Photorelectance investigations of quantum well intermixing processes in compressively strained InGaAsP/InGaAsP quantum well laser structures emitting at 1.55 μm

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We have investigated the effects of interdiffusion and its technological parameters on the subband structure in compressively strained InGaAsP quantum well (QWs) using photorelectance and photoluminescence techniques. p-i-n laser structures with three QWs were grown by gas source molecular beam epitaxy and capped with dielectric films deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition and annealed using a rapid thermal annealing process. A numerical real-time wave-packet propagation method including static electric field, strain in the wells and barriers, and error function interface diffusion modeling is used to calculate the transition energies for the diffused QWs. It has been shown that the shift of the energy levels due to the interdiffusion related changes of the well confinement potential profile is a consequence of two competing processes: a change of the well width and an effective increase of the band gap energy resulting in a net blueshift of all optical transitions. Moreover, it has been found that quantum well intermixing does not significantly influence the built-in electric fields distribution. © 2006 American Institute of Physics. [DOI: 10.1063/1.2209787]

I. INTRODUCTION

Photonic integrated devices based on InGaAsP multiple quantum well (MQW) structures are of particular importance due to the dramatic increase in demand for long wavelength optical communications. Currently, InGaAsP/InP quantum well structures are used for a variety of optoelectronic devices, such as electro-optic modulators for fiber optic communication, infrared detectors, or lasers for operation near the 1.55 μm wavelength region. This value is especially important from the telecommunication point of view, because it lies within a telecommunication window, with characteristic low dispersion and minimal absorption in silica glass fiber, which enables more data to be sent over longer distances. On the other hand, selective area band gap tuning is crucial for monolithic integration of photonic devices. Selective regrowth (SR) and selective area epitaxy (SAE) are two possible techniques that can be used for these purposes. Postgrowth quantum well intermixing (QWI) technique is another approach, by which the absorption edge is changed through interdiffusion of the well and barrier regions in a quantum well structure. Thus, it has attracted much attention for its use in the integration of optoelectronic and photonic devices, since band gap tuning by QWI is a much simpler and more versatile fabrication process as compared to the regrowth methods. Many different approaches to implementing QWI have been proposed, such as laser-induced disordering (LID), photoabsorption-induced disordering (PAID), impurity-free intermixing, which is often called impurity-free vacancy-enhanced disordering (IFVD). In our case plasma enhanced chemical vapor deposition (PECVD) technique is used for the deposition of a dielectric film (SiO₂ or SiO₃Nₓ), which introduces vacancies into the laser structure.

Also studies of QWI can yield fundamental information, such as rates of diffusion, the role of defects, and strain in the diffusion process and on the properties of strongly nonsquare quantum wells.

Among the various QWI techniques, IFVD is believed to be one of the most promising, since there is no damage or impurity-related drawback. The IFVD technique involves the deposition of a thin layer of dielectric (SiO₂ or SiO₃Nₓ) film on the samples and subsequent thermal annealing usually by rapid thermal annealing (RTA). Both of these processes create strain beneath the cap layer. This strong interface strain leads to group-III outdiffusion and defect formation which leads to interdiffusion between the QW and adjacent barrier leading to change in the shape of QW potential.

QWI has been the object of intensive theoretical and experimental studies since the early 1980s. However, most of the studies concerning the intermixing behavior have been performed for GaAs/AlGaAs QW structures and little work has been done on the intermixing behavior of InP based QW structures. The latter is more complex because both group-III and group-V atoms can participate in the intermixing process and many problems remain unsolved, especially for intermixed InGaAsP/InGaAsP (quaternary/quaternary)
QWs in the presence of a built-in electric field. Only a few reports have been published on the optical properties compressively strained InGaAsP/InGaAsP QWI in the presence of a built-in electric field.27–33 Most of the interdiffusion coefficients have been investigated by photoluminescence (PL),36,37 x-ray diffraction (XRD), Raman spectroscopy (RS),38 secondary ion mass spectroscopy (SIMS),39 transmission electron microscopy (TEM), and cross-sectional scanning tunneling microscopy (STM).40 Photoreflectance (PR), as an optical (i.e., contactless and nondestructive) modulation spectroscopy, has been proven to be a very powerful technique for studying semiconductor low dimensional structures. Its success comes from the fact that it is a very effective and highly sensitive absorption-type experiment which allows investigation of both the ground and excited states related optical transitions, including those with very small oscillator strength such as those that are nominally parity forbidden. The method remains effective in the case of small oscillator strength such as those that are nominally forbidden. The method remains effective in the case of small oscillator strength such as those that are nominally parity forbidden. The method remains effective in the case of small oscillator strength such as those that are nominally parity forbidden.

