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Intraband absorption for normal illumination in quantum dot intermediate band solar cells

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ABSTRACT

In the current intermediate band solar cells made with InAs quantum dots (QDs) in GaAs, the transitions by absorption of photons between the intermediate band and the conduction band for illumination normal to the cell surface is very weak or, more often, undetectable. We model the QD as a parallelepiped potential well and calculate the envelope function of the electron wavefunctions. By obtaining the dipolar matrix elements we find that, with the present shapes, this absorption is forbidden or very weak. Deeper QDs with smaller base dimensions should be made to permit this absorption.

1. Introduction

The intermediate band (IB) solar cell was proposed [1] to increase the efficiency of solar cells. In an IB solar cell, three absorption bands can produce electron–hole pair generation: the VB→CB (VB, valence band; CB, conduction band) transitions (the only one in single gap cells, i.e. cells unmodified with quantum dots) and two successive VB→IB and IB→CB transitions. A very high detailed balance efficiency limit of about 63% versus 41% for a single junction solar cell was calculated.

Prototype cells have been manufactured by several groups using InAs quantum dots (QDs) in a GaAs matrix [2–6] with a top efficiency of over 18% [6]. However, thermal and tunnel escape, rather than a second photon, are responsible for the IB→CB transition, also called intraband transition (because in these QDs the IB is detached from the CB) and, if this happens, the current will be increased but at the expense of a lower voltage. Two photons are necessary for thermodynamic reasons if the voltage is to be higher than the quantum efficiency (QE) threshold [7].

The choice of QDs instead of quantum wells (QWs) is in part to avoid the continuum of states represented by travelling functions in the (x, y) plane that might provide an easy thermalization of the IB and the CB. But further to this, it is known that the IB→CB transition is forbidden (see for instance [8], p. 155) in QWs for vertical photons (not so for photons travelling in the (x, y) plane). That is why the quantum dot infrared detectors (QDIDs) [9] came in as an attempt to substitute the QWID.

In our QD IB cells, two-photon quantum efficiency (QE) experiments have been carried out to verify experimentally the desired mechanism [10] that, although present (in several batches differing in QD size, composition, etc.), has been found to be very weak, about three orders of magnitude below the VB→IB, and only measurable at temperatures below 80 K (when thermal escape is reduced). The purpose of this paper is to determine whether there is some fundamental reason that prevents the desired optical IB→CB transitions. There might indeed be a technological reason: the IB is not sufficiently doped as to permit a partial filling of the IB—a condition [1] necessary for the optical IB→CB transition—but even in cases of proper doping (determined by capacitive experiments) the two-photon current is small or undetectable.

2. Eigenfunctions and eigenvalues

In the $\boldsymbol{k}\cdot\boldsymbol{p}$ approximation the wavefunctions of the electrons in presence of a QD are described by an envelope function that modulates the periodic part $u_0(\boldsymbol{r})$ of the material Bloch function (for $\boldsymbol{k}=0$) that carries the atomic details. In the case of an intraband transition the one-band approximation is adequate [11]; at least for qualitative and semiquantitative analyses. The envelope function is the eigenfunction of the following Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\varphi + V(\mathbf{r})\varphi = E\varphi \tag{1}$$

where m is the effective mass of the electrons in the CB and $V(\mathbf{r})$ is the minimum of the CB.

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The purpose of this paper is to get a qualitative insight so that the mathematics will be simplified as much as possible. Thus, in this equation we are considering a scalar effective mass (spherical CB minimum) constant everywhere (we take the geometrical mean of the effective masses of the dot and barrier materials) and a square potential well whose height is the offset U of the CB bottom in the QD and host materials. The strain effects and piezoelectric potentials that are very important in a quantitative analysis are disregarded here. The shape of the low potential region (the QD) is usually admitted to be a strongly truncated [12], squat, quadrangular pyramid but we shall use a shallow squared box of dimensions $2a$, $2b$, and $2c$.

Later we shall justify the use of the separation-of-variables method. Thus, we set $\psi(x,y,z)=\alpha(x)\beta(y)\gamma(z)$. Each one-dimensional function must then be the solution of a one-dimensional Schrödinger equation with a symmetric one-dimensional potential well. This is a simple problem that can be found in any quantum mechanics textbook (for the one-dimensional case). We describe it here to set the nomenclature. In the case of $\gamma(z)$the potential will be 0 for $|z|<c$ and U outside this region. A similar discussion can be made for the $\alpha(x)$ and $\beta(y)$ functions. For $\gamma(z)$ the confined one-dimensional solutions inside the $(-c, c)$ interval will be the well-known odd ($\sin(k_z z)$) or even ($\cos(k_z z)$) functions that, for $z>c$, have to be matched for function and derivative continuity with exponential functions of the type $\exp(-k_z z)$ and its odd or even symmetrical for $z<-c$. Calling $\zeta^2=(2m/\hbar^2)U$, we obtain $k_z^2=(2m/\hbar^2)E_z$and $\kappa_z^2=\zeta^2-k_z^2$ to verify the Schrödinger equation inside and outside the well. To verify the continuity of the logarithmic derivative, $-\tan(k_z c)=k_z c/\sqrt{\zeta^2c^2-k_z^2c^2}$ and $\cot(k_z c)=k_z c/\sqrt{\zeta^2c^2-k_z^2c^2}$ must be fulfilled for odd and even wavefunctions, respectively. These equalities are represented in Fig. 1 (with data of one of the cells actually measured). The grey curve $k_z c/\sqrt{\zeta^2c^2-k_z^2c^2}$ has a vertical asymptote for $\zeta^2c^2=k_z^2c^2$. This means that there are a finite number of confined states. The bigger the well dimension c the further to the right in the figure is the asymptote located and more solutions (energy levels) appear, as can be seen by comparing Fig. 1(a) and (b). At the same time, the bigger the c the smaller the energy interval between energy levels (because $\Delta k_z c\approx\pi/2$ and $k_z\propto\sqrt{E_z}$).

