Polarization field effects on the electron-hole recombination dynamics in $In_{0.2}Ga_{0.8}N/In_{1-x}Ga_xN$ multiple quantum wells

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The effect of the polarization field in wurtzite $In_{0.2}Ga_{0.8}N/In_{1-x}Ga_xN$ ($x>0.8$) multiple quantum wells is studied from first principles. The pyroelectric and piezoelectric fields naturally present in the system due to its wurtzite structure are strong enough to reduce the interband recombination rate in an ideal quantum well. We suggest that composition fluctuations, observed in the active region of actual devices, provide the necessary confinement for an improved recombination rate and lasing. © *1997 American Institute of Physics.* [S0003-6951(97)03147-1]

In the wake of the recent demonstration of a nitride-based semiconductor blue laser,[1] there have been continuous efforts by a number of experimental groups to develop laser structures and understand their basic properties.

The basic mechanism that has been proposed for the stimulated emission in InGaN-based lasers is linked to the formation of localized regions of higher In concentration in the active region of the multiple quantum well (MQW). These regions are responsible for localized trapping centers where the stimulated emission process takes place.[2] The fluctuations in the In concentration are an intrinsic property of $In_xGa_{1-x}N$ alloys due to the difficulties in growing alloys with sufficiently random mixing.[3] A major difficulty in producing efficient nitride-based lasers is the control of the growth of such regions.

Although detailed knowledge of the properties of the active regions will prove to be important for a complete understanding, insights into the functioning of the blue laser diode can be gleaned from calculations of MQWs composed of ideal alloys. In this letter, we show that in the ideal structures recombination processes suffer from an inefficiency that is related to the intrinsic character of the multiple quantum wells. On the basis of the observations of Narukawa *et al.*,[2] it appears that the localization induced by the composition fluctuations overcome these intrinsic limitations due to their particular confinement properties.

Because of its low symmetry, the wurtzite system displays pyroelectric and piezoelectric behavior.[4] The macroscopic polarization in the material comprising the active region of the MQW gives rise to a net electric field perpendicular to the plane of the well. This field, if strong enough, will induce a spatial separation of the electron and hole wave functions in the well. As the charge density concentrates near the walls of the well, the wave function overlap decreases and the interband recombination rate is reduced (the so-called Stark effect). Similar behavior has been observed in II-VI MQWs in an electric field.[5] The geometry chosen for our theoretical device is a periodically repeated MQW confinement heterostructure, consisting of $In_{0.2}Ga_{0.8}N$ well layers (active region) and $In_{1-x}Ga_xN$ barrier layers, grown on a GaN substrate (GaN in-plane lattice constant). Values of $x=1.0$, 0.95, and 0.9 were considered. This structure closely follows the experimental structure which is used to demonstrate the first blue laser.[1] We have estimated the effect of the field in the active region of such a superlattice and find it of sufficient magnitude to substantially influence the stimulated recombination rate of holes and electrons in wells of physical thickness comparable to those in current devices.

The standard *ab initio* plane-wave pseudopotential method was employed in the calculations. The energy cutoff for the plane-wave expansion was 50 Ry to ensure convergence of the nitrogen pseudopotential. We used six special k points for the calculations in the wurtzite structure.[6] The Perdew-Zunger parametrization[7] of the Ceperley-Alder form[8] of the exchange-correlation energy was used. Nonlocal, norm-conserving pseudopotentials[9–11] were included through the Kleinman-Bylander approach.[12] For Ga, we used a recently developed norm-conserving pseudopotential, which includes a nonlocal core correction and permits an efficient description of the gallium species without the need for an explicit treatment of the $3d$ electrons.[4] For N, we chose a neutral configuration as the atomic reference. The alloys were modeled using the virtual crystal approximation. We considered $4+4$ superlattices in the wurtzite structure, assuming the in-plane lattice parameter of GaN (3.20 Å). Our previous work on GaN/AlN interfaces[4] demonstrated that strain effects on the interface are significant. Because of the large mismatch between GaN and InN, the effects of strain in alloys, with even low In composition, are expected to be large. Consequently, strain effects cannot be neglected. Band offsets were calculated following Baldereschi *et al.*[13] In order to correct for the well-known LDA underestimation of the band gaps, the conduction band offsets were corrected by using a Vegard's law approach for the scissors operator. The calculation of the polarizations in the epilayers proceeded along the lines of Refs. 4 and 14.

In each of the heterojunctions analyzed, the strain present in the system was determined via a total energy minimization of the c/a parameter. The results are shown in Table I together with the energy gaps in the different strained alloys. At equilibrium, GaN and InN have the same c/a ratio.[4] In the interfaces between alloys, however, the c/a deviates considerably from the equilibrium value, as anticipated from the size of the lattice mismatch. The size of the gap in the strained alloys decreases with increasing indium

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TABLE I. c/a parameter and E_{gap} for $In_{1-x}Ga_xN$. The equilibrium GaN in-plane lattice parameter was chosen. The value of u was assumed to be unchanged and equal to its equilibrium value in GaN (0.376). The gaps were corrected using a Vegard's law approach for the scissors operator.

	c/a	E_{gap} (eV)
GaN	1.63	3.50
$In_{0.05}Ga_{0.95}N$	1.65	3.50
$In_{0.1}Ga_{0.9}N$	1.67	3.41
$In_{0.2}Ga_{0.8}N$	1.71	3.19

composition, as expected, ranging from 3.5 eV in pure GaN to 3.2 eV in strained $In_{0.2}Ga_{0.8}N$.

