Intersubband transitions in dilute (In,Ga)(As,N)/(Al,Ga)As multiple quantum wells analyzed within a three-band \textit{k}·\textit{p} model

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We study the influence of nitrogen (N) on the intersubband absorption spectra of dilute (In,Ga)(As,N)/(Al,Ga)As multiple quantum wells (MQWs). For MQWs with 6 nm well width and Al_{0.33}Ga_{0.67}As barriers, the main absorption band at 1365 cm\textsuperscript{-1} exhibits with increasing N content a slight redshift in contrast to an expected blueshift, a remarkable decrease of the intensity, and a strong asymmetric broadening on the high-frequency side. In addition, a minor absorption feature appears on the high-frequency side. For MQWs with 3 nm well width and Al_{0.42}Ga_{0.58}As barriers, the strong asymmetric main absorption band at 1820 cm\textsuperscript{-1} exhibits with increasing N content a blueshift, a decreasing intensity, and a minor absorption feature on the low-frequency side, which cannot be attributed to an intersubband transition by only taking into account the effect of N on the discontinuity of the conduction band edges in the MQWs. We analyze the transition energies within a three-band \textit{k}·\textit{p} band-anticrossing model for heterostructures. Because of the presence of the localized N state in the quantum well, a set of N-like states is formed in each quantum well due to the confinement. These N-like states couple to the original quantum well states, and mixed subbands are formed. The dependence of the calculated wave numbers for bound-to-bound as well as bound-to-continuum intersubband transitions on the nitrogen content are in good agreement with the experimental data.

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I. INTRODUCTION

The incorporation of small amounts of nitrogen on anion sites in III-V semiconductors leads to a remarkable reduction of the band gap ($E_G$), which makes such alloys technologically important for optoelectronic devices for wavelengths between 1.3 and 1.55 \mu m. The reduction of $E_G$ is well described within the so-called two-band \textit{k}·\textit{p} band-anticrossing (BAC) model introduced by Shan et al.\textsuperscript{1} The Hamiltonian of this model takes into account the coupling between the extended states at the conduction band edge $E_{C[\text{GaAs}]}$ of GaAs at $\Gamma$ and the localized nitrogen (N) state at $E_N$ above $E_C$. This coupling causes the formation of two mixed conduction subband branches at $E_+$ and $E_-$, which exhibit an anticrossing behavior. The redshifted lower branch at $E_-$ is responsible for the decrease of the energy of the conduction band edge and the strong increase of the effective mass of the conduction-band electrons in Ga(As,N). O’Reilly and Lindsay\textsuperscript{2,3} have proposed an extended version of the BAC model, which is based on a three-band \textit{k}·\textit{p} approximation and includes, besides the coupling between the conduction band edge and the averaged N-state, also the valence band edge of GaAs at $\Gamma$. Therefore, this three-band BAC model already takes into account nonparabolicity effects in GaAs leading to more confined states at a given width of a quantum well than predicted by the two-band model. Furthermore, this three-band \textit{k}·\textit{p} model shows that $E_V$ remains nearly unaffected. Therefore, the band offset between GaAs and Ga(As,N) changes only the conduction band edge $E_{C}$, which decreases with increasing N content, causing an increasing conduction band offset $\Delta E_C=\left[E_{C[\text{GaAs}]}-E_{C[\text{Ga(As,N)}]}\right]$ in Ga(As,N)/GaAs multiple quantum wells (MQWs).

On the one hand, intersubband transitions in thick layers of dilute Ga(As,N) and in Ga(As,N)/GaAs heterostructures have been frequently studied.\textsuperscript{4} On the other hand, the increase of $\Delta E_C$ in Ga(As,N)/(Al,Ga)As heterostructures should be of comparable technological importance for optoelectronic devices for the mid-infrared region as the reduction of $E_G$ for near-infrared optoelectronic devices. For instance, in Ga(As,N)/(Al,Ga)As quantum-cascade lasers, an increasing $\Delta E_C$ should reduce leakage currents from the upper laser level into other levels including continuum states and, therewith, improve the performance of such lasers. However, there are only a few reports by Guzmán et al.\textsuperscript{5} and Duboz et al.\textsuperscript{6} who studied the influence of N on intersubband transitions (ISTS). Moreover, in these investigations, the experimental data were analyzed only within the simplified two-band BAC model, i.e., only by taking into account the increasing band offset with increasing N content and not the coupling between the N states and the conduction band.