This work presents an extensive experimental investigation supported by theoretical calculations of InGaAsP/InGaAsP compressively strained QWs placed in the p-i-n junction of a 1.55 μm laser structure. Photoreflectance and photoluminescence measurements have been used to examine the influence of the IFVD QWI process and its technological parameters such as the RTA conditions, dielectric deposition parameters, and dielectric composition on the energy shift of electron and hole levels in the active region of the device. The origin of the derived shifts is discussed and the influence of the QWI on built-in electric fields and optical quality of investigated structures has been considered. Moreover, a detailed interpretation of the optical transition from the compressively strained and quantum well intermixed InGaAsP QWs in the presence of a built-in electric field is presented.

II. EXPERIMENTAL DETAILS

Samples used in this study were grown by gas source molecular beam epitaxy (MBE) on n-doped (100) InP substrates. The laser structure is shown schematically in Fig. 1. The active region is composed of three 1.1% compressively strained 5-nm-thick QWs of In0.76Ga0.24As0.85P0.15 separated by In0.76Ga0.24As0.52P0.48 barriers lattice matched to InP substrate. The compositions have been chosen so that the In/Ga ratio remains constant throughout the wells and barriers. This “partial” laser structure is completed with 80 nm upper and lower cladding layers of In0.76Ga0.24As0.39P0.61 and In0.76Ga0.24As0.52P0.48, respectively, and capped with undoped InP, In0.55Ga0.45As, and InP layers.

The InP layer was removed before the deposition of the SiO2 or Si3N4 films. Silicon dioxide was deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD). The technical details of the deposition system have been described elsewhere.35,42 Three sets of samples were used in this QWI study: (i) structures from the first set have been used to investigate the effect of the RTA temperature (560–780 °C); (ii) the second set explores how the dielectric deposition condition, specifically microwave power of ECR-PECVD process (650–900 W) changes the amount of intermixing; and (iii) how the composition of the dielectric cap layer impacts the properties of QW’s after RTA. Results for all processed samples have been compared to those of as-grown reference samples. When carrying out the optical characterization the dielectric film and next two layers (In0.55Ga0.47As and InP) were removed by chemical etching. Photoreflectance measurements were performed in the so called bright configuration, where the sample was illuminated at near normal incidence by white light from a halogen lamp (100 W) serving as a probe beam source. The 488 nm line of an Ar+ (20 mW) laser was used as the photomodulation beam (pump beam) in PR measurements as well as in PL measurements as an excitation source. The detected light was dispersed through a 0.55 m focal length single grating monochromator and detected by a thermoelectrically cooled InGaAs photodiode. All the measurements presented in this work were performed at the room temperature.

III. THEORETICAL CONSIDERATIONS

We assumed in our model that Fick’s second law is obeyed in QW and barrier layers and all atom movements on the same sublattice have the same diffusion coefficient. In this work, since the structure has identical group-III concentrations in the well and barrier, only the diffusion of group-V atoms is assumed. This assumption is also in agreement with results presented by Lee et al.31 and Teng et al.,32 where they suggest that interdiffusion in InGaAsP/InGaAsP QWs is due to diffusion of P into and As out of the QW.43

For a nonsquare In0.51Ga0.49As1−xP1−x QW, the group-V atom composition can be described by the following equation:

\[
\text{InP: } 250 \text{Å; ud}
\]

\[
1.15Q (800 \text{ Å; } p=5\times10^{-7} \text{ cm}^{-2})
\]

\[
1.24Q (700 \text{ Å; ud})
\]

\[
3xQW (50 \text{ Å well; 100 Å barrier; ud})
\]

\[
1.15Q (800 \text{ Å; } n=5\times10^{-7} \text{ cm}^{-2})
\]

\[
\text{InP (5000 \text{ Å; } n=1\times10^{10} \text{ cm}^{-2})}
\]

\[
\text{Substrate n-type InP}
\]

FIG. 1. Layer structure of the investigated samples. Active region: three In0.76Ga0.24As0.39P0.61 mixed InGaAsP QWs in the built-in p-i-n electric field of the doped cladding layers. 1.15Q-In0.76Ga0.24As0.85P0.15 and 1.24Q-In0.76Ga0.24As0.61.
\[
\chi_v(z) = 1 - \frac{1 - x}{2} \left[ \text{erf} \left( \frac{L_z + 2z}{4L_d^\nu} \right) + \text{erf} \left( \frac{L_z - 2z}{4L_d^\nu} \right) \right],
\]

