Physica E 41 (2009) 1466–1468

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Concentration and band offset dependence of the electronic basic transition of cubic $In_xGa_{1-x}N/In_yGa_{1-y}N$ quantum wells

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A R T I C L E I N F O

Article history:
Received 20 September 2008
Received in revised form
9 April 2009
Accepted 14 April 2009
Available online 21 April 2009

PACS:
73.21.Fg
71.20.Be
71.20.Nr

Keywords:
Quantum wells
Electronic structure
Semiconductor compounds

A B S T R A C T

We calculate the transition energy from the first level of holes to the first level of electrons for cubic $In_xGa_{1-x}N/In_yGa_{1-y}N$ quantum wells. We employ the empirical tight binding approach with an sp^3s^* orbital basis, nearest neighbour interactions and the spin–orbit coupling, together with the surface Green function matching method. For the alloy, we use the virtual crystal approximation. We take into account the strain in the well. We assume a value of 0.65 eV for the InN bandgap and 3.3 eV for the GaN gap. Using a value of 20% for the valence band offset, we study the transition energy behaviour varying the well width for the sets of concentrations $x = 0.3$, $y = 0.02$ and $y = 0.05$; $x = 0.15$, $y = 0.05$; and $x = 0.16$, $y = 0$. For the concentrations $x = 0.16$, $y = 0$, we also study the influence of the band offset using values of 20%, 50% and 80% for the valence band offset. We compare our calculations with experimental data from hexagonal and cubic quantum wells, and with other theoretical calculations for cubic quantum wells. The comparison of the calculations with the experimental results from hexagonal quantum wells is good. The theoretical energy transitions are 0.35–0.5 eV higher than those obtained experimentally for cubic quantum wells.

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1. Introduction

The III–V GaN, AlN and InN nitrides, and their alloys, have received considerable attention in the last 10 years due to their potential in the fabrication of optoelectronic devices for optical communications, solar cells, transistors, optical disks and lighting. In particular, the bandgap of InN has been subject to controversy. The last InN bandgap reported value is 0.65 eV or less [1], very different to the first one suggested (1.9 eV). This extends the usable bandgap energy of the nitrides and their alloys from 0.65 to 6.2 eV. Thus, in principle, emitting devices from infrared to ultraviolet, including the whole visible region, can be fabricated. The nitrides crystallize in the stable hexagonal (wurtzite) structure, but they also can be grown in the metastable cubic (zincblende) structure. The bandgap of zincblende InN is close to that of wurtzite InN within 1% [2]. Currently, nitride-based quantum wells are grown along the polar *c*-direction of the wurtzite structure, where there is a large internal electric field which causes a shift of optical transitions and a reduction in the oscillator strength, reducing the efficiency of optoelectronic devices which employ quantum wells [3,4]. Quantum wells grown with cubic structure in a (0 0 1) direction would be attractive because they do not have internal electric fields [3]. Experimental works about blue emission laser diodes based on hexagonal $In_xGa_{1-x}N/In_yGa_{1-y}N$ quantum wells have been reported with low concentrations of In in the barriers [3,5]. There are also recent results about cubic $In_xGa_{1-x}N/GaN$ quantum wells with green emission [3]. In this work, for zincblende (0 0 1) $In_xGa_{1-x}N/In_yGa_{1-y}N$ quantum wells, we calculate the 1h–1e transition energy as a function of the well width, for the sets of concentrations, $x = 0.3$, $y = 0.02$ and $y = 0.05$; $x = 0.15$, $y = 0.05$; and $x = 0.16$, $y = 0$. For quantum heterostructures, the band offset (BO) has a central role in devices design. There is experimental and theoretical information that for a hexagonal InN/GaN interface the proportion of the valence BO (VBO) is approximately 20% [6]. In case of the cubic interface the information about the VBO is more limited and, apparently, there is no experimental information. Theoretical estimations give values between 0.3 and 0.77 eV [7,8] which, for the bandgap values we use for InN and GaN, the proportion of the VBO is between 10% and 30% approximately. On the other hand, the BO at a heterojunction can be controlled by doping the interface [9,10]. So, we have also made the calculations varying the BO value in order to study its effect on the transition energy. We have made the calculations using the empirical tight binding (ETB) approximation, together with the surface green function matching (SGFM), taking into account the strain in the well and the

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doi:10.1016/j.physe.2009.04.016

spin–orbit effect. Our ETB parameters (ETBP) give values of 0.65 and 3.3 eV for the bandgaps of InN and GaN, respectively. We compare our results with experimental data from hexagonal and cubic quantum wells, and other theoretical calculations. The paper is organized as follows, in Section 2 we give the methodology employed in the calculations; Section 3 is devoted to the results and discussions. Finally, conclusions are depicted in Section 4.