In this paper, we investigate the influence of N on ISTs in dilute (In,Ga)(As,N)/(Al,Ga)As and Ga(As,N)/(Al,Ga)As MQW structures. The experimental results are analyzed within a three-band \textit{k}·\textit{p} BAC model for heterostructures, where we focus on the IST energies. The paper is organized as follows: In Sec. II, the samples and the experimental setup are described. The intersubband absorption (ISA) spectra are presented in Sec. III. In Sec. IV, the three-band \textit{k}·\textit{p} BAC model for ISTs in heterostructures is described. This model is applied in Sec. V to analyze the experimental spectra focusing on the transition energies of the ISA bands. Finally, we summarize the results and conclude in Sec. VI.

II. SAMPLES AND EXPERIMENTAL SETUP

In order to study the influence of nitrogen on ISTs, we have measured the ISA spectra of (In,Ga)(As,N)/
(Al, Ga)As MQWs. These samples were grown on semi-insulating (Si) GaAs substrates by molecular-beam epitaxy (MBE) as described in Ref. 7. Each MQW consists of 50 periods with a nitrogen content \( N_N = 4\% \). The wells of the MQWs are doped with Si, where the Si concentration \( n_{Si} \) increases from \( n_{Si} = 2 \times 10^{19} \text{ cm}^{-3} \) for \( N_N = 0.1\% \) to \( n_{Si} = 5 \times 10^{18} \text{ cm}^{-3} \) for \( N_N \geq 2\% \) in order to compensate for the increasing electrical passivation of the Si donors with increasing \( N_N \). The concentration \( n \) and mobility \( \mu \) of the free carriers were determined by Hall measurements, while the spatial distribution of the free carriers in the MQWs were verified by capacitance-voltage (C-V) measurements.

The experimentally determined carrier concentrations at room temperature agree with the nominal values. At \( T = 300 \text{ K} \), the Hall mobility decreases from about \( \mu = 1700 \text{ cm}^2/\text{V} \cdot \text{s} \) for samples without N to about \( 400 \text{ cm}^2/\text{V} \cdot \text{s} \) for MQWs with 0.1\% N and decreases even further to values between 200 and 100 \( \text{cm}^2/\text{V} \cdot \text{s} \) for samples with \( N_N \geq 0.8\% \). This dependence of \( \mu \) on \( N_N \) at \( T = 300 \text{ K} \) is interpreted in the following way. In samples without N, scattering of electrons on longitudinal optical phonons as well as on ionic impurities is dominating, while with increasing N content electrons are more and more scattered by N-related defects including alloy scattering and potential fluctuations due to N clusters.\(^7\)-\(^10\) With decreasing temperature down to about 77 K, the mobility of the N-containing samples remains almost constant (predominantly defect scattering), whereas for 10 K < \( T < 77 \text{ K} \) weak localization determines the mobility. Below 10 K, hopping conduction prevails.\(^7\)-\(^10\)

We have studied two sets of MQWs. In the first set (MQWs I), the wells also contain In with \( N_{In} = 3N_N \) in order to compensate for the strain due to the N atoms. The well width \( d_w \) was chosen to be 6 nm. The barriers consist of Al\(_{0.33}\)Ga\(_{0.67}\)As with a thickness \( d_b = 10 \text{ nm} \). Measurements on different MQWs have shown that an In content of \( N_{In} = 12\% \) in the wells does not substantially change the ISA spectra. Therefore, in the second set of samples (MQWs II), the wells are grown without In. The well width \( d_w \) was chosen to be 3 nm, and the barriers consist of Al\(_{0.42}\)Ga\(_{0.58}\)As with a thickness \( d_b = 10 \text{ nm} \). All samples were analyzed by x-ray diffraction, which indicates that the actual length of the periods, the N content of the wells, and the composition of the barriers agree well with the nominal data. In the following, we will focus on as-grown samples, because a rapid thermal annealing of the MQWs for temperatures below 850 °C, which usually improves the interband emission characteristics,\(^11\) does not significantly change the ISA spectra.

The ISA spectra were measured by two methods. First, a single transmission of polarized light at oblique incidence (angle of incidence \( 60^\circ \)) through plane parallel samples was detected. Second, in order to considerably improve the signal-to-noise ratio, the transmission was studied through waveguide-shaped samples (45° facets and 7 internal reflections). Measurements were carried out at room temperature as well as for selected samples at \( T = 77 \text{ K} \) using a Fourier-transform spectrometer (Bruker IFS 66v). The spectra recorded for \( p \)-polarized light \( (T_p) \) were normalized to the ones for \( s \)-polarized light \( (T_s) \). The obtained \( T_p/T_s \) spectra of the samples were additionally normalized to the \( (T_p/T_s)_0 \) spectrum of a SI-GaAs reference substrate in order to remove any effects due to the prepolarization of the Fourier-transform spectrometer as well as the SI-GaAs substrate. For the detection of the weak and very broad absorption bands, the measurements were carried out for different sample and polarizer orientations (vertical and horizontal), and the final spectra were obtained by averaging over all \( T_p/T_s \) spectra.