where \( z \) is the coordinate in growth direction with origin \((z = 0)\) at the center of the nonsquare QW, and \( L_z \) is the as-grown well width. The range of the disordering process is characterized by the interdiffusion length \( L_d = t_a D(t_a) \), where \( t_a \) is the annealing time. The as-grown QW is defined by \( L_d = 0 \) and a small value of \( L_d \) corresponds to a partially broadened QW, while a large value of \( L_d \) corresponds to extensive interdiffusion, and \( L_d \rightarrow \infty \) corresponds to the situation where the QW is completely smeared out. The value of the electric field was estimated to be \( \sim 57 \text{kV/cm} \) assuming the pinning of Fermi level at the acceptor and donor levels in the surrounding cladding layers. This value is also confirmed by the analysis of the observed Franz-Keldysh oscillations, details of which will be presented in Sec. IV F. The influence of the electric field on confined electrons may vary with depth for the same value of the electric field due to different effective barrier and hence different tunneling probability. For the shallow enough QWs the carriers can behave as if they are in the strong electric field regime, where the out tunneling probability is high and cannot be neglected in the calculations. Additionally, carriers in the intermixed QW could be accelerated in the well by the quasi-electric fields produced by the composition gradients. \(^2\) Thus, in order to describe the QW states properly and to include the tunneling effects, the time-dependent Schrödinger equation (TDSE) needs to be used.

The energies for three QWs in the presence of the applied electric field have been studied using real-time wave-packet propagation method \(^\text{45,46}^\) (RTWPM) which relies on the direct numerical integration of the TDSE. The finite difference form of the effective mass approximation is used in a well-established Ben-Daniel and Duke expression for the position-dependent-mass kinetic-energy operator. \(^47,48^\) The confinement potential profile is defined as follows

\[
V(z = z_{\text{min}} + \Delta l)_{e,h} = B_{e,h} \left[ E_{\text{ee}}^G \chi_{\text{ff}}(z), E_{\text{ff}}^G \chi_{\text{ff}}(z) \right] - E_{\text{ff}}^G(m,n)
\]

+ \( qFz + V_{\text{strain}}(z) \),

where \( z_{\text{min}} \) is the beginning of a computational grid. \( V_{\text{strain}}(z) \), involves biaxial and shear components of strain and was calculated according to Ref. 49 from which the effective mass \( m \) and energy band gap expression were also taken. We also assumed that only the band-offset ratio is a semifree parameter and after employing a fitting procedure to all samples (see Sec. IV) its value has been obtained to be \( VBO=70\% \). This is similar to the values cited by other authors. \(^\text{33,50}^\)

The remaining material parameters have been taken as constant and well known values. \(^\text{39}^\) More theoretical details will be published elsewhere. \(^\text{51}^\)

Figure 2 shows the numerically obtained potential for different interdiffusion lengths. It can be seen that the post-growth structure modification changes the profile of the well from squarelike to paraboliclike, so that the well becomes shallower and wider and tunneling probability for carriers increases. In Fig. 2 it can also be seen that in the case of three QWs in the electric field, in-direct optical transitions are possible which will be discussed in the next paragraphs.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Interpretation of PR features

Figure 3(a) presents PR spectra obtained for the as-grown InGaAsP/InGaAsP QW laser structure. The spectrum can be divided into two regions related to different parts of the structure: QW region and region related to so called Franz-Keldysh oscillations connected with the existence of built-in electric fields \(^52^\) and related, respectively, to \( 1.24Q \) and \( 1.15Q \) cladding layers.

The part of PR spectrum between 0.97 and 1.3 eV is associated with band gap transitions in bulklike \( 1.24Q \) and \( 1.15Q \) layers. PR resonances related to these layers include the so called Franz-Keldysh oscillations (FKOs) which are associated with a built-in electric field existing in these lay-
ers or at interfaces of these layers. In the case of 1.24Q layers, we expect an almost homogenous electric field because these layers are undoped and are placed between p-type and n-type layers (see Fig. 1). In the case of 1.15Q layers, an inhomogeneous electric field could be expected because these layers are doped. We will discuss this in more detail in the last section.

Considering the QW-related part, beside the fundamental transition at 0.782 eV three additional transitions are observed. Figure 4(a) also shows the PL spectrum (thin line). In photoluminescence only one peak associated with QW emission is observed. It is related to the transition between the first electron and the first heavy hole levels (subbands) and is asymmetric with a high energy tail. This is a characteristic feature of a free carrier recombination taking place at room temperature.

