Three-dimensional assemblies of semiconductor quantum dots in a wide-gap matrix providing an intermediate band for absorption

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Citation: Journal of Applied Physics 112, 114320 (2012); doi: 10.1063/1.4767377
View online: http://dx.doi.org/10.1063/1.4767377
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/112/11?ver=pdfcov
Published by the AIP Publishing

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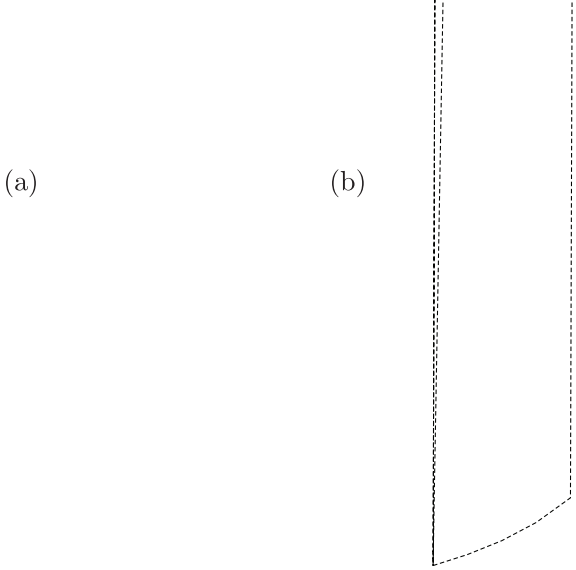
$$v_\alpha(\ ) = \boldsymbol{I}_{0,\alpha} \frac{^2 - \boldsymbol{I}_{1,\alpha}}{\boldsymbol{I}_{2,\alpha} \boldsymbol{J}_{3,\alpha}{}^2 - 1}. \tag{5}$$

The material and atom specific parameters for InAs, GaAs, InP, GaP, and their alloys are the same as those given in Refs. 2, 23, and 24, while for InSb and GaSb we used the values provided in Table III.



such that the sequence of tensile-compressive strain—$\lambda_{film} < \lambda_0 < \lambda_{mat}$—leads to zero overall in-plane stress?

We briefly revisit in this section two methods of strain balance determination, using atomistic and continuum elasticity (AE and CE). We show, with a specific example of an InAs/(In,Ga)P quantum well system, that, in many cases, the CE results are not completely reliable, since this method is too "far sighted," missing significant contributions of interatomic coupling in the limit of thin layers.

A. [illegible]

In order to predict the desired geometry, that is, the appropriate $_{mat}/_{film}$ ratio, one has to calculate the elastic strain energy $E =$ of the epitaxial combination of the two materials, where is the volume of the sample. The stress and strain tensors $\underline{\sigma}$ and $\underline{\varepsilon}$ are related by

$$\underline{\sigma} = \frac{\partial}{\partial \underline{\varepsilon}} = \frac{1}{} \frac{\partial E}{\partial \underline{\varepsilon}}. \tag{6}$$

Choosing a frame of reference with its -axis along the growth direction, the in-plane components of the stress tensor $\underline{\sigma}$ can be calculated after imposing the condition that the system is relaxed along , i.e., that the surface and all the interfaces are stress-free.[2]

Here, we calculate directly the elastic energy E and the density on an atomistic level by making use of the VFF functional, Eq. (1). From this, the stress tensor $\underline{\sigma}$ can be obtained by numerical evaluation of the energy gradient entering Eq. (6). For a given film material (fixed lattice constant λ_{film} and thickness $_{film}$), one varies the composition and thickness of the matrix material evaluating, at each point, the resulting in-plane stress. Determining the zeros of this quantity provides the thickness $_{mat}$ corresponding to a strain-balanced $_{mat}/_{film}$ combination.