### III. INTERSUBBAND ABSORPTION SPECTRA OF MQWS

For samples without nitrogen, the transmission spectra for a single light pass exhibit a minimum due to ISA, where the transmittance \( T = (T_p/T_s)/(T_p/T_s)_0 \) decreases to about 88\%. The full width at half maximum (FWHM) is about 150 cm\(^{-1}\). For the MQWs with \( N_N > 0.1\% \), the ISA minimum becomes much less pronounced (its value decreases to 98\%). At the same time, the minimum becomes much broader (FWHM \( \approx 400 \text{ cm}^{-1} \)), i.e., the absorption becomes very weak. Therefore, we will only discuss ISA spectra of (In, Ga) \( \times (\text{As},N)/(\text{Al,Ga})\text{As} \) MQWs using the much more sensitive internal reflection method on waveguide-shaped samples. For presenting these spectra, we use the absorbance as given by \( A = -\ln(T_p/T_s) \) corrected by the background signal given by \( +\ln(T_p/T_s)_0 \).
are 3.5 for $N_N = 0.1\%$, 6 for 0.3\%, 7 for 0.8\%, 8 for 1\%, and 9 for 2.4\%.

frequency side a strong asymmetric broadening. This trend continues in the ISA spectrum for the sample with $N_N = 0.3\%$, which shows besides the very broad band at $v_0 = (1212 \pm 10) \text{ cm}^{-1}$ a second absorption band at $v_1 = (2930 \pm 30) \text{ cm}^{-1}$, where the intensity of both absorption bands is already remarkably reduced with respect to the ISA band of the MQW without N. With increasing $N_N$ up to 1.6\%, the small decrease of $v_0$ continues, and the spectral feature at $v_1$ disappears due to broadening effects. Finally, for the samples with $N_N \geq 2.2\%$, the wave number $v_0$ slightly increases with increasing $N_N$ and reaches the value $v_0 = (1405 \pm 10) \text{ cm}^{-1}$ for $N_N = 4\%$.

The ISA spectra of the MQWs II are shown in Fig. 2 for increasing N content recorded at 300 K. The spectrum of the sample without N shows a pronounced absorption band at $v_2 = (1820 \pm 15) \text{ cm}^{-1}$. However, in contrast to the ISA spectrum of the MQW I with $N_N = 0$, the main ISA band for the MQW II with $N_N = 0$ exhibits already a strong asymmetric broadening on the high-frequency side. For the spectrum of the sample with $N_N = 0.1\%$, the main ISA band is clearly blueshifted, and the asymmetry on the high-frequency side persists. With a further increase of $N_N$, the intensity of the ISA bands remarkably decreases, and on the low-frequency side of the band at $v_2$ a weak very broad absorption feature appears at $v_3 = 1900 \text{ cm}^{-1}$. Finally, in the spectrum of the sample with $N_N = 2.4\%$, the main ISA band disappears, the low-frequency feature remains, and a new feature appears at about 2750 cm$^{-1}$.

For 77 K, the dependence of the ISA spectra on the nitrogen content is almost the same as for 300 K. We believe that this observation can be explained as follows. First, due to the high concentration of free carriers in the samples, the electron gas is nearly degenerate. Therefore, the electron distribution in the occupied first subband as well as in the almost unoccupied second subband hardly changes with decreasing temperature down to 77 K. Second, as discussed in Sec. II, the strong scattering of the electrons on N-related defects for the N-containing MQWs does not change for temperatures between 77 and 300 K. Therefore, the large FWHM of the ISA bands remains with decreasing temperature down to 77 K.

IV. THREE-BAND k·p HAMILTONIAN FOR Ga(As,N)/(Al,Ga)As MQWs

The small redshift observed in MQWs I and II with increasing N content is the essential experimental result. This is in contrast to an expected blueshift, if the influence of N is only taken into account on the band offset. Therefore, we will focus on analyzing the IST energies as a function of $N_N$. The second important feature of all ISA bands of the MQWs with $N_N > 0.2\%$ is the remarkable reduction of their intensity and the strong increase of their FWHM. We believe that these features are predominantly caused by the strong scattering of electrons on N-related defects (cf. Sec. II) and are not determined by the oscillator strengths of these ISTs. Therefore, a quantitative description of the line shape requires a scattering theory for the free carriers on N-related defects, which is beyond the scope of this investigation.