The part of the PR spectrum related to InGaAsP QW region (0.75–0.95 eV) of the as-grown structure could be satisfactorily fitted by four resonances. The transition energies have been obtained using a least-square fit to the low-field Aspnes’ third derivative form of the Lorentzian line shape.\(^{54}\)

\[
\frac{\Delta R}{R}(E) = \text{Re} \left[ \sum_{j=1}^{n} C_j \cdot e^{i\theta_j (E - E_j + i \cdot \Gamma_j)^{-m_j}} \right].
\]

where \(n\) is the number of optical transitions and spectral functions used in the fitting procedure, \(C_j\) and \(\theta_j\) are the amplitude and phase of the line shape, \(E_j\) and \(\Gamma_j\) are the energy and the broadening parameter of the transitions, respectively, while \(m_j\) is the parameter related to the type of the transition and dimensionality of the critical point of the density of states. We have assumed \(m=3\), which corresponds to one electron absorption in two dimensional systems. Figure 3(a) presents PR spectra (open circles) of the as-grown compressively strained InGaAsP/InGaAsP QWs structures together with the fitting curves (bold line). Figure 4(b) shows numerically obtained overlap integral intensities as well as the moduli of the individual resonances (thin line) obtained according to Eq. (4)

\[
\Delta \rho(E) = \frac{|C|}{[(E - E_0)^2 + \Gamma^2]^{m/2}}.
\]

The plot of the modulus of individual resonances makes analyses clearer, because we have a set of well defined peaks instead of superimposed derivativelike curves and it gives the relative intensities of the transitions in arbitrary units, allows comparison of these results with numerically obtained overlap integrals.

It is well known that the Gaussian line shape is more appropriate for inhomogeneous type of broadening but other authors\(^{54}\) and our experience with the fitting procedure both show that Lorentzian and Gaussian lines give the same transition energy within experimental error. Additionally, assuming \(m=3\) in the fit the procedure simulates with a good agreement a Gaussian line shape.\(^{54,55}\) Therefore, we selected Lorentzian line shape which gives a simple formalism for the moduli instead of a complex expression for third derivative of Gaussian line-shape and makes analyses clearer.

The time-dependent Schrödinger equation was used to explain, the origin of the observed PR features shown in Fig. 3(a). On the basis of the calculations, it has been concluded that, for as-grown structure, only one electron state, three heavy hole, and one light hole states are confined in the QW. For clarity the direct optical transition are labeled as follows: \(h\)-i heavy hole energy level, \(lh\)-j light hole energy level, and \(e\)-k electron energy level, where parameters \((i,j,k)\) are integer values, describing the order of the energy levels. The confinement of carriers becomes much weaker as the potential becomes shallower due to interdiffusion processes, and additionally tilted in the internal electric field. Also the energy states of the carriers are not stationary anymore (the respective wave functions are leaking out of the wells) and nominally forbidden optical transitions become possible. For instance, \(\Delta n \neq 0\) transitions and/or indirect transitions in the real space have a finite oscillator strength which increases with an increasing electric field and/or diffusion rate,\(^{51}\) and can be detected in the experiment. For the indirect transitions the notation is as follows: index \(U\), means upper, and \(L\) lower transition (see Fig. 2).

The first resonance at 0.782 eV (calculated value is 0.781 eV) is associated with the \(h1\)–e1 transition (a direct one in the real space). Also, the obtained value of overlap integral for this transition [see Fig. 3(b)] is largest. Generally, the \(h2\)–e1 transition is parity forbidden for an ideally symmetric QW, but in this case the built-in electric field of the \(p-i-n\) structure breaks the selection rules and this transition becomes observable. However, it was not clearly observed in the experiment, but the untypical shape of the high energy part of the first resonance (only for the as-grown structure) suggests the existence of this transition at about 0.830 eV. From theoretical considerations, this transition was expected at 0.833 eV. Also in this region an indirect transition \((Lh3\)–e1) was predicted at 0.822 eV, which can merge with
FIG. 5. Room temperature PR spectra of InGaAsP QWs for different interdiffusion conditions (annealing temperature, ECR-PECVD microwave power, and cap stoichiometry) reflected as a different values of energy shift of fundamental transition from 15 up to 55 meV.

The understanding of the observed effects much clearer. From our present more sophisticated and detailed theoretical field so only the stationary Schrödinger equation was used simple effective mass approximation for a single associated with the resonance, at 0.892 eV

$h_2-e_1$ transition. For these two transitions the overlap integrals, for the as-grown sample, are almost equal to zero, which confirms the experimental result.