The calculated electronic properties for the strained interfaces are summarized in Table II. The interfaces are all of type I and there are no electrically active interface states in the gap. In general, an increase in the In concentration in the barrier layers leads to a decrease in the band offsets; this amounts to a decrease in the depth of the potential well that confines the carriers to the active region.

In a polar material, the macroscopic polarization, P, manifests itself through the appearance of a macroscopic electric field, F, related to the polarization via the dielectric constant of the material: $F=-P/\epsilon_0\epsilon$. Macroscopic polarization and electric fields present in a single epilayer of the MQWs are summarized in Table III. For the dielectric constants we used $\epsilon(\mathrm{GaN})=9$ and $\epsilon(\mathrm{InN})=15$;[15] dielectric constants for the alloys were obtained through a Vegard's law approach. The only field needed to estimate recombination rates is the one present in the active layers, but since the knowledge of the polarization fields in the barrier layers is needed for the evaluation of the red shift of exciton energies measured in actual devices,[2] the values of the field in the barrier are also given.[16] It is important to note that the size of the field spontaneously present in nitride MQWs is roughly one order of magnitude larger than the fields used in typical experiments (see for instance Ref. 5).

In order to quantify the effect of the field, we modeled the MQW as an effective infinite quantum well within the framework of the effective mass approximation.[17,18] In the low-field limit, which largely applies to the nitride MQWs of width less than 5 nm, the values for the energy shift of the ground state $\Delta E_1^{(2)}$ and the variational expression for the wave functions obtained from second order perturbation theory are[18]

$$\Delta E_1^{(2)}=\frac{1}{24\pi^2}\left(\frac{15}{\pi^2}-1\right)\frac{m^*e^2F^2W_{\mathrm{eff}}^4}{\hbar^2}, \tag{1}$$

and

TABLE II. Valence (VBO) and conduction (CBO) band offsets of the different MQWs studied. The gaps were corrected using a Vegard's law scissors operator. Units are meV.

	VBO	CBO
$GaN/In_{0.2}Ga_{0.8}N$	−102	194
$In_{0.05}Ga_{0.95}N/In_{0.2}Ga_{0.8}N$	−99	203
$In_{0.1}Ga_{0.9}N/In_{0.2}Ga_{0.8}N$	−63	151

TABLE III. Calculated polarization (P) and absolute value of the macroscopic electric field (F) in the different strained epilayers.

	(P (10^{-2} C/m^2)	$\lvert F\rvert$ (kV/cm)
GaN	0.45	564
$In_{0.05}Ga_{0.95}N$	0.58	704
$In_{0.1}Ga_{0.9}N$	0.81	952
$In_{0.2}Ga_{0.8}N$	1.16	1019

$$\psi(z)=N(\beta)\cos\left(\frac{\pi z}{W_{\mathrm{eff}}}\right)\exp\left[-\beta\left(\frac{z}{W_{\mathrm{eff}}}+\frac{1}{2}\right)\right], \quad \frac{|z|}{W_{\mathrm{eff}}}<\frac{1}{2}, \tag{2}$$

respectively. W_{eff} is the effective width of the well as defined below, N is a normalization factor, and β a variational parameter. The electric field is denoted by F and m^* is the effective mass. A Vegard's law procedure was used for the effective masses in the alloys.[2] We chose for the electrons: $m^*(\mathrm{GaN})=0.27$,[19] $m^*(\mathrm{InN})=0.11$;[19] for the holes: $m^*(\mathrm{GaN})=0.8$,[19] $m^*(\mathrm{InN})=1.5$.[20] It is known that the behavior of a MQW in an electric field is not modeled with sufficient quantitative accuracy by an infinite well whose width is the physical thickness. This has been attributed to the fact that the energies of the lowest confined states in a well of finite height are significantly different from the infinite well energies, even at zero field. It has been shown that choosing effective widths W_{eff} for the infinite well to match the lowest energy states in zero field provides a remarkably good description of the system in an electric field.[17] For thin wells, we determined the effective width by ensuring that there be a discrete level in the well for the calculated barrier height in the Kronig-Penney model. For both electrons and holes, typical values for the effective widths range between 2.0 nm and 3.5 nm. For well widths in which the previous condition was automatically satisfied, the physical width has been used.

With these parameters, we can compute the overlap integral between electron and hole wave functions, namely

$$M_{e-h}=\int_{-\infty}^{+\infty}\psi_e(z)\psi_h(z)dz, \tag{3}$$

and estimate the reduction in the recombination rate, which is proportional to the square of the overlap, M_{e-h}^2.