While the MQWs I contain indium in the wells, this is not the case for the MQWs II. However, for the MQW I with the largest In content, the change in the wave number $v_{12}$ of the IST from the ground $|1 \rangle$ to the first excited subband $|2 \rangle$ is smaller than the uncertainty of the experimental value $v_0$. Therefore, in the following, we will ignore the influence of indium on the conduction band structure, and the energies of the subbands are only calculated for Ga(As,N)/(Al,Ga)As MQWs within a three-band k·p approximation. This three-band k·p model takes into account the effect of N on the conduction band structure and the nonparabolicity in the Ga(As,N) wells as well as the (Al,Ga)As barriers. The conduction band structure of each individual layer within a heterostructure is described by the tight-binding Hamiltonian

$$
\hat{H} = \begin{pmatrix}
E_N + \alpha_N k_z^2 & V_{NC} - \alpha_C k_z^2 & P_{Nk_z} \\
V_{NC} - \alpha_C k_z^2 & E_C - \alpha_C k_z^2 & P_{Ik_z} \\
P_{Nk_z} & P_{Ik_z} & E_V + \alpha_V k_z^2 
\end{pmatrix}
$$

(1)

where $k_z$ denotes the component of the wave vector along the growth direction of the MQWs. $E_N$, $E_C$, and $E_V$ are the energies of the original states, taking into account that their energies are slightly changed due to the N incorporation (disorder and band tails, formation of clusters, partial breakdown of k-selection rules, etc.). The coefficients $\alpha$ are related to the effective masses of the different states. For the localized N state, a very flat dispersion is used, which corresponds to a very large effective mass. The coupling between the original states is described by the off-diagonal coefficients $V_{NC}$, $P_N$, and $P_I$. The coupling between the N state and the conduction (valence) band edge disappears for $N_N = 0$ because $V_{NC} \propto \sqrt{N_N} (P_N \propto \sqrt{N_N})$ is assumed. The constant $P_I$ accounts for the coupling between the conduction and valence edges.
in GaAs at $\Gamma$ and is independent of $N_N$. The (Al,Ga)As barriers are also described by the Hamiltonian in Eq. (1), with all $N$-depending terms as well as $E_N$ being set to zero. The parameters used in the calculation are given in Ref. 12.

For bulk GaAs, $N_k=0$, the Hamiltonian in Eq. (1) has three solutions, $E_+, E_-$, and $E_3$

$$E_k(N_k, k_z = 0) = \frac{E_N + E_C}{2} \pm \frac{1}{2} \sqrt{(E_N - E_C)^2 + 4V_N^2(N_k)}$$

and $E_3 = E_V$.

Figure 3(a) shows the anticrossing behavior of the mixed conduction band branches $E_+$ and $E_-$ versus $k_z$ in bulk GaAs, $N$ for $N_k=0, 0.5, and 1\%$ according to Eq. (2), while in Fig. 3(b) the values $E_+$ and $E_-$ are plotted versus $N_k$. The energies $E_+$ and $E_-$ describe the pseudogap between the conduction branches for a given $N_k$ at $k_z=0$ as already described within the two-band model.\textsuperscript{1,2}

In order to calculate the eigenstates for the heterostructure, we switch to real space by replacing in Eq. (1) the momentum $k_z$ by its quantum-mechanical operator $(1/i)\partial/\partial z$.\textsuperscript{13} By assuming periodic boundary conditions for the whole structure (such as in a MQW or superlattice), we can apply a discrete Fourier transformation. The wave functions for the subbands of the complete structure are then given by

$$\Psi_{k,v}(z) = \frac{1}{d} e^{ik_z z} \sum_{n,j} e^{k_p,n,j} \exp \left( \frac{2\pi i j}{d} z \right) \mathbf{u}_n,$$

where $d$ denotes the period of the MQW or superlattice, $v$ the subband index, $j$ the Fourier expansion index, and $\mathbf{u}_n$ ($n = 1, 2, 3$) the base vectors of the three-band $k\cdot p$ model. In this basis, the eigenvalue equation for the heterostructure can be written as

$$\sum_{n',j'} H_{n,j',n'}(k_z) c_{k,v,n,j'} = E_{k,v} c_{k,v,n,j},$$

with the matrix elements denoted by

$$H_{n,j,n'}(k_z) = \left[ \sum_{n,j} e^{k_v z} \mathbf{u}_n \right] \cdot \mathbf{u}_n \exp \left( \frac{2\pi i j}{d} z \right),$$

where $j_0 = \pm q_z$, $-1/2 \leq q_z \leq 1/2$, and $k_z = 2\pi q_z/d$. The matrix elements $\langle u_n \vert H(z) \vert u_{n'} \rangle$ of the Hamiltonian that describes the MQW structure are analytically calculated assuming that the confinement potentials are constant within each layer. Putting everything together, the eigenstates of the complete MQW structure are calculated from the eigenvalue equation of a Hermitian matrix