The third resonance at 0.878 eV (theoretical value 0.883 eV) is associated with $l h_1-e_1$ transition. The fourth resonance, at 0.892 eV (0.900 eV from calculation), is associated with the $h_3-e_1$ transition. For these transitions, there is reasonable agreement between the calculated and experimentally obtained resonances [see moduli on Fig. 3(b)]. The sample differences are probably due to the complicated shape of PR spectra. In addition, there are three QW’s in the investigated structure, which can have slightly different widths which will reflect in broader and overlapping resonances. The complex shape of a line in the region of higher energies can also arise from the fact that the 1.24 Q transition (0.97 eV) where the low energy part of the FKQ can merge with higher order quantum well transitions. Additionally, as can be observed from Fig. 3(b), in this spectral range there are other very weak indirect transitions predicted from theory which can merge with the direct transitions, i.e., $l h_1-e_1$ and $h_3-e_1$. This complex line shape in high energy region of QW will be discussed in more detail in the next paragraph. On the other hand, since results for the fundamental transition are in excellent agreement with theoretical ones it seems that disagreement for higher excited states could be due to oversimplification in theoretical modeling of the diffusion, and in consequence, modeling of the potential shape.

Interpretation of the order of PR resonances differs from that one presented in our previous work28–30 in which we used simple effective mass approximation for a single as-grown QW structure and neglected the influence of the electric filed so only the stationary Schrödinger equation was solved. Our present more sophisticated and detailed theoretical model has changed the former interpretation and made the understanding of the observed effects much clearer. From a comparison of the systematic experimental results with the-

oretical calculations (see also the discussion in Sec. IV E and Fig. 15) of the interdiffused QW in the presence of the built-in electric field the time-dependent Schrödinger equation was necessary to get satisfactory agreement with all results.

Following the QWI process all the photoreflectance spectral feature are altered. First of all, the PR signal related to the 1.24Q layer changes significantly (see Fig. 4). We suppose that the main origin of the changes is a change in the phase of PR resonance. The change in phase could be caused by the interdiffusion of atoms across 1.24Q/1.15Q interface. Such atom migration does not change the band gap energy of 1.24Q and 1.15Q layers because of their thickness. However, it can change the band bending at the interface and the refractive index of the dielectric layer. This would influence the phase of PR resonance or produce a small change in the internal electric field, which will change the period of the FK oscillations. These oscillations will be used to determine the built-in electric field and changes of this field with the interdiffusion process.

As is observed in Fig. 4, which presents the as-grown and annealed QW at 780 °C, SiO$_2$/N$_y$ cap layer, the post-growth modification of the QW changes the potential shape and, in consequence, shifts the energy levels in the well; however, the order of PR resonances is not changed. The energy shift of the fundamental transition ($h_1-e_1$) will be used as a measure of the interdiffusion intensity, i.e., changes of the potential shape. A blueshift of 55, 25, and 42 meV for the ground state transition, $l h_1-e_1$, and $h_3-e_1$ transitions, respectively, has been obtained. These phenomena will be discussed in detail in the following sections.

Figure 5 presents a set of PR spectra obtained for samples after interdiffusion process. As can be observed for the stronger interdiffusion (reflected in the larger blueshift of the fundamental transition) the second weak resonance interferes with the first resonance, which is related to the fundamental transition, and thus is very difficult to analyze. Also it can merge with the indirect transitions for which overlap integral increase a bit with interdiffusion. Due to these reasons, in the remaining part of our work, $h_2-e_1$ transition will not be considered. As can also be seen in Fig. 5, for the interdiffusion, which produces a blueshift of about 15 meV and more, higher parts of obtained PR spectra start to get complicated. First of all, the overlap integral for the indirect transition ($U h_2-e_1$) increases rapidly and it has to be taken into consideration (dashed vertical thin line). This transition can coincide with the $h_3-e_1$ one. Additionally, the overlap integral of the $h_4-e_1$ transition is not zero. It is due to the fact that fourth heavy hole confined level appears when the width of the quantum well increases enough. However, at the same time, the confinement potential gets shallower which will also reflect in a weaker confinement of carriers. Thus the origin of this transition is more complex. It has been suggested that it could be an above barrier transition for which the wave function is localized above the well.
B. Influence of annealing on the QW optical transitions

In the IFVD process, the dielectric deposition parameters, and subsequent RTA treatments control the QWI process.

Figure 6 shows PL spectra of InGaAsP QW structures recorded at room temperature. The line shape of the emission peak is asymmetric with a tail at high energy side, which is typical of free carrier recombination at room temperature.56,57 It seems that annealing for 60 s at 580–780 °C enhances PL intensity by a factor of 1.5–2.0. The enhancement of PL intensity is attributed to a reduction of the number of grown-in defects which could result in some nonradiative recombination. In addition, the annealing process blueshifts the emission peak. This phenomenon has been investigated carefully in PR spectroscopy, which can also probe the excited state transitions.

The PR spectra were also obtained on the annealed samples, and Fig. 7 shows the results. Depending on the energy level position in the confinement potential both a blueshift of lower states or redshift of higher states has been observed.