B. [illegible] (001)

The CE provides a relatively simple, alternative way to evaluate the elastic energy and its density entering Eq. (6). As shown by various authors,[2,34,35] the CE-derived strain balance condition only depends on the elastic coefficients of the two materials involved. For the (001) direction, this condition reads

$$\frac{^{(001)}_{mat}}{^{(001)}_{film}} = -\frac{^{(001)}_{film}\,\varepsilon_{\parallel}(\mathrm{film})\,\lambda_{mat}}{^{(001)}_{mat}\,\varepsilon_{\parallel}(\mathrm{mat})\,\lambda_{film}}, \tag{7}$$

where

$$\varepsilon_{\parallel}(\alpha) = \frac{\lambda_0 - \lambda_\alpha}{\lambda_0} \quad \text{for} \quad \alpha \equiv \text{film or mat}, \tag{8}$$

and

$$^{(001)}_{\alpha} = {}_{11,\alpha} + {}_{12,\alpha} - \frac{2\,{}^{2}_{12,\alpha}}{{}_{11,\alpha}} \quad \text{for } (001), \tag{9}$$

with $_{11,\alpha}$, $_{12,\alpha}$ the elastic constants of the film and matrix materials. Obviously, the strain balance ratio of Eq. (7) shows no thickness dependence of the constituents (film or matrix) in its right-hand side.

We compare here AE and CE determination of the strain balance condition for an InAs quantum well (QW) deposited on a GaAs(001) substrate embedded in an (In,Ga)P alloy matrix. The thickness of the QW is kept fixed while the composition and the thickness of the barrier are sought for the strain balance condition appropriate to each QW thickness. Our results are shown in Fig. 2(b) where the corresponding lattice constants of the QW and the substrate are also indicated, labeled by vertical bars. The way the results of such calculations are to be interpreted is the following: one picks a certain QW thickness, e.g., 2 MLs, and reads, from the top axis, a desired composition ^{x} of the $In_xGa_{1-x}P$ matrix. The corresponding ordinate of the 2 ML curve provides the ratio $_{mat}/_{film}$ for which the two layers are at strain balance condition. Using the matrix lattice constant determined this way, in conjunction with that of the substrate and of the film, allows a direct estimation of the in-plane strain. The basic principle of strain balance becomes now obvious: at a fixed film-substrate compressive strain, the smaller the tensile

of 23 at. %. Contrary to the expectations, the QDs size reduction is accompanied by a red-shift of the PL peak. This reduction of the HOMO-LUMO separation is mainly due to a raise in energy of the initial (hole) state. Indeed, our calculations for epitaxially strained $GaAs_{0.8}Sb_{0.2}$ alloy shows a 0.21 eV upwards shift of the VBM as compared to GaAs. As a consequence, the InAs hole states are now energetically below the Ga(As,Sb) matrix VBM. This result is in agreement with the [illegible] results of Ban [illegible].[13] who also obtain a zero hole levels offset ΔE_v, a very encouraging result for IBSC. As can be seen in Fig. 3(c), also $\Delta E_{\cdot} = E$ is increased, 0.39 eV, as compared to the benchmark system InAs/GaAs. This is caused by the higher energy (on an absolute scale) of the CBM in the strained $GaAs_{0.8}Sb_{0.2}$ as compared to GaAs. The single-particle HOMO-LUMO separation (corresponding to $E_{\cdot}$) for $InAs/GaAs_{0.8}Sb_{0.2}$ QD we obtained is 1.01 eV, showing no change versus InAs/GaAs. In contrast, the calculations of Ban [illegible].[13] give a 1.14 eV value, slightly higher than ours. From the point of view of IBSC functionality, two negative aspects need to be mentioned: (i) the band gap of the matrix (1.40 eV) and thus the expected [illegible] is smaller than in GaAs, and (ii) on a GaAs(001) substrate, both the QD and the matrix are introducing a compressive strain that might accelerate the detrimental strain accumulation when several QD layers need to be grown.

( ) [illegible] 0.3 [illegible]0.7 [illegible] [illegible] . 3( )/: Extremely popular in photovoltaics, this alloy has not yet been studied as potential matrix for a QD system. Known as exhibiting a wide band gap, our calculations show that even under the biaxial strain of the GaAs(001) a large, 2.12 eV, direct band gap can be expected. Despite the hole levels offset being high, 0.42 eV, that would reduce the open circuit voltage, we expect a QD-IBSC based on $InAs/In_{0.3}Ga_{0.7}P/GaAs(001)$ to show improved solar cell characteristics versus the benchmark system. Indeed, such

( ) , , , 0.3 $I_{0.7}$ I $r_{\dagger}^{\lambda}$ $F_{\dagger}$. 4( )/: This system is a variation of system (C) discussed above which, as we could see, along with certain promising features like a wide band gap and a large $\Delta E_{c} = E$, also exhibits an inconveniently large ΔE_{v} (hole levels offset) that drastically reduces the open circuit voltage . The use of InP as a QD material may appear justified by the fact that the valence band offset between InP and GaP is relatively small, the InP VBM lying 0.11 eV above that of GaP.[25] As can be seen in Fig. 4(b), the

