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Indium segregation effects in (111)*B*-grown (In,Ga)As/GaAs piezoelectric quantum wells

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The effect of indium surface segregation on electronic states and excitonic properties is investigated experimentally and theoretically in (111)*B*-grown (In,Ga)As/GaAs strained piezoelectric quantum wells. Thermally detected optical absorption and electroreflectance experiments are performed on two samples grown by molecular beam epitaxy and containing 7 and 14 wells. Excitonic energies and oscillator strengths are calculated by a variational method within the effective mass approximation. The influence of indium segregation on the piezoelectric field strength and the oscillator strength of excitonic transitions is analyzed.
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The growth of high-quality (111)*B*-grown (In,Ga)As/GaAs piezoelectric quantum wells is crucial for the fabrication of blue-shifting electroabsorption modulators, bistables, and low threshold lasers potentially interesting for monolithic blue-green sources.[1–4] To our knowledge, the influence of indium segregation on the electronic properties of such heterostructures is yet to be investigated. A number of studies concerning (111)*B*-grown (In_xGa_{1-x})As/GaAs multiple quantum wells (MQW's) have shown a piezoelectric field value 30% weaker than the theoretical predictions which assumed perfectly abrupt interfaces.[5–7] Because it is now well established that strong indium surface segregation occurs in this system, we investigate the optical effects of modifying the indium composition profile over a large number of monolayers.[8–9]

We report a quantitative analysis of the effects of the indium segregation on the electronic and excitonic properties of two $In_{0.15}Ga_{0.85}As$/GaAs MQW's. The samples are labeled sample 1 and sample 2 and have 7 and 14 wells, respectively. Both samples were grown using molecular beam epitaxy (MBE) on n^+ (111)*B* GaAs substrate misoriented 2° toward the $[2\bar{1}1]$ axis. The detailed sample structure is as follows: a layer of 0.3 μm of n^+ GaAs, a 0.735 μm GaAs undoped region in which the 100 Å $In_xGa_{1-x}As$/150 Å GaAs MQW's are incorporated centrally, and 0.3 μm of p^+ GaAs. Mesa photodiodes 400 μm in diameter allow an optical access through an annular contact on the p^+ region. According to a pyrometer, the substrate temperature during the growth of the quantum wells is 535 °C. The growth rate, of approximately one monolayer per second, was measuared by monitoring the reflection high-energy electron diffraction (RHEED) oscillations provided by a reference sample grown on a (100) GaAs substrate.

Thermally detected optical absorption (TDOA) and electroreflectance (ER) spectra taken from sample 1 are shown in Fig. 1. TDOA is a nonconventional technique based on the detection of the nonradiative de-excitation occurring after absorption. The heating of the sample induced by such nonradiative recombinations is detected at liquid helium temperatures by using a germanium thermometer. TDOA data directly provide the positions of excitonic transitions from the absorption maxima. Three transitions are detected involving the fundamental levels of electrons (e_1) and levels of heavy holes (hh_i with i=1,2,3). The monotonic increase