The eigenfunctions are characterized by their value of $k_z c$. Symbolically we can label them by a quantum number that will be 1 for the solution to the left, 2 for the next one, etc. Even functions correspond to the odd quantum numbers and vice versa.

Similar arguments can be used for $\alpha(x)$ and $\beta(y)$.

The eigenvalues of $\psi(x,y,z)$ are $E=E_x+E_y+E_z-U$ (we subtract U to change the energy origin and to set it at the bottom of the host material CB). Actually, Fig. 1 (a)and (b) are related to the vertical and horizontal dimensions, respectively. There is one eigenvalue for the vertical dimension and five for each horizontal dimension, in total $5\times5\times1=25$. They are represented in Fig. 2. States with quantum numbers $(u,w,1)$ and $(w,u,1)$ have same energy. This degeneracy is removed if the strain field is considered (but the splitting may be not too strong). Note that confined levels above the potential well, called virtual bound states VBS, may occur in three dimensions (never in one dimension) as described in Ref. [13]. Four levels appear as found experimentally [14] and theoretically [5] inside the potential well.

If only one of the dimensions is very large, many closely spaced levels will appear that when the length approaches infinite will form a continuum, as occurs in quantum wires and wells.

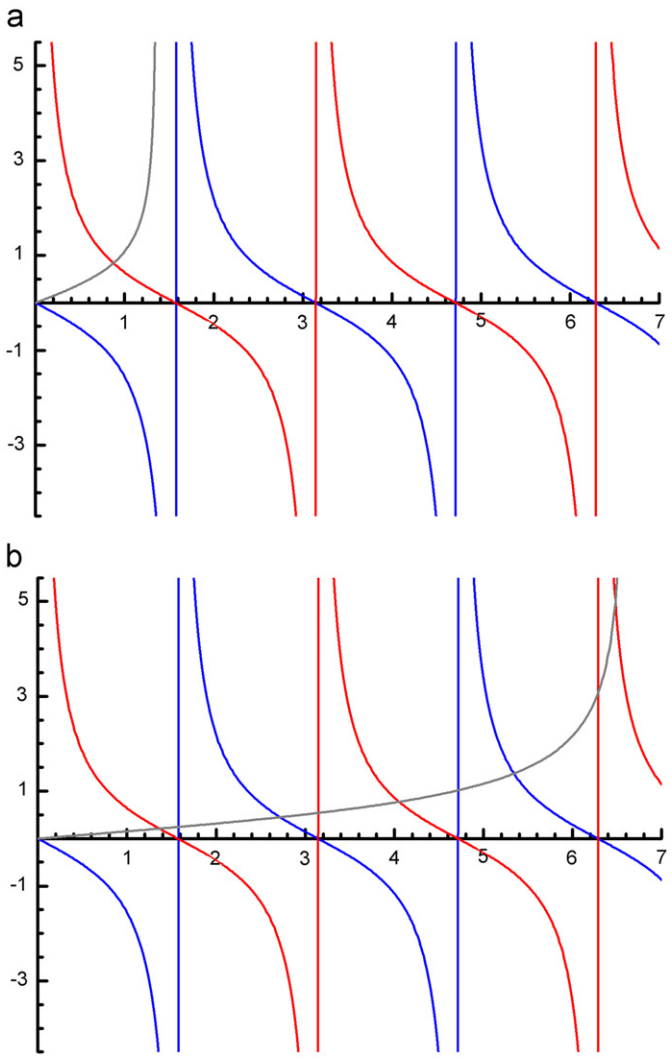

Fig. 1. The two members of the equations $-\tan(k_z c)=k_z c/\sqrt{\zeta^2c^2-k_z^2c^2}$ and $\cot(k_z c)=k_z c/\sqrt{\zeta^2c^2-k_z^2c^2}$ vs. $k_z c$ for $U=0.542$ eV, $m=0.0613$ times the electron mass; (a) $c=1.75$ and (b) $=8.5$ nm. Red curve for odd and blue for even eigenfunctions.

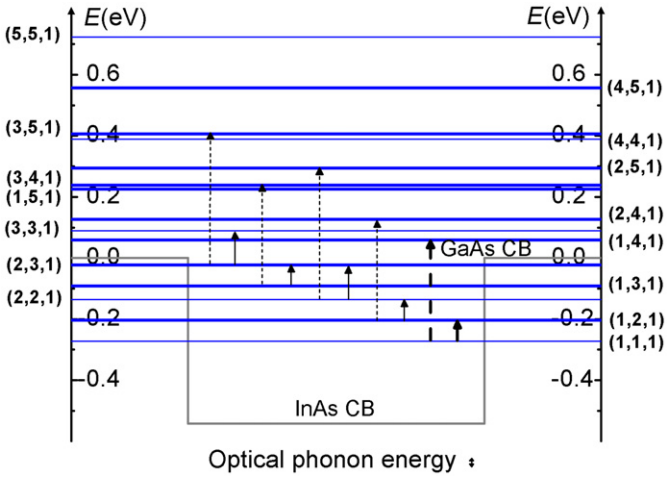

Fig. 2. Horizontal lines: confined state energy levels in an InAs QD in GaAs; thick lines are double degenerated (besides spin degeneracy). Solid/dashed vertical arrows: strong/weak permitted optical absorptions departing from negative energy levels. Thick arrows for absorptions departing from the fundamental state. The energy of an optical phonon is drawn for comparison.