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Effect of giant electric fields on the optical properties of GaN quantum wells

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Spontaneous and piezoelectric fields are known to be the key to understanding the optical properties of nitride heterostructures. This effect modifies the electronic states in the quantum well (QW) and the emission energy in the photoluminescence (PL) spectrum. These fields induce a reduction in the oscillator strength of the transition energy between the confined electron and hole states in GaN/Al$_x$Ga$_{1-x}$N QWs, and dramatically increase the carrier lifetime as the QW thickness increases. In this work, we solve analytically the Schrödinger equation for moderate electric fields when the electron-hole transition energy in the QW is larger than the energy gap of the GaN. Furthermore, the large redshifts of the PL energy position and the spatial separation of the electrons and holes several greater times than the Bohr radius caused by the strong piezoelectric fields are explained using a triangular potential, instead of a square one, in the Schrödinger equation. The transition energy calculations between the electron-hole pair as a function of the well width with the electric field as a fitting parameter are in agreement with the measured photoluminescence energy peaks.

Keywords: Semiconductor quantum wells; electric field; photoluminiscence.

Los campos piezoeléctricos y espontáneos son de gran relevancia en el estudio de las propiedades ópticas en estructuras nitrogenadas. Dichos campos modifican los estados electrónicos en el pozo cuántico y como consecuencia la energía de emisión en los espectros de fotoluminiscencia. Los campos eléctricos presentes en el pozo cuántico, por ejemplo GaN/Al$_x$Ga$_{1-x}$N, inhiben la transición de recombinación entre electrones en la banda de conducción y huecos en la banda de valencia. Además, el corrimiento hacia bajas energías en la posición del pico de fotoluminiscencia y la separación espacial entre electrones y huecos en el límite de campos eléctricos intensos, son explicados usando un pozo de potencial triangular en la ecuación de Schrödinger en lugar de un pozo cuadrado. Las energías de transición obtenidas por este modelo son comparadas con experimentos de fotoluminiscencia.

Descriptores: Pozos cuánticos semiconductores; campo eléctrico; fotoluminiscencia.

PACS: 78.20.Bh; 78.55.-m; 78.67.De

1. Introduction

GaN-based quantum wells (QWs) have been successfully applied in blue and green light emitting diodes as well as in violet laser diodes[1,2]. Despite the poor material quality of epitaxial nitride layers compared to other III-V semiconductors, these devices have shown high performance and high reliability.

Another peculiarity results from the polar axis of the wurzite crystal structure and the strong polarity of III-N bindings. All group-III nitrides in the wurzite phase have a strong spontaneous macroscopic polarization and large piezoelectric coefficients. This has been found from *ab initio* calculations[3,4]. The abrupt variation of the polarization at the surfaces and interfaces gives rise to a large polarization sheet of charges that in turn create internal electric fields of the order of MV/cm. The field-induced linear bending of the band edges causes a spatial variation of confined electrons and holes within the active layers of the devices and has, therefore, important consequences for the optical properties of the nitride-based light-emitting diodes or lasers. It is worth noting that the piezoelectric field present in III-V nitrides appears in the presence of strain, due to epitaxy, for example, while the spontaneous polarization is a property of low-symmetry materials in their ground state, independent of strain, and is absent in zincblende materials (*e.g.* GaAs).

Furthermore, besides the built-in electric field, a strong tendency of indium surface segregation during the growth of In$_x$Ga$_{1-x}$N/GaN QWs result in nonabrupt interfaces and surface compositions different from the bulk. Segregation is a process whereby binding and elastic energy difference between the surface and bulk sites result in the migration to the surface of one species. It has been shown both experimentally[5] and theoretically[6] that the oscillator strength of the QW optical transitions decreases when the segregation process increases due to the spatial separation of the electron and hole pairs by the internal electric field.

Parallel to the progress in the fabrication of optical devices, there have been lively discussions about the optical properties of QWs based on GaN, Al$_x$Ga$_{1-x}$N and In$_x$Ga$_{1-x}$N in the presence of a giant quantum confined Stark effect. Particularly for Al$_x$Ga$_{1-x}$N/GaN QWs, it has been noted for some time that there exists a large red shift of the optical emission spectrum for strained[7] and unstrained[8] GaN QWs. Together with other features, such as energy-dependent decay time of the emission in QW, this has often been interpreted in terms of localization effects, which can be related either to some interface roughness and/or impurities or to the variations of the exciton binding energy as a function of the strong electric field and the thickness of the QW.