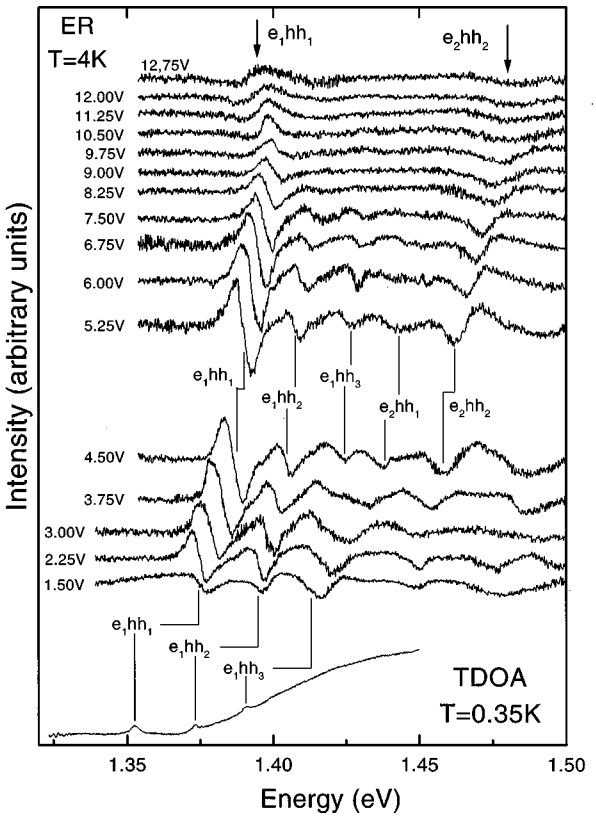

FIG. 1. TDOA spectrum and ER spectra as a function of the reverse applied voltage in the range of 1.50 to 12.75 V, obtained from sample 1. Vertical lines indicate the energy position of excitons. These energy positions have been obtained from the intensity maxima in the absorption lines and from a fitting procedure of the ER spectra.

of the TDOA signal as the energy of the incident photon is increased is attributed to absorption into impurity levels. TDOA enables very weak signals occurring in the high electric field regime to be detected. At zero volt applied bias, ER could detect no transitions associated with the wells because of the weak oscillator strengths and also because of the possibility that carriers recombine in the GaAs barriers where the electric field is weaker.

ER spectra are shown for several reverse bias voltages in the range of 1.50 to 12.75 V where excitonic oscillator strengths are strong enough to enable the signal to be localized accurately. At low voltages (stong in-well electric field), excitonic transitions forbidden from classical selection rules could have comparable or larger intensities than those of the fundamental transition. When the bias increases, the fundamental transition becomes more prominent. When the applied bias is strong enough to cancel the in-well electric field, the excitonic transitions with $\Delta n \neq 0$ disappear. Since the in-well electric field is responsible for the transition energy shifts through the quantum confined Stark effect, it is possible to locate the flat band configuration by the maximum of the fundamental excitonic energy. Finally, the damping of the excitonic features that is clearly seen at very high bias is attributed to carrier escape through the barrier potential tips via field assisted tunneling.[10]

In order to obtain the characteristics of the excitons from the ER spectra, we have analyzed the shapes of these spectra through a multilayer model based on the calculation of the reflection coefficient. The variation of this coefficient induced by the modulation of the electric field is calculated literally by a simple derivation with respect to the dielectric function that is modeled by a standard damped oscillator. Changes in this dielectric function are evaluated by a first derivative expression with respect to the oscillator parameters: energy, broadening, and oscillator strength.[11]

From the examination of Fig. 1, it is difficult to determine accurately the value of the voltage corresponding to the flat band configuration. Therefore, we have used a model in the effective mass approximation to calculate the energy levels and wave functions in the presence of electric fields. This model is coupled with a variational calculation of the excitonic binding energy and oscillator strength. The excitonic trial function used has the following form:

$$\Phi(z_e, z_h, r_{\mathrm{eh}}) = \varphi_e(z_e)\varphi_h(z_h)\exp[-(r_{eh}^2 + (z_e - z_h)^2)^{1/2}/\lambda]. \tag{1}$$

The relative distance between the two particles in the layer plane is given by r_{eh}, and z_e, z_h are the coordinates of the electron and hole along the quantization direction, and $\varphi_e(z_e)$, $\varphi_h(z_h)$ their envelope functions, respectively. The exciton binding energy is determined by minimizing the quantity $\langle\Phi|H_{\mathrm{exc}}|\Phi\rangle/\langle\Phi|\Phi\rangle$ with respect to the variational parameter λ; H_{exc} represents the excitonic Hamiltonian.