$$\hat{H}_{j,j'} = \sum_{m=0}^{n} \left( \begin{array}{cccc} E_{m} + \alpha_{N_m}(2\pi/d)^2 j'^2 & V_{N_m} - \alpha_{N_m}(2\pi/d)^2 j'^2 & P_{N_m}(2\pi/d) j'^2 & \alpha_{V}(2\pi/d)^2 j'^2 \\ V_{N_m} - \alpha_{N_m}(2\pi/d)^2 j'^2 & E_{m} - \alpha_{C}(2\pi/d)^2 j'^2 & P_{V}(2\pi/d) j'^2 & \alpha_{V}(2\pi/d)^2 j'^2 \\ P_{N_m}(2\pi/d) j'^2 & P_{V}(2\pi/d) j'^2 & E_{V} + \alpha_{V}(2\pi/d)^2 j'^2 & \alpha_{V}(2\pi/d)^2 j'^2 \\ \alpha_{V}(2\pi/d)^2 j'^2 & \alpha_{V}(2\pi/d)^2 j'^2 & \alpha_{V}(2\pi/d)^2 j'^2 & \alpha_{V}(2\pi/d)^2 j'^2 \end{array} \right) \times g_{m}(j,j'),$$

where

$$g_{m}(j,j') = \left\{ \begin{array}{ll} (d_m - d_{m-1})/d & \text{for } j = j', \\
\{1/[2\pi(j-j')][\exp(2\pi(j-j)d_m/d) - \exp(2\pi(j-j)d_{m-1}/d)] \text{ for } j \neq j'. \end{array} \right.$$
INTERSUBBAND TRANSITIONS IN DILUTE

FIG. 4. Conduction subband structure for Ga(As,N)/(Al,Ga)As MQWs with \( d_w = 6 \text{ nm} \) and Al\(_{0.33}\)Ga\(_{0.67}\)As barriers (MQWs Ib). (a) \(|\Psi|^2\) calculated for small N content. The thick solid lines represent the original bound states |1\> and |2\> in the quantum well for \( N_N = 0 \). The thin solid lines indicate the N-like states, which are caused by the localized N state at \( E_N \) for very low N content. (b) \(|\Psi|^2\) for \( N_N = 1 \). The lines represent \(|\Psi|^2\) of the mixed subbands formed due to the coupling between the original bound and the N-like states in the quantum well.

The discontinuity of the conduction band structure of Ga(As,N)/(Al,Ga)As MQWs at first, we discuss the data, which were calculated for MQWs with \( d_w = 6 \text{ nm} \) and Al\(_{0.33}\)Ga\(_{0.67}\)As barriers. These heterostructures are labeled MQWs Ib, since they have the same layer structure as the experimentally investigated samples MQWs I, but do not contain In in the wells. Figure 4 shows the calculated band structure for two MQWs Ib. For the MQW Ib without any nitrogen [cf. Fig. 4(a)], the quantum well contains two bound states |1\> and |2\>, which are indicated as thick solid lines. For this MQW, the discontinuity of the conduction band is determined by \( E_c\text{[GaAs]} \) and \( E_c\text{[Al}_{0.33}\text{Ga}_{0.67}\text{As]} \). In Ga(As,N) with very low N content, a localized N state is formed at \( E_N = 1.65 \text{ eV} \) (Ref. 1) indicated in Fig. 4 by the dashed line and included in Eq. (6) by the \( E_N \)-dependent diagonal element. An important consequence of Eq. (6) is that due to the QW confinement the localized N state creates an additional set of N-like states in each quantum well above \( E_N \), which are indicated in Fig. 4(a) as thin solid lines. Due to the large effective mass of the N state and the small energy difference between the barrier and \( E_N \), the energy separation between neighboring N-like levels is smaller than the one between the original quantum well states |1\> and |2\>.