Figure 8 shows the energy shifts obtained from PR spectra for the different optical transitions in InGaAsP QWs as a function of RTA temperature. As can be observed, a change of behavior of “thermal energy shift” from a redshift to a blueshift of the optical transitions occurs for the higher temperature anneal ~720 °C. For the lower anneal temperature a redshift is observed which is greatest, for transitions involving energy levels lying near the top of the well (light hole and third heavy hole), while no shift is observed, within experimental errors, for the \( h_1 - e_1 \) transitions where the energy level lies near the bottom of the well. These behaviors are associated with an increase/decrease of the effective width of QW effectively decreasing/increasing the energy of the confined levels \( E_{LW} \). Above ~720 °C the energy shift rapidly increases with increasing annealing temperature, for all transitions, reaching 15 meV for the fundamental transition at 780 °C. Similar result for QW structure was obtained before by other authors.12 This rapid increase is evoked by temperature which corresponds to the interdiffusion activation energy.

In the presented case, for the ground state transition, in the whole range of temperatures, the blueshift observed in PL (filled stars in Fig. 8) is almost identical, within experimental error, to the one observed in PR (open circles in Fig. 8). The absorption-type experiment, such as photoreflectance, is not sensitive to defect states and a comparison between PL and PR gives information about a character of the recombination process. The Stokes shift between PL and PR features of the fundamental transition was not observed. It means that for all investigated structures the room temperature emission line is attributed to free carrier recombination process without a significant contribution of defect states.

C. Influence of microwave power on the QW optical transitions

Figure 9 shows PR spectra of InGaAsP QW structures with SiO\(_2\) cap layer, recorded at room temperature. Dielectric cap layer was deposited by ECR-PECVD at different microwave powers. The whole structure was later annealed at 780 °C. It has been observed that increasing the microwave power increases the blueshift for the fundamental transition (Fig. 9) but decreases the PL intensity (Fig. 10). The decrease of PL intensity is attributed to a reduction of the
number of confined electrons in the QW region due to thermal escape, which is more efficient for strongly interdiffused QWs, where energy levels are closer to the top of the QW. In the PR spectra the blueshift, associated with a shift of the energy level, is observed for all transitions, but its value is different for all of them. For the ground state transition \( \text{h1} \rightarrow \text{e1} \) the blueshift reaches up to 55 meV. The other two transitions \( \text{h3} \rightarrow \text{e1} \) and \( \text{h1} \rightarrow \text{e1} \) are less shifted, 25 and 42 meV, respectively. The results show that the lowest energy transition is most sensitive to the postgrowth modification. For the case of the ground state transition, over the whole range of microwave powers, the blueshift observed in PL (filled stars in Fig. 11) is almost exactly the same as the shift observed in PR (open circles in Fig. 11). The conclusion is similar to those obtained for annealed samples showing the weak influence of the defect states on emission signal.

A study of the influence of microwave power shows that an increase in the microwave power from 600 to 900 W causes an increase in the blueshift (about 55 meV for the fundamental transition), while at the same time it decreases the PL yield (by a factor of 4) from the sample. Thus, in practical applications, the choice of microwave power should be made based on a balance between demands for emission energy and intensity.

D. Influence of cap layer composition on the QW optical transitions

A significant difference in the amount of blueshift for the QW optical transitions is observed for samples with different stoichiometry of the SiO\(_x\)N\(_y\) cap layer. Figure 12 proves that the dielectric cap plays an important role in the atom migration process. This comparison shows that the existence of the dielectric film induces an enhancement of the blueshift of the fundamental transition from 15 (uncapped annealed sample) to 65 meV. For other transitions \( \text{h1} \rightarrow \text{e1} \) and \( \text{h3} \rightarrow \text{e1} \) the presence of the dielectric film induces values of the blueshift up to 45 and 48 meV, respectively. The changes in the stoichiometry of the cap layer are reflected in the changes in refractive index, which can be used as an identifier of the cap layer composition. The observed energy shifts versus refractive index of the cap layer are presented in Fig. 13.

The structures were annealed at 780 °C for 60 s and capped, with different compositions of SiO\(_x\)N\(_y\) film. A microwave power of 500 W was used to deposit the dielectric caps.
As the refractive index increases, the value of the blue-shift also increases following the parabolic trend, up to the maximum value of \(-6.5\) meV for the fundamental transition in the case where \(n=1.66\) (and \(n=1.69\) for \(lh1-e1\)). Similar results have previously been obtained for the ground state for \(n=1.63\).58

Good correlation between the amount of Ga (and In) incorporated into the dielectric film with the amount of blueshift have been shown for various annealing temperatures and times,34 meaning that a dissolution of group-III species into the dielectric films directly correlates with the physical process that enhances the QWI. However, blue shift for the films of different compositions is not simply related to the amount of Ga (and In) outdiffused into the dielectric. Hazell et al.34 proposed that annealing-induced Ga (In) vacancies, produced at the dielectric/semiconductor interface, due to Ga (In) out diffusion into the dielectric, are responsible for the enhancement of the QWI process in the InGaAsP structures. Because of the identical group-III (Ga, In) composition of the QWs and adjacent barrier it has been proposed that group-V (P, As) atoms can induce the QWI process through interstitial migration.59,60 This exchange of group-III vacancies on group-V interstitials is a consequence of the kick-out mechanism.61 This mechanism will produce intermixing through As–P exchange. However, for different SiO

stress shrinks the free space in the porous dielectric layer, which is a reservoir for outdiffused atoms, leading to the decrease of QWI.