2. Methodology

We have calculated the band structure of bulk cubic GaN and InN using the ETB approximation with an sp^3s^* basis of atomic orbitals, first neighbours interactions and taking into account the spin–orbit coupling, following the usual guidelines [11,12]. In Table 1 are listed the ETBP of the binary compounds. The corresponding ETBP for the alloy were calculated employing the virtual crystal approximation (VCA) [11], for the various values of the concentration. For the concentrations we use, the lattice constant of the material of the well ($In_xGa_{1-x}N$) is perceptibly larger than that of the barrier ($In_yGa_{1-y}N$). We assume that the material of the barrier preserves its lattice constant and the material of the well adjusts its lattice constant to that of the barrier; then, the well experiences a compressive biaxial strain. We incorporate this effect scaling the InGaN ETBP through the equation

$$E'_j = E_j(r/r_0)^{-\eta}_{\alpha\beta} \quad (1)$$

where α and β represent the type of orbitals for the ETBP in Table 1. Quotient r/r_0 is the distance between the atoms in the strained lattice over the distance between the atoms in the lattice without strain. The values of the $\eta_{\alpha\beta}$ exponents could be obtained from a fitting to experimental data of gap dependence on strain. Experimental information for the gap dependence of the cubic nitrides is limited and it is difficult to make a fitting. We have adjusted the exponents to data of the gap dependence of GaN on biaxial strain, obtained from first principles calculations [13]. For InN, we have assumed the same qualitative dependence of its gap as that of GaN. The values of the exponents that reproduce better the variation of the gap under biaxial compressive strain are $\eta_{ss} = \eta_{pp} = 9.0$ for InN and $\eta_{ss} = 4.5$, $\eta_{pp} = 3.3$ for GaN. For the rest of orbitals we use $\eta_{\alpha\beta} = 2.0$ for the two compounds. The theoretical treatment of the heterostructure is made by means of the SGFM method [14], which incorporates appropriately the effect of the two interfaces of the well.

3. Results and discussion

The lattice parameters of GaN and InN, we considered 4.5 and 4.98 Å, respectively; these values, together with the elastic constants were taken from Refs. [15,16]. We used the VCA in order to obtain the ETBP, the lattice constants, the elastic constants and the exponents of the scaling for the InGaN alloys. The ETBP are given in Table 1. We calculated the energy of the 1h–1e transition in the center of the Brillouin zone (BZ) for (0 0 1) $In_xGa_{1-x}N/In_yGa_{1-y}N$ wells, varying the number of monolayers of the well from 2 to 20. One monolayer has two atomic layers, one of anions and one of cations. Fig. 1 shows the results for the concentrations $x = 0.15$ and 0.3, $y = 0.05$, using the same VBO established for hexagonal InN/GaN interfaces of 20%. We see that the energy transition reduces when the well width increases, because the hole and electron energy levels go closer to the bottom of the well potential. In the limit, when the well width goes to infinity, the energy transition approaches to the values of the gaps for $In_{0.15}Ga_{0.85}N$ (2.87 eV) and $In_{0.3}Ga_{0.7}N$ (2.51 eV) strained to the barrier of relaxed $In_{0.05}Ga_{0.95}N$. The reason is that the electrons and holes would be free particles and their basic state would be the bottom of the well potential. The monolayers thicknesses for strained $In_{0.15}Ga_{0.85}N$ and $In_{0.3}Ga_{0.7}N$ are 2.312 and 2.387 Å, respectively. We see from Fig. 1 that for a fixed concentration of In for the barriers, the energy transition reduces when the concentration of In for the well increases because the gap of $In_xGa_{1-x}N$ decreases. We also show in Fig. 1 the experimental results, taken from Kuroda and Tackeuchi [4], for the photoluminescence (PL) emission energy of hexagonal $In_{0.2}Ga_{0.8}N/In_{0.03}Ga_{0.97}N$ and $In_{0.12}Ga_{0.88}N/In_{0.03}Ga_{0.97}N$ multi-quantum wells (MQW) with well widths of 25 and 40 Å, respectively. Additionally, Fig. 1 presents the experimental results of Nagahama et al. [5] for a hexagonal $In_xGa_{1-x}N/In_{0.05}Ga_{0.95}N$ MQW with a well width of 25 Å. Modifying the concentration x of In for the well, they can change the emission wavelength from 440 to 463 nm, which corresponds an energy from 2.82 to 2.68 eV. They do not mention the range of variation of x, but the range of energy emission of their wells corresponds approximately to a variation of x from 0.17 to 0.23 in our calculations. We see that the comparison of experimental data from these hexagonal quantum wells with our calculations is good.