V. COMPARISON OF THE CALCULATED INTERSUBBAND TRANSITION ENERGIES WITH EXPERIMENTAL DATA FOR Ga(As,N)/(Al,Ga)As MQWS

In this section, we apply the solution of the eigenvalue problem of the matrix given in Eq. (6) to the conduction band structure of Ga(As,N)/(Al,Ga)As MQWs. At first, we discuss the data, which were calculated for MQWs with \( d_w = 6 \text{ nm} \) and Al\(_{0.33}\)Ga\(_{0.67}\)As barriers. These heterostructures are labeled MQWs Ib, since they have the same layer structure as the experimentally investigated samples MQWs I, but do not contain In in the wells. Figure 4 shows the calculated band structure for two MQWs Ib. For the MQW Ib without any nitrogen [cf. Fig. 4(a)], the quantum well contains two bound states |1\> and |2\>, which are indicated as thick solid lines. For this MQW, the discontinuity of the conduction band is determined by \( E_c\text{[GaAs]} \) and \( E_c\text{[Al}_{0.33}\text{Ga}_{0.67}\text{As]} \). In Ga(As,N) with very low N content, a localized N state is formed at \( E_N = 1.65 \text{ eV} \) (Ref. 1) indicated in Fig. 4 by the dashed line and included in Eq. (6) by the \( E_N \)-dependent diagonal element. An important consequence of Eq. (6) is that due to the QW confinement the localized N state creates an additional set of N-like states in each quantum well above \( E_N \), which are indicated in Fig. 4(a) as thin solid lines. Due to the large effective mass of the N state and the small energy difference between the barrier and \( E_N \), the energy separation between neighboring N-like levels is smaller than the one between the original quantum well states |1\> and |2\>. For N\(_N\) > 0.3\%, the energy of the bottom of the quantum well shifts according to Eq. (2) from \( E_{c[\text{GaAs}]} \) to \( E_{c[N_N]} \), whereas the energy of the top of the quantum well increases from \( E_{c[\text{Al,GaAs}]} \) to \( E_{c[N_N]} \). While in Ref. 6 only the increase in the band offset was taken into account in the calculation of the subband energies for (In,Ga)(As,N)/GaAs MQWs, the three-band \( k \cdot p \) model in Sec. IV explicitly includes the nonparabolicity and the coupling of the states at \( E_c \) and \( E_v \) with the ones at \( E_N \), which is described in Eq. (6) by the N-dependent off-diagonal elements. For \( N_N = 0 \), this coupling disappears. However, for \( N_N > 0 \), these off-diagonal terms cannot be neglected anymore. Due to this coupling, the N-like states in the quantum wells mix with the original ones already present for \( N_N = 0 \). \(|\Psi|^2\) of these mixed subbands is shown by the lines in Fig. 4(b) for \( N_N = 1 \% \).

In Fig. 5, the calculated subband energies \( E_i(N_N) \), where \( i = 1, 2, \ldots, 3(2j_{\text{max+1}}) \) denotes the index of the newly formed mixed subband, are plotted as solid and dotted lines for the MQWs Ib. For a better overview, the high-frequency as well as the low-frequency conduction band branches of Ga(As,N) (\( E_c \) and \( E_v \), respectively) are also included in the figure as dashed lines, while the original energies of the bottom and the top of the quantum well (\( E_{c[\text{GaAs}]} \) and \( E_{c[N_N]} \), respectively) are indicated as dash-dotted lines. The newly formed mixed bound states exhibit alternating anticrossings and crossings with increasing energy as expected from the symmetry of the subbands (cf. Fig. 5). However, the anticrossing behavior is not the subject of the present study. Figure 5 clearly shows the formation of the mixed subbands as well as their redshift with increasing \( N_N \).

The calculated wave number \( n_{12}(N_N) = E_{12}(N_N)/E_{11}(N_N) \) for the IST from the ground |1\> into the first excited subband |2\> is plotted in Fig. 6 as a solid line. The redshift of all newly formed mixed subbands causes the important effect...
then slightly increases. In Fig. 6, the measured wave number  for the main absorption band ( for the high-frequency absorption feature) in the ISA spectra of the MQWs I shown in Fig. 1 is marked as dots (squares). The solid line indicates the calculated wave number  for the IST from the ground into the first excited subband. The dashed (dotted) line denotes the IST from the ground state into the continuum above the  barriers [above the upper pseudogap at  for the (GaAs, N) wells]. Note that the gaps in the solid line reflects the minigap in the conduction subband structure of Fig. 5.

that the IST energy  decreases very rapidly with increasing nitrogen content for . With a further increase of , the value of  reaches a minimum at  and then slightly increases. In Fig. 6, the measured wave numbers  for the main ISA band of the MQWs I are marked as dots. These data were taken from the maxima of the main absorption band in the ISA spectra shown in Fig. 1. Figure 6 shows that the calculated values  for the MQWs I are in good agreement with the measured N dependence of  for the MQWs I. Therefore, we attribute the main absorption band in the ISA spectra of the MQWs I to the IST from the ground state into the first excited subband [2]. Note that deviations between the calculated and the measured energies may occur for several reasons. First, electron-electron interactions, in particular the depolarization shift, are neglected in the calculations. Second, the coupling between plasmons and ISTs is not taken into account. Third, the influence of In on the conduction band structure is not included as mentioned above. Fourth, due to the large width of the ISA minima, the uncertainty of the  values is rather large. Furthermore, the strong asymmetry of the absorption minima may result in some systematic deviations. Fifth, due to the strong free-carrier scattering as indicated by the broad minima in the ISA spectra in Figs. 1 and 2, the coupling between the N-like and the original quantum states in the wells may by reduced, which causes an additional frequency shift for the intersubband excitations, which is not taken into account in this study. Such damping effects reduce the anti-crossing of any coupled elementary excitations in a solid.

