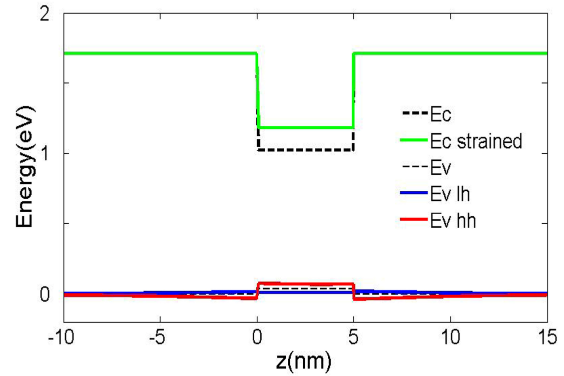

Figure 3: $InP_{0.87}Sb_{0.13}$ dot in $Al_{0.57}In_{0.43}As$ matrix on GaAs substrate.

Barrier	X	Dot	y
$Al_{1-x}In_xAs$	[0.37]	$Ga_{1-y}In_yP$	[0.87 →1.0]
	[0.37→0.43]	$InAs_{1-y}P_y$	[0.8→ 1.0]
	~0.5	$InAs_{1-y}P_y$	~0.6

Table 2: Material combinations on GaAs substrate for fully strained barrier.

Barrier	x	Dot	y
$Al_{1-x}Ga_xSb$	[0.79→0.88]	$InAs_{1-y}Sb_y$	[0.58→0.73]
$Al_{1-x}In_xAs$	0.2	$InP_{1-y}Sb_y$	[0.71→0.74]
$Al_{1-x}In_xAs$	0.59	$InAs_{1-y}P_y$	0.37

Table 3: Material combinations on InP substrate for fully strained barrier.

In the case of fully strained barrier the effect of compressive strain in the barrier tends to minimize the valence band offset as well as increases the barrier band gap, which is favorable for the material search with the constraints mentioned in section three. The conduction band edge in the barrier is raised from its unstrained case when the barrier lattice constant is higher than that of substrate as shown in figure 4 due to the compressive strain. On the other hand in the barrier fully relaxed case the barrier band gap does not change much.

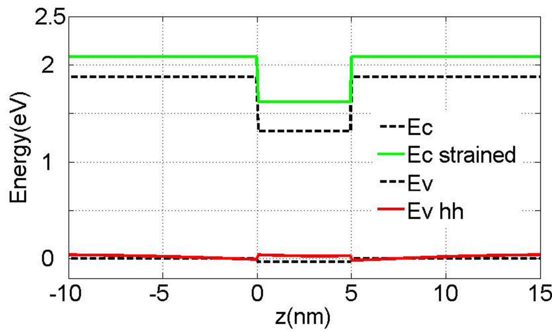

Figure 4: InP QD in $Al_{0.63}In_{0.37}As$ matrix on GaAs substrate (barrier fully strained).

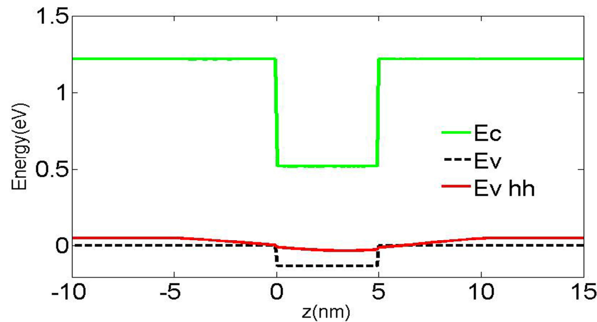

Figure 5: $InAs_{0.41}Sb_{0.59}$ QD in $Al_{0.21}Ga_{0.79}Sb$ barrier on InP substrate (barrier fully strained).

A few specific material combinations on a GaAs substrate for the case of fully strained barrier are listed in table 4 and those for the case of fully relaxed barrier are listed in table 5. In both the cases the efficiencies listed are at 1000 solar concentration calculated from detailed balance scheme for AM 1.5 solar spectrum.

Barrier	Dot	E_G Bar (eV)	E_G Dot (eV)	Eff (%)
$Al_{0.63}In_{0.37}As$	$Ga_{0.13}In_{0.87}P$	2.08	1.67	48
$Al_{0.63}In_{0.37}As$	$Ga_{0.05}In_{0.95}P$	2.08	1.65	48
$Al_{0.63}In_{0.37}As$	InP	2.07	1.65	48
$Al_{0.62}In_{0.38}As$	$InAs_{0.11}P_{0.89}$	2.05	1.55	49
$Al_{0.6}In_{0.4}As$	$InAs_{0.15}P_{0.85}$	2.0	1.52	48
$Al_{0.50}In_{0.50}As$	$InAs_{0.41}P_{0.59}$	1.77	1.30	53

Table 4: Barrier/Dot materials combinations on a GaAs substrate (barrier fully strained) with corresponding efficiencies.

Barrier	Dot	E_G Bar (eV)	E_G Dot (eV)	Eff (%)
$Al_{0.57}In_{0.43}As$	$InP_{0.87}Sb_{0.13}$	1.71	1.14	58
$Al_{0.54}In_{0.46}As$	$InP_{0.85}Sb_{0.15}$	1.62	1.09	57
$Al_{0.51}In_{0.49}As$	$InP_{0.83}Sb_{0.17}$	1.54	1.05	56

Table 5: Barrier/Dot materials combinations on a GaAs substrate (barrier fully relaxed) with corresponding efficiencies.

5. CONCLUSION

The strain has significant effect in band structure of nanostructure materials. Material combinations for QD intermediate band solar cell with negligible valence band offset are presented taking strain into account. It is found that the material combinations for the optimum band gaps are limited by the ability to get negligible VBO. The theoretical efficiency of these material combinations as calculated for AM1.5 solar spectrum with detailed balance scheme is obtained up to 58% under x1000 solar concentration.

References

[1] A. Luque, A. Marti, Phys. Rev. Lett. , 78 (1997) 5014.
[2] A. Martí, L Cuadra, A. Luque, IEEE Trans. Electron devices Vol.49. no.9, (2002) 1632.
[3] M. Y. Levy, C. Honsberg, IEEE Transactions on Electron Devices vol 55, no. 3, (2008) 706.
[4] Stephen P. Bremner, Michael Y. Levy, Christiana B. Honsberg Applied Physics letters 92, (2008) 17110.
[5] D.Bimberg, M. Grundmann, N. N. Ledentsov, Quantum dot Heterostructures, John Wiley and Sons.
[6] Y. Nabetani, T. Ishikawa, S. Noda and A. Sasaki, J. Appl. Phys.71, 347.
[7] L Ouattara et all Nanotechnology 15 (2004) 1701.
[8] G. S. Pearson, D.A Faux, J. Appl. Phys.,88 (2000) 730.
[9] T. B. Bahder, Phy. Rev. B 45 (1992)1629.
[10] Craig Pylor, Phys. Rev.B 57 (1998) 7190.
[11] Chris G. Van de Walle, Phys. Rev. B 39 (1989) 1871.
[12] I. Vurgaftman, J.R Meyer, L.R Ram-Mohan, J. Appl. Phys. 89 (2001) 5815.