It has been shown that these calculations using abrupt interfaces and taking the in-well electric field as an adjustable parameter lead to a piezoelectric field discontinuity of 165 kV cm^{-1}. This results in a poor description of the behavior of the excitonic transitions involving excited levels of holes.[12] The theoretical value for the piezoelectric field F_{piezo} is 225 kV cm^{-1} for $x=0.15$, and for a piezoelectric constant e_{14} deduced from a linear interpolation between the values of those of the two binaries, InAs and GaAs, at room temperature.

Indium surface segregation, which occurs during the MBE growth, can be invoked to explain this discrepancy. The resulting chemical modulation strongly modifies the band structure of the quantum wells and thus the energy levels. This segregation is an exchange mechanism between the surface and the bulk phases. Indium atoms are less bounds than gallium atoms and thus the indium fraction in the surface monolayer becomes larger than that in the bulk. In order to build the concentration profile, a thermodynamical equilibrium segregation model appears to be relevant.[9] For the high temperature-grown samples investigated here, Dehaese *et al.* have shown that there are no kinetic limitations to the segregation phenomenon.[13] Assuming that the exchange of atoms is limited to the last nucleated monolayer (bulk phase) and the surface adatoms, surface and bulk indium fractions x_s and x_b are linked by

$$x_s(1-x_b)/x_b(1-x_s) = \alpha/(1-\alpha), \tag{2}$$

where α is an exchange coefficient that incorporates all the causes of segregation, such as the difference between the bulk and surface free energies. In this treatment, the monolayer thickness is defined by the width separating two successive planes containing indium atoms and can be calculated to be $a_0/\sqrt{3}$, where a_0 is the lattice parameter of the GaAs substrate.

In the band structure calculations, strain, piezoelectric field, and effective masses are calculated in all monolayers which contain indium atoms. The e_{14} value, which varies with the indium concentration, is estimated in each monolayer. We assume a linear variation with the indium composition and we use the same fractions of the e_{14} values of the two binaries to determine the slope. The in-well and barrier electric fields are calculated by considering that a well consists of a set of monolayers, each containing a different indium fraction. For each well, there are n_{ML} monolayers which contain indium atoms; monolayer i has a thickness $l_W(i)$ and a piezoelectric field $F_{\mathrm{piezo}}(i)$. If N is the number of wells within the MQW structure, the total potential drop across the intrinsic region caused by the p-i-n field (V_{pin}) and eventually by the applied electric field (V_{app}) can be expressed as the sum of the potential variations across the barriers and the wells:

$$V_{\mathrm{app}} + V_{\mathrm{pin}} = L_b F_b + N\sum_{i=1}^{n_{\mathrm{ML}}} l_W(i)F_{\mathrm{piezo}}(i), \tag{3}$$

where L_b is the total width of pure GaAs. The piezoelectric field discontinuity in each monolayer can be related to the total electric field in this monolayer $F_W(i)$ by

$$F_{\mathrm{piezo}}(i) = F_b - F_W(i). \tag{4}$$

From Eqs. (3) and (4) it is possible to evaluate $F_W(i)$ for each monolayer and therefore to build the band structure of the MQW's.

The exchange coefficient used to fit the experimental data is taken to be 0.95. It provides segregation energies consistent with previous values reported in the literature for (100)