In the MQWs I containing N, several mixed subbands are formed as discussed above and shown in Figs. 4(b) and 5.

FIG. 6. Semilogarithmic plot of the measured (symbols) and calculated (lines) wave numbers for ISTs in Ga(As, N)/(Al,Ga)As MQWs with  and AlGaAs barriers (MQWs I and Ib) vs N content. The wave number  for the main absorption band ( for the high-frequency absorption feature) in the ISA spectra of the MQWs I shown in Fig. 1 is marked as dots (squares). The solid line indicates the calculated wave number  for the IST from the ground into the first excited subband. The dashed (dotted) line denotes the IST from the ground state into the continuum above the  barriers [above the upper pseudogap at  for the (GaAs, N) wells]. Note that the gaps in the solid line reflects the minigap in the conduction subband structure of Fig. 5.

Therefore, we also expect transitions from the ground state  into higher subbands than the second one, but with a decreasing oscillator strength with increasing subband separation. We assume that these transitions cause the strong asymmetric broadening on the high-frequency side of the main ISA band at  shown in Fig. 1. Furthermore, for sufficiently high N concentration ( 0.3%), the density of the higher subband levels becomes large enough in order to also enable ISTs from the ground state  into the continuum above the barrier  for the MQWs I calculated for small N content. The thick solid line represents the original bound state  for very low N content. The lines represent  for the mixed subbands formed due to the coupling between the original bound and the N-like states in the quantum well.

FIG. 7. Conduction subband structure for Ga(As, N)/(Al,Ga)As MQWs with  and AlGaAs barriers (MQW II). (a) |\Psi|^2 calculated for small N content. The thick solid line represents the original bound state  in the quantum well, which is already present for . The thin solid lines indicate the N-like states, which are caused by the localized N state at  for very low N content. (b) |\Psi|^2 calculated for . The lines represent |\Psi|^2 of the mixed subbands formed due to the coupling between the original bound and the N-like states in the quantum well.

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the wells, which are shown for small values of $N_{\text{N}}$ in Fig. 7(a) as thin solid lines. The coupling of these states with the original bound state in the well results in the formation of several new mixed subbands with the corresponding $|\Psi|^2$ shown in Fig. 7(b) for the MQW II with $N_{\text{N}}=1\%$. The energies of these new mixed subbands for the MQWs II are plotted in Fig. 8 as a function of $N_{\text{N}}$ as solid and dotted lines. Figure 8 shows that within the three-band $k\cdot p$ model more than one bound state is present in the wells of the MQWs II for $N_{\text{N}}\approx 0.3\%$. Therefore, we expect also a bound-to-bound IST $|1\rangle \rightarrow |2\rangle$ in the MQWs II, if the N concentration and, therewith, the density of states of the new mixed subbands is sufficiently large.

In Fig. 9, the calculated (measured) energies for different ISTs in the MQWs II are shown versus $N_{\text{N}}$ as symbols. At first, we analyze the main ISA band at $v_{12}$, which is indicated in Fig. 9 by the dots. The dotted line in Fig. 9 represents the calculated energies for the IST from the ground state $|1\rangle$ into the quasicontinuum above the Al$_{0.42}$Ga$_{0.58}$As barriers, which is denoted by $v_{1\text{ex}}$. For the MQW II with $N_{\text{N}}=0$, the calculated value of $v_{1\text{ex}}$ agrees exactly with the measured one indicating that the main ISA band is due to such a bound-to-continuum transition above the Al$_{0.42}$Ga$_{0.58}$As barriers. This assignment is also supported by the strong asymmetric broadening on the high-frequency side of the main ISA band (cf. Fig. 2), which is typical for such a transition. With increasing $N_{\text{N}}$, the energy of the bottom of the quantum well decreases according to $E_c(N_{\text{N}})$ resulting in an increasing wave number $v_{1\text{ex}}$ for this IST. For $N_{\text{N}}\approx 1\%$, the energy $E_c(N_{\text{N}})$ of the upper conduction band branch exceeds the one of the barriers $E_{c}(\text{Al}_{0.42}\text{Ga}_{0.58}\text{As})$. Therefore, the IST now occurs from the ground state $|1\rangle$ into the continuum above the pseudogap at $E_c(N_{\text{N}})$ of the Ga(As,N) wells. In Fig. 9, this IST is denoted by $v_{1\text{IN}}$ (dotted line). A comparison of the measured wave number $v_{12}$ of the main ISA band (dots) with the calculated values $v_{1\text{IN}}$ for the MQWs II suggests that the main ISA band at $v_{12}$ is caused by such a bound-to-continuum IST for $N_{\text{N}}\approx 1\%$.