Thus, for the low values of the refractive index (low stress in SiO

E. Energy levels

Figure 15(a) summarizes all the obtained results for the transition energies in the active part of the structure, i.e., the QWs. It presents the values of energies of optical transitions both for the ground state and excited states, obtained from the PR experiment (points) and from theoretical calculations (lines). These values change versus interdiffusion process intensity. The degree of the QW intermixing intensity is directly associated with the energy shift of the ground state transition.

It is known that the energy level positions should change with changes of the width and/or the change of the depth of the QW. It is expected that with the increase of the ground
state energy shift, the QW profile should change from a narrow and deep squarelike shape to a broad and shallow parabolicike shape. This behavior should also be reflected by a change in the distance between the energy levels. This conclusion is expected, but it has not been observed so far experimentally for InGaAsP-based QWs. Up to date, investigations of similar structures have mainly used the photoluminescence technique which detects only the ground state energy shift, the QW profile should change from a narrow and deep squarelike shape to a broad and shallow parabolicike shape. This behavior is expected, but it has not been observed so far experimentally for InGaAsP-based QWs. Up to date, experiments have mainly used the photoluminescence technique which detects only the ground state energy shift, the QW profile should change from a narrow and deep squarelike shape to a broad and shallow parabolicike shape. 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\[
\Delta E = \Delta E_{\text{con}} + \Delta H_{\text{con}} + \Delta \text{bg}.
\]

In the first stage [see Fig. 15(b)] of the intermixing process \((L_d \ll L_W)\), for wide wells the majority of the energy shift due to RTA results from changes in the confinement energy \(E_g \sim L_W^2\) due to changes in the QW effective width.

Since the ground-state energies of electrons and heavy holes are located near the bottom of the well (beneath the effective width), they will experience a narrowing of the well width and their energies should increase as the well shape is changed by RTA, giving rise to the small blueshift of the fundamental transition. However, for narrower well widths, electron and heavy hole-ground state energies are already significantly increased due to spatial confinement and approach the barrier energy (i.e., they are near the top of the well, above the effective width). Above this effective width carriers will be less confined after RTA—“seeing” a wider quantum well, and so their energies will be lowered, giving rise to the redshift of the fundamental transition in this regime.

For the cases presented in this paper, both of these tendencies can be observed because of the possibility of detecting excited states in the QW using PR.

In the second stage of QWI \((L_d \sim L_W)\), the energy shift is dominated by changes in the value of the band gap [see Fig. 15(b)] due to changes of the well composition resulting from diffusion of P into and As out of the QW.\(^{44}\) Finally, a rapid increase in the blueshift is observed for all transitions.

In Fig. 15(a), it can be seen that the ground state interband transition energy, which is defined as \(E_{h1-e1} = E_{h1} + E_{e1} + E_{hl}\), increases monotonically with an increase of the blueshift of the fundamental optical transition. In this case all presented results are in excellent agreement with theoretical calculation presented as bold line in Fig. 15(a). The \(lh1-e1\) transition energy increases much more slowly and up to about 20 meV (medium interdiffusion regime) is well resolved in the experiment. Additionally, \(h3-e1\) transition in this regime is well resolved and its energy decreases slowly, which in consequence, decreases the distance between the \(h3, lh1,\) and \(h1\) energy levels. This behavior is due to the fact that for the \(h1-e1\) transition two processes (changing of the band gap and decreasing of the QW width) add to each other giving a strong blue shift. In the case of higher order energy levels, i.e., \(h3\) and \(lh1\) these two processes compensate and the blueshift is smaller.

For interdiffusion which resulting in a blueshift of more than 20 meV, the \(lh1-e1\) and \(h3-e1\) transitions cannot be clearly resolved from the experiment. This is mostly due to the fact that the \(h4-e1\) transition and the indirect \(Uh2-e1\) transition appears which was discussed in the previous sections. This is the reason for the wide distribution of parameters obtained from the fitting procedure in this regime.