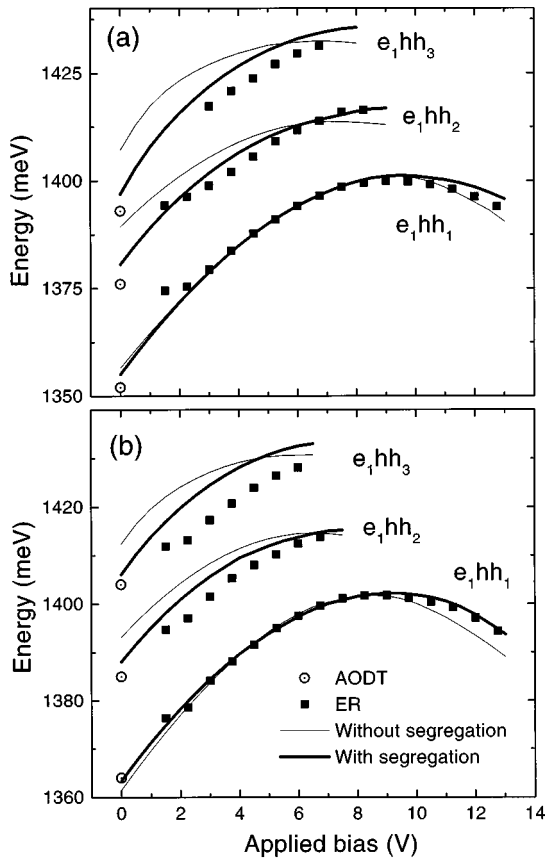

FIG. 2. Experimental excitonic energies obtained by TDOA and from ER spectra of sample 1(a) and sample 2(b) are plotted with dot center and filled square symbols, respectively, as a function of applied bias for the fundamental and two excited excitonic transitions. Lines are obtained by including (thick lines) or neglecting (thin lines) indium segregation.

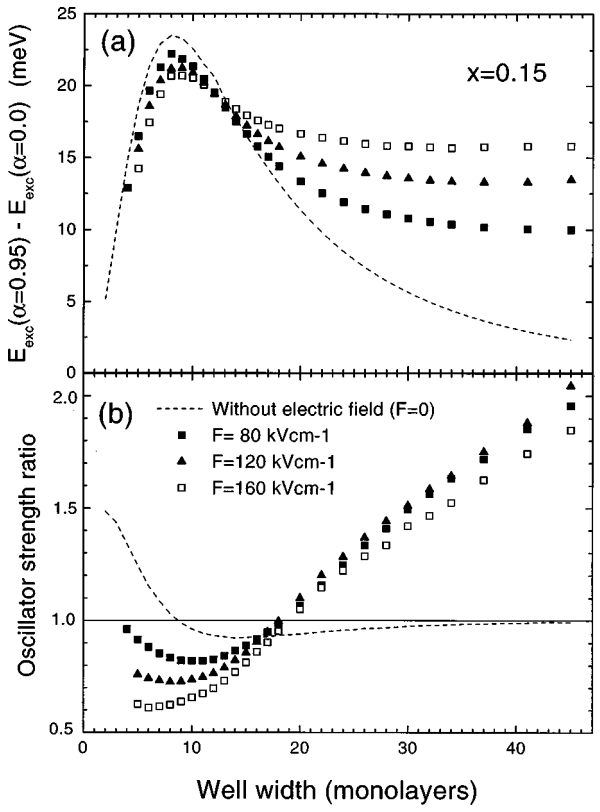

FIG. 3. (a) The difference between the e_1hh_1 excitonic transition energies calculated with segregation ($\alpha=0.95$) and without segregation ($\alpha=0$) is reported as a function of the well width for several values of the in-well electric field F. (b) The ratio of the corresponding oscillator strengths is also reported.

$In_xGa_{1-x}As/GaAs$ heterostructures.[9,14–15] Indium segregation blueshifts the fundamental transition energy and increases the electron and heavy hole wave function overlap as reported by Disseix *et al.* in the case of (100) growth.[16] This phenomenon is enhanced in the piezoelectric (111) quantum wells by the presence of a strong electric field: the heavy hole wave function is pushed toward the center of the well, increasing the overlap.

Figure 2 shows the experimental energies deduced from the TDOA and ER experiments as a function of applied bias for sample 2. Theoretical fits are also displayed considering abrupt or gradual interfaces due to segregation processes. These adjustments include the binding energy variation induced by changes in the in-well electric field by bias. In the case of segregation the binding energies have been recalculated because of the modified carrier localization. The transitions involving excited levels of heavy holes are better described if segregation is included. This is due to the fact that segregation widens the top of the wells leading to the narrowing of the heavy hole levels. In this way, hh_2 and hh_3 levels are closer to the hh_1 level when segregation is taken into account.