Recently, GaN/AlN QW structures were grown by plasma-assisted molecular-beam epitaxy by taking advantage of the surfactant effect of Ga. The QWs show PL emission as a function of the well width with photon energies in the range between 4.2 and 2.3 eV, *i.e.* the emission becomes lower than the band gap of GaN bulk and varies linearly for wide wells ($>$1nm)[9]. The internal electric field strength in GaN/AlN QWs of the order of 10MV/cm deduced from the dependence of the PL experiments is in agreement with the theoretical prediction by Bernardini *et al.*[3].

In this work, we present an alternative way which takes into consideration the energy shift due to strain, dependence temperature of the ban-gap and the presence of internal electric field in the QW. The electron-hole transition energy in the QW is calculated using the variational electron and hole wave functions for the following cases:

(a) the transition energy in quantum well is larger than the GaN energy band-gap (moderate piezoelectric fields), and

(b) in the limit of strong internal electric field when the QW's emit at energies lower than the GaN bulk energy.

Under these approximations, the built-in electric field is used as a fitting parameter when compared with the experimental PL peak of GaN single quantum wells.

2. Theoretical model

Since our study is based on the comparison of the PL spectra with the calculated transition energies, the model of the well and barrier profile to include in the Schrödinger equation is presented here. We will consider the case of a single QW with built-in electric fields embedded in strain-free barriers. We assume that the potentials are proportional to e*Fz* in the QW and flat in the barriers, F being the piezoelectric field, e the electron charge, and z the coordinate along the growth axis. Within this approximation, the transition energy between the confined electron and the hole states is given by

$$\delta E = E_g + E_e + E_{hh} \tag{1}$$

where E_g is the effective band gap in the strained GaN layer at temperature T, and is given by the expression

$$E_g = E_g^0 + \Delta E - \frac{\lambda T^2}{\xi + T}, \tag{2}$$

with E_g^0 the band gap of unstrained GaN at $T = 0°$ K and ΔE is the energy shift due to strain. The third term in Eq. (2) accounts for the band-gap dependence on the temperature where λ is an empirical constant and ξ is sometimes associated with the Debye temperature[10]. This expression has been successfully applied in describing $E_g(T)$in many semiconductors. E_e and E_{hh} are the electron and heavy hole confinement energy, respectively.

In PL experiments of GaN/Al$_x$Ga$_{1-x}$N QWs, the most important information is that the emission energy decreases strongly with increasing QW width. At a certain critical QW thickness (for a fixed internal electric field), the emission energy passes below the GaN band-gap energy. Considering quantum confinement effects alone, one expects all QW peaks to be strongly blueshifted with respect to the GaN energy gap. Hence, the pronounced redshift of the larger width QW is a clear indication of a strong electric field present in the QWs.

In order to estimate the amplitude of this electric field, F, we have performed calculations within the effective mass approximation of the QW ground state for the electron and the hole transition energy as a function of the well thickness a for various input values of F. Figure 1 shows the energy

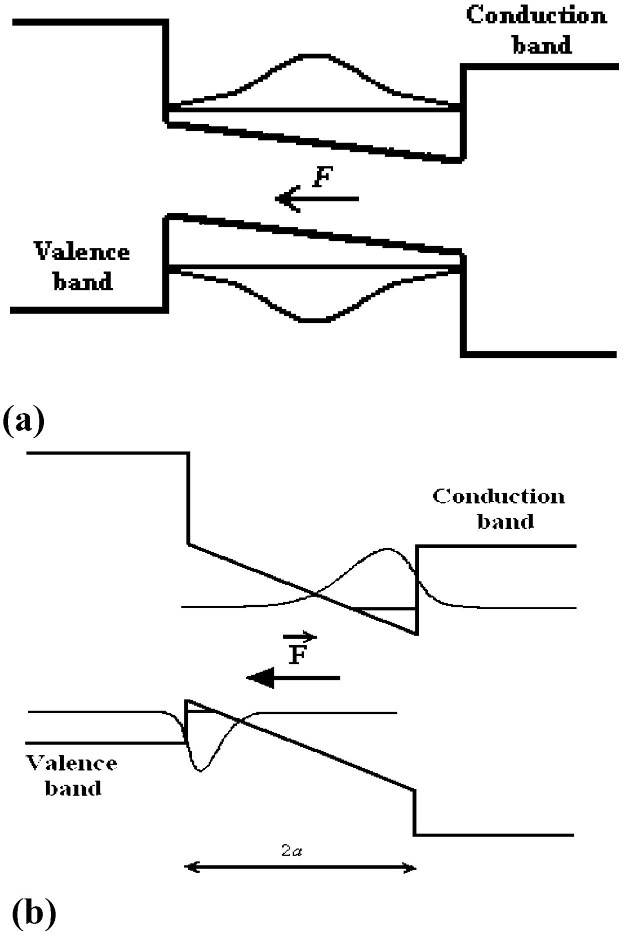

FIGURE 1. Schematic picture of the energy levels and wave functions of the electrons and holes in strained quantum well with (a) moderate and (b) strong fields.