In Fig. 2, we present the results for the concentrations $x = 0.3$, $y = 0.02$ and 0.05 for a VBO of 20%. The concentration of In is the same for both wells but is different for the two barriers. The gap for $In_{0.3}Ga_{0.7}N$ strained to the barrier of $In_{0.02}Ga_{0.98}N$ is 2.53 eV and the monolayer thickness is 2.395 Å. In this case, the gap for this well is bigger than that of $In_{0.3}Ga_{0.7}N/In_{0.05}Ga_{0.95}N$ because the biaxial compressive strain is bigger due to the higher

Table 1
ETBA and S–O parameters (in eV).

	$E(s,a)$	$E(p,a)$	$E(s,c)$	$E(p,c)$	$E(s^*,a)$	$E(s^*,c)$
GaN	−12.9156	3.2697	−1.5844	9.1303	14.0000	14.0000
InN	−12.9856	2.5832	−0.5244	8.6268	15.0000	15.0000
	$V(s,s)$	$V(x,x)$	$V(x,y)$	$V(sa,pc)$	$V(sc,pa)$	$V(s^*a,pc)$
GaN	−8.8996	5.4638	8.7208	6.7152	7.3524	7.8440
InN	−4.0018	4.7207	6.6133	2.8693	5.4793	9.0339
	$V(pa,s^*c)$	λ_a	λ_c	Δ_0		
GaN	2.3827	0.003	0.015	0.018		
InN	3.0511	0.003	0.002	0.010		

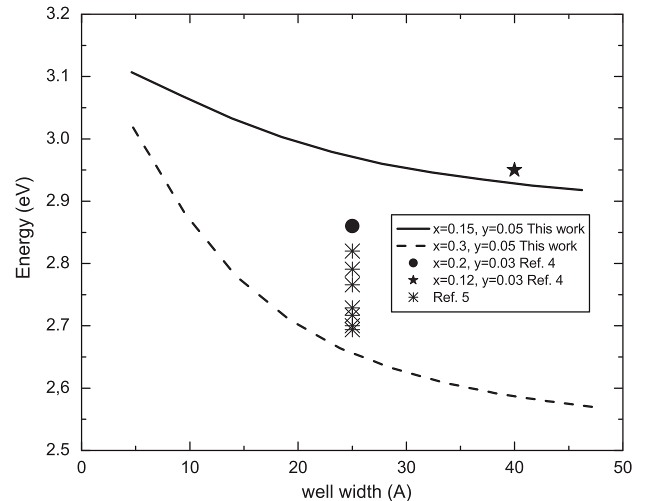

Fig. 1. Transition energies 1h–1e as a function of the well width and for two values of x and the same y. Experimental results are also shown (see text).

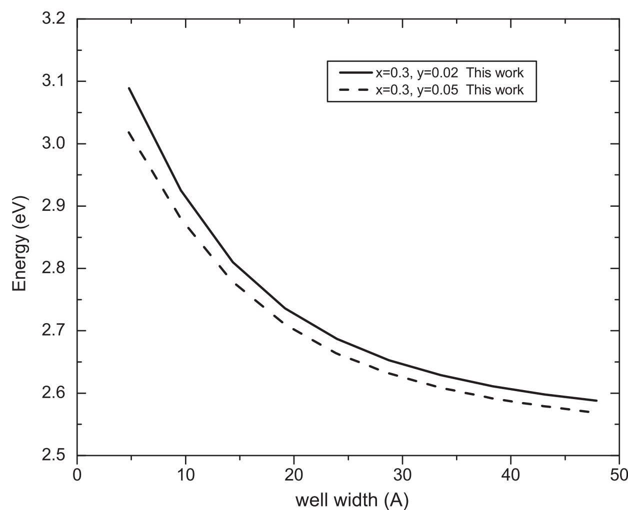

Fig. 2. Transition energies 1h–1e as a function of the well width and two values of y and the same x.