In addition, the piezoelectric field deduced from these fits is larger (F_{piezo} $(x=0.15)=190\pm10$ kV cm^{-1}) than that in the case of a square composition profile ($F_{\text{piezo}}=165\,\text{kV}\pm10\,\text{kV cm}^{-1}$). This result is of fundamental interest because it shows that a great part of the discrepancy between experimental and theoretical value of the piezoelectric field ($220\,\text{kV cm}^{-1}$) can be explained by segregation. This effect combined with the pyroelectric effect described by Bahder *et al.* that e_{14} increases with temperature, can totally account for the disagreement in the e_{14} value for $In_xGa_{1-x}As$.[6] It has to be noted that the piezoelectric constant value for $In_{0.15}Ga_{0.85}As$ deduced from the interpretation of our experimental data including the In segregation ($e_{14}=0.124\,\text{C m}^{-2}$) is found to be greater than the experimental values reported in the literature.[5–7,17–19]

The effects of indium surface segregation on excitonic properties calculated by using the trial function described in Eq. (2) are illustrated in Fig. 3. The upper part of the figure shows its effects on fundamental excitonic transition energy. It is worth noting that by increasing the in-well electric field the indium segregation blue shift is enhanced. The strongest is the quantum confined Stark effect, the strongest is the segregation effect. This behavior accounts for the observations of Ilg and Ploog:[8] They report a stronger blue shift of photoluminescence peaks in the case of (111) growth axis heterostructure than (211) or (311), and of course (100) grown structures. They concluded that enhanced indium segregation occurs by crystallographic orientation. Since the piezoelectric field is larger in the case of (111) planes than that in the (211) and (311) planes, our results demonstrate that the increase of the energy is mostly due to the exhaltation of

the segregation effect under built-in electric field rather than the increase in the segregation phenomenon itself. However, a slight increase of the segregatin phenomenon with crystallographic orientation can be expected assuming that the piezoelectric field being generated reduces the incorporation of indium into the growing $In_xGa_{1-x}As$ layer.

Another interesting observation is that this effect of indium segregation is observed even for very wide quantum wells. For thin wells, the trend follows that of a square well because the carrier wave function is delocalized; so for thin wells the electric field and the indium segregation effects on band structure are seen as very weak and localized perturbation. When the well thickness increases, carriers are pushed toward opposite sides of the quantum wells. Confinement of electrons and holes occurs even for very thick wells because of the strong electric field which makes the shape of the wells triangular at each side. This triangular shape and resulting confinement energy are almost independent of the well thickness. Therefore, segregation effects under an electric field do not vanish for thick wells, as they do in the absence of any electric field. To illustrate this point, Fig. 3(b) shows the evolution of the oscillator strength ratio, defined as the value of the oscillator strength with segregation ($\alpha = 0.95$), divided by that obtained without segregation ($\alpha = 0$), as a function of the well thickness for the fundamental e_1hh_1 excitonic transition. For thin wells, the broadening of the top of the well induced by segregation enables an enhanced carrier separation by the in-well electric field and induces a decrease of the oscillator strength ratio. For larger thicknesses, the hole wave function is pushed toward the center of the well because the segregation increases the wave function overlap and consequently the oscillator strength value. The same behavior is observed for excitonic transitions involving excited levels such as e_1hh_2 or e_1hh_3, but in this case the magnitude of the effect is drastically reduced because of the larger spatial extension of carriers located on hh_2 and hh_3 levels.

In conclusion we have shown how segregation affects electronic states and excitonic properties in (111)*B* $In_xGa_{1-x}As/GaAs$ MQW structures. As a result, piezoelectric field determination based on energy level calculations must account for this phenomenon. The electroreflectance experiments are analyzed within this framework and the e_{14} value is found to be higher than the previous determinations. It is also shown that the presence of a strong in-well electric field enhances segregation effects by modifying its action on electronic states confined in the quantum wells.

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