In Fig. 1, we show the recombination rate as a function of the width of the well in the polarization field. For a thickness of about 2.0 nm the recombination rate is of the order of 80%, but drops very quickly as the size of the active region is increased, and is zero for wells of 4.0 nm. The recombination rate also decreases as the barrier height is decreased, and is lowest in the $In_{0.2}Ga_{0.8}N/In_{0.1}Ga_{0.9}N$ heterostructure.

In light of the present results, it is clear that lasing should be substantially reduced in such devices. However, lasing is observed to occur quite readily in devices in which composition fluctuations were measured in the active region.[2] We suggest from this observation that the composition fluctuations can provide the necessary confinement for an improved recombination rate at any well widths greater than those of the quantum dot sizes. In particular, we estimate, on the basis of our calculations of the band offsets, that

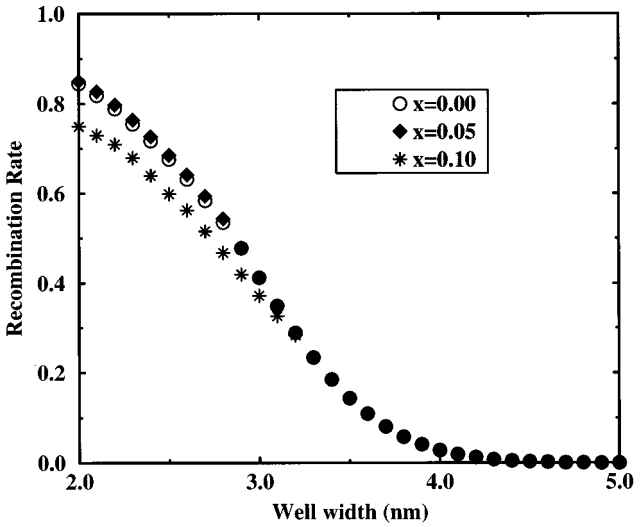

FIG. 1. Recombination rate for electrons and holes vs the well width given the calculated polarization field in the active layer. The zero-field limit for each width has been taken as the reference. Different curves refer to different barrier layers, as specified in the legend.

a composition fluctuation of the order of 10%–20% in the active region is enough to confine the carriers in a spherical quantum dot with a diameter of a few nm.[2,21]

A further effect of the polarization field is the redshifting of the exciton energies with respect to pure GaN. This can be estimated from Eq. (1). The behavior is summarized in Fig. 2, where the absolute value of the correction for electrons and holes in the $In_{0.2}Ga_{0.8}N/GaN$ superlattice is shown. Very little difference has been observed in the other cases, since the shift is dependent on the field that is intrinsic to the active layer. Small variations in the effective widths due to different barrier heights do not appreciably change the results. Corrections of the order of tenths of meV are to be expected in active layers of thickness between 2.0 and 3.0 nm. This shift must be taken into account in order to properly assign the excitonic transition energies measured in experiments (see for instance Ref. 2).

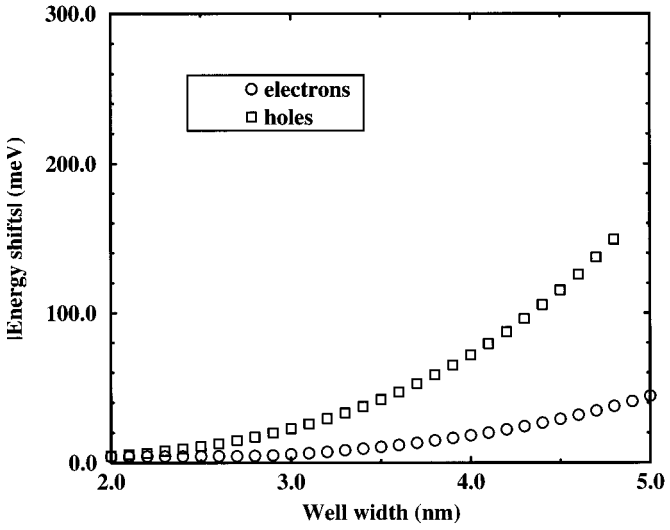

FIG. 2. Absolute values of the energy shifts vs the well width for the calculated polarization field in the active layer. The actual sign of the correction will be negative for electrons and positive for holes.

In conclusion, we have shown using first-principles calculations and a variational model for the description of the MQW, that the spontaneous electric field due to the intrinsic pyro-electric and piezoelectric character of wurtzite nitride semiconductors is strong enough to reduce the interband recombination rate by a measurable degree in quantum wells of dimensions comparable to those used in actual devices. This effect should be taken into account in the engineering of high performance devices. In particular, a confinement mechanism is needed to counteract the polarization field. Finally, we have suggested that the confinement provided by regions of high indium concentration, which effectively form quantum dots,[2] can overcome the negative effect of the polarization field and can be important for lasing.

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