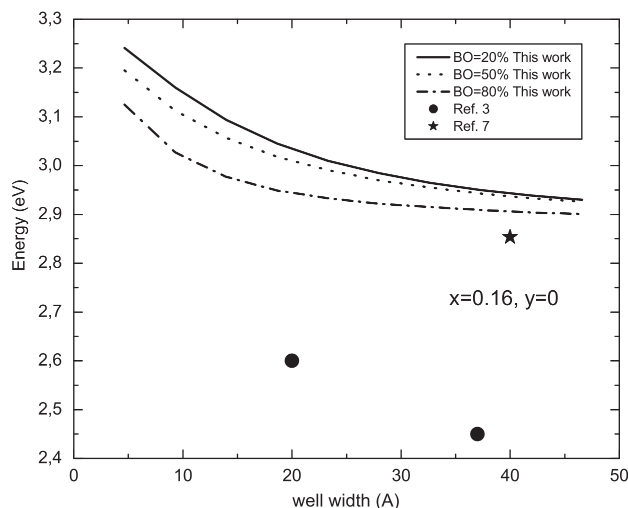

Fig. 3. Transition energies 1h–1e as a function of the well width and BO for $x = 0.16$ and $y = 0$.

concentration of Ga in the barrier. For a semiconductor, when the biaxial compressive strain increases, the gap increases. This causes the increase of the energy transition observed in Fig. 2 when the In concentration decreases in the barrier.

Finally, in order to study the effect of the VBO value, we present in Fig. 3 the transition 1h–1e for the concentrations $x = 0.16$, $y = 0$ for values of 20%, 50% and 80% of the VBO. The gap for $In_{0.16}Ga_{0.84}N$ strained to the barrier of GaN is 2.88 eV and the monolayer thickness is 2.329 Å. We see that when the VBO increases, the energy transition decreases, which is more pronounced for narrow wells. For biaxial compressive strain, at the center of the Brillouin zone, the heavy hole valence band is higher than the light hole band. We think that the decrease of the energy transition when the VBO increases, is due to a smaller effective mass of the electrons than that of the heavy holes. When the VBO increases, the depth of the well for electrons decreases and the first level of energy for electrons decreases more, comparatively, than the increase of the first level of holes. The net effect is a decrease of the 1h–1e energy transition when the value of the VBO increases. We also present in Fig. 3 theoretical and experimental data for cubic quantum wells taken from the literature. The theoretical datum is taken from Bhouri et al. [7], which was calculated using the envelope wavefunction approximation; as we can see, our results are in good agreement with that of Bhouri. The experimental data are taken from Li et al. [3] for the PL emission energy of cubic $In_{0.16}Ga_{0.84}N$/GaN MQW for two well widths. We see that the theoretical energy transitions are 0.35–0.5 eV higher than those obtained experimentally. The exciton binding energy for quantum wells is a few tens of meV and cannot explain the discrepancy. One possible reason would be that the gap for cubic GaN is significantly lower than that of the hexagonal one.

4. Conclusions

We have calculated the 1h–1e transition energy in the center of the BZ, for (0 0 1) cubic $In_xGa_{1-x}N/In_yGa_{1-y}N$ quantum wells for different values of x and y and for the band offset. We found that when the well width increases, the energy transition decreases and goes to the value of the gap of the $In_xGa_{1-x}N$ alloy of the strained well. For a fixed concentration of In in the barrier, increasing the In concentration in the well causes a reduction of the energy transition. Likewise, for a fixed concentration of In in the well, an increase of the In concentration in the barrier induces a reduction of the energy transition. Besides that, an increment of the valence band offset decreases the energy transition. The agreement of our results is good with other theoretical results for cubic wells and with experimental data from hexagonal quantum wells, but the calculations are higher by 0.35–0.5 eV than experimental data from cubic quantum wells.

Acknowledgements

This work was partially supported by the VIEP-BUAP and Secretaría General de la UAZ.

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