FIG. 15. (a) Experimentally and numerically obtained energy level position vs interdiffusion intensity (reflected in the blueshift of the fundamental transition), (b) schematically presented stages of the interdiffusion process.
F. Influence of the postgrowth treatment on p-i-n built-in electric field

For moderate electric fields, the PR spectrum exhibits a series of oscillations, termed as FKOs, as shown in Fig. 16. In PR, the built-in electric field is modulated through the photoinjection of electron-hole pairs via a chopped incident laser beam. The sample surface or p-i-n electric field can be determined from the position of FKO extremes. It is worth noting here that the FKO conditions cannot be met in the QW region of the sample (carriers cannot be accelerated along the QW growth direction which is parallel to FKO), thus FKO signal must be related to the bulk region of the heterostructures. After Shen and Pollack, it has been assumed that FKOs are heavy-hole dominated.

To evaluate the built-in electric field, a PR spectrum can be analyzed by using the asymptotic representation of the Airy function on the FKO analysis. The inset of Fig. 17 shows the quantity \( (4/3\pi)(E_g-E_j)^{3/2} \) plotted as a function of refractive index for the related FKOs enabling a precise evaluation of the internal electric field when the analysis is performed for a single critical point. The solid lines are the least-square fits to a linear function, which yield the value of the electric field for the surface region to be in the range from 47 up to 57 kV/cm, for different QWI conditions. From small variations in the values of the electric field resulting from the different conditions of the QWI process (presented in the inset of Fig. 17) it can be concluded that the built-in surface electric fields (associated with FKOs from 1.15Q region) do not change significantly after the QWI process. However, investigated structures include a second built-in p-i-n junction electric field, which is more important from an applications point of view. As a consequence of existence of this field a superposition of different FKO periods has been observed. Moreover, the existence of the surface electric field (FKOs from 1.15Q region) prevents us from using the previous method to estimate the value of this p-i-n junction electric field. To overcome this problem, we performed a line shape analysis using the fast Fourier transform (FFT) of the PR spectrum. The oscillation frequency \( f(eV^{-3/2}) \) of the FKO is given by

\[
f = \frac{2(2\mu)^{1/2}}{3\pi e\hbar}. \tag{6}
\]

The relation between \( f \) and \( F \) indicates that the signals coming from the different interfaces with various electric fields can be resolved in the FFT spectrum. A typical FFT spectra of the InGaAsP laser structure signal are shown in Fig. 17. It can be seen that the signals from the p-i-n junction and from the surface are clearly resolved. The values of the built-in electric fields calculated using FFT are 54 and 48 kV/cm for surface (1.15Q) and the p-i-n junction (1.24Q), respectively. Results obtained by both methods are in agreement with previous estimations determined for the as-grown structure, when the field was calculated based on Fermi level pinning and its value was found to be 57 kV/cm.

V. CONCLUSIONS

In this work it has been shown how the QWI process can affect the optical transitions in a QW laser structure. Here, the influence of the technological parameters such as annealing temperature, microwave power of the ECR-PECVD process, and the stoichiometry of the cap layer, on the optical properties of InGaAsP QW have been investigated. It has also been shown that the control of these parameters is an attractive way to achieve band structure modification.

The time-dependent Schrödinger equation has been solved for the InGaAsP diffused QW in the electric field of the p-i-n junction and used to explain the origin of the observed PR resonances. It has been experimentally found for
InGaAsP QW structures that an increase in interdiffusion causes the energy levels to change in different ways, mostly depending on the energy level position in the well. This result was confirmed by comparison with theoretical calculations.

The influence of RTA conditions has been also analyzed. Around 720 °C, a change in the energy shift of the optical transitions occurs. Below this temperature, for excited state transitions, a redshift occurs, associated with an increase in the effective width of the QW accompanied by a decrease of the energy of the confined levels. Above 720 °C the energy of the confined levels. Above 720 °C the energy shift rapidly increases with the increase in annealing temperature and changes to blue-shift for all transitions at 780 °C. This increase is evoked by temperature, which corresponds to the “interdiffusion activation energy,” beginning to change the content of the active region. These correlations significantly.

In addition, a blueshift was also observed for samples capped with dielectric deposited with different microwave powers in the ECR-PECVD process, as well as for samples with cap layers of different stoichiometries. In this case the ground state transition was observed to be the most shifted while the other transitions were clearly less affected.

Moreover, for samples having a dielectric cap deposited by ECR-PECVD with enhanced microwave power, the Stokes shift between PL and PR features of the fundamental transition was not observed. This means that enhancing the microwave power of the ECR-PECVD process increases value of the blueshift but does not alter the quality of the layers.

Finally, the values of the built-in junction electric field were determined for all postgrowth modified samples using two methods, both of which indicated that during QWI processes the built-in junction electric field does not change significantly.

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