In the following, we analyze the wave numbers $v_{12}$ of the low-frequency spectral feature in the ISA spectra of the MQWs II with $N_{\text{N}}\approx 0.8\%$ (cf. Fig. 2). The values of $v_{12}$ are marked in Fig. 9 by squares. The appearance of this spectral feature below the bound-to-continuum transition at $v_{12}$ must be due to a second bound state in the quantum well, which is predicted by our three-band BAC model as shown in Fig. 8 for $N_{\text{N}}>0.3\%$. The calculated wave number $v_{1\text{IN}}(N_{\text{N}})$ for the $|1\rangle \rightarrow |2\rangle$ IST for the MQWs II is indicated as the solid line in Fig. 9. This plot shows that the additional low-frequency absorption feature at $v_{3}$ measured for the MQWs II with $N_{\text{N}}=2.4\%$ approaches the calculated values $v_{1\text{IN}}$ for the additional absorption feature at $E_c(N_{\text{N}})$ of the Ga(As,N) wells. In Fig. 9, this IST is denoted by $v_{1\text{IN}}$.

FIG. 8. Calculated energies for the subbands of Ga(As,N)/(Al,Ga)As MQWs with $d_w=3$ nm and Al$_{0.42}$Ga$_{0.58}$As barriers (MQWs II) vs N content (solid and dotted lines). The dashed-dotted lines represent the conduction band edges for GaAs and Al$_{0.42}$Ga$_{0.58}$As, while the dashed lines indicate the energies $E_c(N_{\text{N}})$ and $E_v(N_{\text{N}})$ for the two conduction band branches of Ga(As,N) [Eq. (2)]. The IST from the ground state $|1\rangle$ into the first excited subband $|2\rangle$ is indicated by $v_{12}$. FIG. 9. Semilogarithmic plot of the measured (symbols) and calculated (lines) wave numbers for ISTs in Ga(As,N)/(Al,Ga)As MQWs with $d_w=3$ nm and Al$_{0.42}$Ga$_{0.58}$As barriers (MQWs II) vs N content. The wave number $v_{12}$ for the main absorption band (dashed line) is denoted by $v_{1\text{IN}}$. A comparison of the measured wave number $v_{3}$ of the main ISA band (dots) with the calculated values $v_{1\text{IN}}$ for the MQWs II suggests that the main ISA band at $v_{3}$ is caused by such a bound-to-continuum IST for $N_{\text{N}}\approx 1\%$.
VI. SUMMARY AND CONCLUSIONS

The effect of the quantum well confinement on a localized N state creates a number of N-like states in each quantum well of (In,Ga)(As,N)/(Al,Ga)As MQWs. Due to the coupling of these N-like states with the original well states, new mixed subbands are formed in the conduction band structure of the MQWs. This effect essentially modifies the energies of the bound-to-bound as well as bound-to-continuum ISTs. The intensity and the width of the ISA spectra are clearly well of.

In addition, the strong modification of the conduction band structure in Ga(As,N)/(Al,Ga)As quantum-cascade structures has to be taken into account for the design of N-containing GaAs-based quantum-cascade lasers.

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12In the calculation, the following parameters were used for the uncoupled states in the wells: \( E_N = E_{N_0} - (\gamma - \kappa)N_N \), \( E_C = E_{C_0} - (\alpha - \kappa)N_N \), and \( E_V = E_{V_0} + \kappa N_N \), where \( E_{C_0} = 1.42 \text{ eV} \), \( E_{V_0} = -0.02 \text{ eV} \), \( E_{N_0} = 1.65 \text{ eV} \), \( \gamma = 1.55 \text{ eV} \), \( \kappa = 3.89 \text{ eV} \), and \( N_N \) (in %)/100 (Ref. 2). Coupling coefficients: \( V_{NC} = \beta \sqrt{N_N} \), where \( \beta = -2.3 \text{ eV} \) (\( P_N = \beta_0 \sqrt{N_N} \), with \( \beta_0 = -0.983 \text{ eV Å} \)), \( P_1 = 9.753 \text{ eV Å} \) (Refs. 2 and 3). Dispersion parameters: \( \alpha_N = (1.099 - 885 N_N^{1/2}) \text{ eV Å}^2 \), \( \alpha_C = 6.047 \text{ eV Å}^2 \), \( \alpha_V = 1.683 \text{ eV Å}^2 \), and \( \alpha_{NC} = -3.112 \text{ eV Å}^2 \) (Ref. 2). (Al,Ga)As barrier parameters: \( E_N = V_{NC} = P_N = 0 \), \( P_1 = 9.753 \text{ eV Å} \). MQWs I: \( E_{C_0} = 1.73 \text{ eV} \) and \( E_{V_0} = -0.17 \text{ eV} \), MQWs II: \( E_{C_0} = 1.8 \text{ eV} \) and \( E_{V_0} = -0.20 \text{ eV} \).