band profile in the QWs. In the narrow QW, for moderate piezoelectric fields as shown in Fig. 1a, electrons and holes are strongly confined leading a large overlap between electron and hole wave functions. This results in a transition energy larger than the GaN band-gap emission photon energy. In contrast, for sufficient large QWs, the electrons and holes are weakly confined and the spatial separations between electrons and holes strongly depend on the internal electric fields (above 1 MV/cm)[7-9] in the wells. A large electric field in the wells induce a large separation between electrons and holes, leading to a PL energy emission lower than that bulk GaN and a long PL decay time (see Fig. 1b).

To quantify the effects of the electric fields on the PL peak energy larger than the GaN band-gap, we consider the finite quantum well potential within the framework of the effective mass approximation (see Fig. 1a) as follows:

$$V(z)=\begin{cases} eFz, & |z|<a \\ \\ V_0 & otherwise \end{cases}, \qquad (3)$$

where F≠0 in the QW and F=0 within the barriers. The electron energy is found by solving the Schrödinger equation with Eq.(3) and employing a variational approach with the first bound level, $\varphi_{0,}$ in the well at $F=0$; the variational ground state is given by[11]

$$\varphi(z)=N_\beta(1+\beta z/2a)\varphi_0(z), \qquad (4)$$

where β is the variational parameter and

$$N_\beta=\left[1+(\beta/2a)^2\left\langle z^2\right\rangle\right]^{-1/2},$$

a normalization factor with $\left\langle z^2\right\rangle=\left\langle\varphi_0\left|z^2\right|\varphi_0\right\rangle$. Then, using Eq.(3), we obtain the bound state energy whose value must to be minimized:

$$E_e(\beta)=E_{0e}+N_\beta\left[\frac{2e\beta F\langle z^2\rangle}{2a}+\frac{\hbar^2\beta^2}{2m_e(2a)^2}\right], \qquad (5)$$

where E_{0e} is the zero-field ground state energy for electrons and

$$\beta=\frac{2a\hbar^2}{4eFm_e\langle z^2\rangle^2}\left[1-\sqrt{1+16e^2F^2m_e^2\langle z^2\rangle^3/\hbar^4}\right]. \qquad (6)$$

Thus the induced energy shift for electrons due to the piezoelectric field can be expressed as $\delta\varepsilon=E_e(\beta)\text{-}E_{0e}$, which decreases with the built-in electric field in the QW. A similar process can be done for the holes' well potential to obtain the ground state energy in the presence of an electric field.

On the other hand in the limit of a strong electric field such that the PL emission energy is below the GaN band-gap energy, a confined triangular potential is used for electrons and holes to calculate the fundamental transition energies (see Fig. 1b). Again, simple analytic wave functions make calculations of properties of QWs more convenient than they would be if numerical self-consistent solutions or cumbersome analytical solutions like Airy functions had to be used [12]. For that reason approximate solutions have been widely used in triangular QWs calculations. The simplest of this, proposed for inversion layers by Takada and Uemura [13], is

$$\chi(z)=\left[\frac{3b^3}{2}\right]^{1/2} ze^{-(bz)^{3/2}/2}. \qquad (7)$$

The parameter b is determined by minimizing the electron energy for a given QW thickness and effective electron mass. Because of the simplicity of the wave function, it is easy to evaluate the expectation value of the Hamiltonian. The energy of the lowest band is

$$E_e(b)=\frac{5\Gamma(\frac{2}{3})}{16}\frac{\hbar^2b_e^2}{m_e}+\Gamma(\frac{2}{3})\frac{10eF}{9b_e},$$

and

$$b_e=\left(\frac{16eFm_e}{9\hbar^2}\right)^{1/3}, \qquad (8)$$

where $\Gamma(z)$ is the Gamma function. Then substituting Eq. (8) in Eq. (1), the PL energy peak as a function of the piezoelectric field and the thickness of the QW can be written as

$$\delta E=E_g-2eaF+\frac{5}{12}\Gamma\left(\frac{2}{3}\right)\left(\frac{6e\hbar F}{m^{*1/2}}\right)^{2/3}$$

where

$$\left(\frac{1}{m^*}\right)^{1/3}=\frac{1}{m_e^{1/3}}+\frac{1}{m_h^{1/3}} \qquad (9)$$