( ) [illegible] $GaAs_{0.6}Sb_{0.4}$ [illegible] (001) [illegible]- [illegible] [illegible] 5( )/: As a result of the biaxial strain, the VBM of $GaAs_{0.6}Sb_{0.4}$ on InP(001) is lifted as compared to Ga(As,Sb) on GaAs(001). This leads to a similar beneficial effect as for the InAs/Ga(As,Sb) system (B): the hole levels offset ΔE_v is zero. Another positive aspect of this system is that the electron levels offset remains practically of the same size as in InAs/GaAs. A serious problem, however, is the low predicted value, 1.03 eV, of the band gap E of the Ga(As,Sb) under biaxial strain. An alternative to remove this inconvenience might be provided by the alloying of the matrix, e.g., with Al, and thus enhancing the band gap of the matrix.

III. C[illegible] S[illegible]

Taking a prototype geometry for a QD-matrix-substrate system, we have calculated the energy level alignments for a series of III-V compounds and alloys and evaluated their potential to provide the desired offsets required for a QD-IBSC implementation. In doing so, we used a multi-band atomistic pseudopotential approach, with a high level of accuracy and prediction ability. Our investigations started from a widely used QD-IBSC benchmark system, InAs/GaAs, and analyzed the evolution of the relevant energy differences: band-gap, electron, and hole level offsets, HOMO-LUMO separation, upon compositional changes of the (i) dot and (ii) matrix materials. We surveyed some of the "usual suspects" amongst the III-V systems and compared their electronic structure against that of the benchmark system as well as from the point of view of the ideal case of a maximum efficiency. In addition, we have performed atomistic elasticity calculations for an InAs/(In,Ga)P/GaAs(001) quantum well to determine the strain balance condition for such a structure. These results have shown that the simple methodology provided by continuum elasticity is limited in validity for the case of thin layers.

Our investigations have shown that, technological difficulties notwithstanding, some QD-matrix-substrate systems could make the subject of more detailed experimental and theoretical investigations owing to their positive prognosis for a QD-IBSC realization. The systems we found to fulfill these characteristics are (in QD/matrix notation):

(i) In(As,Sb)/GaAs with the IB formed by the dot-confined holes and positioned 0.34 eV above the GaAs VBM. With an adequate choice of the substrate the system could be strain balanced, while matrix alloying with Al may lead to an increase of the main band gap.

(ii) $InAs/In_{0.3}Ga_{0.7}P$ with the IB formed by dot-confined electron levels, and with a wide, direct band-gap matrix. We have shown, by AE calculations, that such a material combination can be strain balanced on a GaAs(001) substrate. Moreover, the matrix remains a direct band gap semiconductor even under this biaxial strain. From all the investigated systems, these QD-matrix-substrate combinations came to the closest agreement with the E /E values prescribed for the ideal maximum efficiency under concentrated radiation.

(iii) $InAs/GaAs_{0.6}Sb_{0.4}/InP(001)$ is yet another system with a potential for strain balance exhibiting a zero hole levels offset. This is equivalent to no "energy offset caused" loss in the open circuit voltage, which, in turn, could be enhanced by appropriate alloying of the matrix.

We have restricted our study to a quite common class of semiconductors, formed by the III-V group elements. Without exhausting all possibilities, our calculations have shown that, while several combinations appear to be quite promising, it is nevertheless necessary to extend the search for appropriate QD-IBSC materials beyond this class. Targeting solely the desired characteristics mentioned here—appropriate energy level alignment and preventing large strain accumulation in QD stacks—a minimum set of design principles can be summarized as follows: (veerf.2405.5((com7.2(d)3910.53.6(i)7.ze)15.2.zewe
tions.Hadot.6(a)10.5(t.7(n)12.4(gc2(d)0(o)13.7(s)0(s)16r6.1(o)0TJ0 -1.201

ideally zero $I_{,}$ $\mathcal{S}$ strain-induced band edge effects have been taken into account. In this context, it is worth mentioning that, regardless of the sign of the biaxial strain (tensile or compressive), the splitting of the Γ_{15v} levele6D2.084.2285.0286 0l95.2(tw)21.31llsr