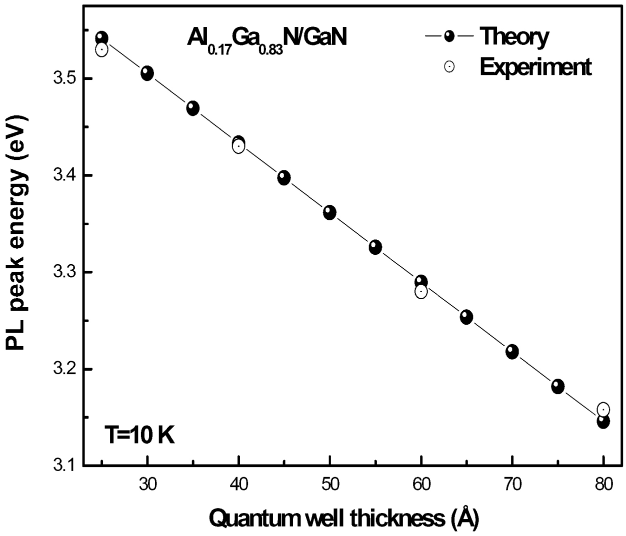

FIGURE 2. PL energy of $Al_{0.17}Ga_{0.83}N$/GaN QWs as a function of the well width. The experimental data are well accounted for by Eq. (8) taking into account an internal electric field of 719 KV/cm.

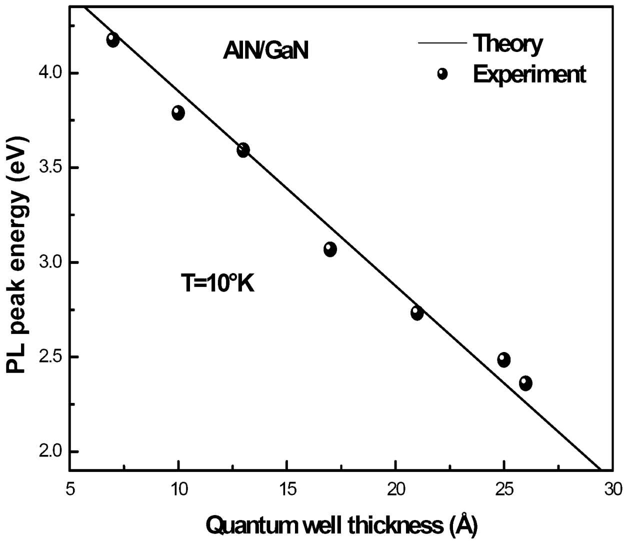

FIGURE 3. Variation in the PL emission energy as a function of the QW width. The solid line represents the calculations of the emission energy with an electric field of 10 MV/cm.

As can be observed from Eq.(9), the PL energy peak is a linear function of $2a$ and, for the thickness of the QW and strong electric fields such that $\delta E < E_g$, the energy involved in the electron-hole recombination is lower than the band gap of the QW.

The variation of the QW emission energy with the QW thickness is shown in Fig. 2. The solid lines represent the results of the theoretical calculations, Eq.(9), of the fundamental transition energies of the triangular QW. The experimental data were taken from Ref. 8 of unstrained GaN QWs with $\mathrm{Al}_x\mathrm{Ga}_{(1-x)}\mathrm{N}$ barriers and x=0.17. The effective mass for electrons is assumed to be $0.22m_0$ and for holes $2m_0$. In Eq.(2) λ=*8.84* 10^{-4} eV/° K and ξ=*874 K.* Excitonic effects were neglected since an estimate showed that the excitonic binding energies are weak (a few tens of meV) even for thin QWs due to the electric field–induced spatial separation of electrons and holes[13]. In order to take into account the sizable Stokes shift, 0.6 Γ_{inh} was subtracted from the calculated transition energies (assuming that the absorption linewidth is similar to the observed PL linewidth)[7,9] where Γ_{inh} is the experimental PL linewidth.As shown in Fig.2 the theoretical model of transition energy between the confined electron and hole sates as a function of the well width is in agreement with the measured PL energy peaks for an electric field of 719 kV/cm and an energy strain given by ΔE=*0.02 eV.*

In Fig. 3, the PL energy of GaN/AlN QW, s is plotted as a function of the well width[9]. The internal electric field was used as a fitting parameter. We find our calculations in good agreement with the experimental PL emission energies for an internal electric field of *F=10 MV/cm.* and ΔE =*0.18 eV.* As the calculations show the transition energy decreases linearly with increasing QW width in agreement with the experimental results reported in the literature.

3. Conclusions

In conclusion, we have developed a simple theoretical model to explain the optical properties of GaN QWs in the presence of an internal electric field. It is shown that the PL energy peaks below the band gap of GaN decrease linearly as a function of the QW thickness. The overall agreement between the calculations and the experiments clearly shows the presence of giant internal electric fields resulting from the interplay of the piezoelectric and spontaneous polarizations in the well.

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