Absorption spectroscopy on Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As multi-quantum-well heterostructures. II. Subband structure

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The subband structure of Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As multi-quantum-well heterostructures (MQWH’s) lattice matched to InP, grown by molecular-beam epitaxy, was determined by absorption and magnetoabsorption experiments for well widths ranging from 2.3 to 13.8 nm. A comparison to theoretical models (parabolic single-band and coupled six-band envelope-function approximations) reveals the necessity of taking the nonparabolicity of the conduction band as well as of all the valence subbands into account. The equal values for the reduced effective mass and the electron effective mass, obtained by Shubnikov-de Haas and cyclotron-resonance experiments, show that the highest valence-subband mass is much larger than the theoretical assumption from decoupled valence subbands. In view of the complete subband structure the best theoretical description is given by using a conduction-band offset $\Delta E_c = 500$ meV as determined by capacitance-voltage measurements in the literature. For this value the calculated subband transition energies are about 10% higher than the experimental results.

I. INTRODUCTION

The determination of the subband structure in multi-quantum-well heterostructures (MQWH’s) is of fundamental interest for the understanding of the quantumized energy levels in these structures and thus for a precise band-structure design of the respective MQWH. One parameter, which enters the theoretical description of the subband structure, is the band offset of the conduction and valence bands, respectively. The conduction-band offset $\Delta E_c$, for the Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As material system has been determined by capacitance-voltage ($C-V$) measurements on $N$-type Al$_{0.48}$In$_{0.52}$As/$n$-type Ga$_{0.47}$In$_{0.53}$As heterojunctions to be $\Delta E_c = 500 \pm 50$ meV or $(70 \pm 7)\%$ of the total band-gap difference $\Delta E_g = 700$ meV.$^1$ As for the GaAs/Al$_x$Ga$_{1-x}$As system the actual value of the band offset has become controversial as a result of theoretical fits of the subband transition energies in absorption and luminescence experiments in limited well-width ranges. For a 10-nm QWH the conduction-band offset was determined to be $\Delta E_c = 440$ meV.$^2$ In contrast, luminescence measurements of the energy separation of electron-to-heavy-hole and electron-to-light-hole subband transitions in very narrow quantum wells ($L_z = 1.43$ and 1.91 nm) yielded a valence-band offset of $\Delta E_v = 0.15 \Delta E_g$.$^3$ However, in the latter study, the Al$_{0.48}$In$_{0.52}$As barrier material was not lattice matched to the InP substrate, thus giving rise to considerable strain effects in the samples. The influence of the strain on the reported results as well as the determination of the given precise well widths were not presented in that study.

The other important parameters which strongly influence the theoretical subband structure are the carrier effective masses. The electron effective mass in Ga$_{0.47}$In$_{0.53}$As quantum wells has been studied by cyclotron-resonance experiments in Ga$_{0.47}$In$_{0.53}$As/InP systems for well widths larger than 8 nm (Ref. 4) and very recently by magnetoabsorption experiments in the Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As system for one well width of $L_z = 15$ nm.$^5$ These experiments demonstrate the necessity of taking into account the nonparabolicity of the Ga$_{0.47}$In$_{0.53}$As conduction band. Furthermore, Rogers et al.$^6$ reported a heavy-hole mass of $m_{hh} = 0.075 \pm 0.010$ for $L_z = 15$ nm, which is substantially larger than that for the bulk material.

In this second part of our work we will present the entire subband structure of the Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As MQWH system for well widths down to 1.4 nm. The experimental subband spacing has been determined by absorption and photoluminescence experiments. The energy positions of the different subband transitions will be compared to theoretical values based on the parabolic single-band envelope-function approximation (EFA) and on the coupled six-band EFA. The influence of the different parameters such as the conduction- and valence-band offsets and the three-dimensional (3D) carrier effective masses in the theoretical models will be discussed. The importance of the carrier effective masses for the theoretical description of the subband structure will be pointed out. Measurements of the reduced effective mass by magnetoab-
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II. RESULTS AND DISCUSSION

A. Theoretical models

Using the parabolic single-band EFA and the boundary conditions given by Bastard\(^1\) the solution of the stationary Schrödinger equation yields the following two equations for the eigenvalues of the quantized energy levels (see, for example, Ref. 8):

\[ k_n \tan(k_n L_z/2) = k_m^* m_n^* / m_p^* , \quad n \text{ odd} \]
\[ k_n \cot(k_n L_z/2) = -k_m^* m_n^* / m_p^* , \quad n \text{ even} \]

(1)

where \( k_n^2 = 2m_n^* E_n / \hbar^2 \), \( k_m^2 = 2m_m^* (V - E_n) / \hbar^2 \), \( m_n^* \) (\( m_m^* \)) is the effective mass in the well (barrier) layer, \( V \) the potential well depth, and \( E_n \) the energy eigenvalue.

The calculations for the electron and heavy- and light-hole eigenvalues in the framework of the coupled six-band EFA were performed in the limit of \( k_1 = k_2 = 0 \) (\( k_3 = 0 \)).\(^3\) In this case the heavy-hole valence band is completely decoupled from the other bands and shows a parabolic dispersion. In contrast, for the electron and light-hole bands, coupling and thus nonparabolicity of the bands has been explicitly taken into account.

In the theoretical models the carrier effective masses and the conduction- and valence-band offsets of Ga\(_{0.47}\)In\(_{0.53}\)As and Al\(_{0.48}\)In\(_{0.52}\)As enter as important parameters. The conduction-band offset \( \Delta E_c \) has been determined by People et al.\(^1\) to be \( \Delta E_c = 0.5 \pm 0.05 \text{ eV} \) or \( (70 \pm 7)\% \) of \( \Delta E_g \), respectively, at room temperature from \( C-V \) measurements on \( N\)-type-Al\(_{0.48}\)In\(_{0.52}\)As/\( n\)-type-Ga\(_{0.47}\)In\(_{0.53}\)As heterojunctions. From magnetoabsorption experiments on a bulk Ga\(_{0.47}\)In\(_{0.53}\)As epitaxial layer Alavi et al.\(^10\) reported the following values for Ga\(_{0.47}\)In\(_{0.53}\)As at 5 K determined directly from the measurements:

\[ E_g = 0.813 \pm 0.001 \text{ eV} \]
\[ 1/\mu_{el}^* = 26.5 \pm 0.5 \]
\[ 1/\mu_{eh}^* = 44.0 \pm 1.0 \]

where \( \mu_{el}^* \) (\( \mu_{eh}^* \)) are the reduced effective masses for electron and heavy hole (electron and light hole). Using the electron effective mass of \( m_e^* = 0.041 \pm 0.001 \), as determined by Nicholas et al.\(^11\) we obtain the following effective-hole masses for bulk-type Ga\(_{0.47}\)In\(_{0.53}\)As:

\[ m_{hh} = 0.47 \pm 0.09 \quad \text{and} \quad m_{lh} = 0.051 \pm 0.05 \% \].

Therefore, the heavy-hole mass of this material is determined very precisely.

Alavi et al. described the band structure of Ga\(_{0.47}\)In\(_{0.53}\)As using a set of parameters for a quasi-Ge model (Ref. 10 and references therein). This parameter set yielded the following values for the Luttinger parameters: \( \gamma_1^* = 11.01 \) and \( \gamma_2^* = 4.18 \). Therefore, for the case of \( k_1 = 0 \), the effective masses of the valence bands in Ga\(_{0.47}\)In\(_{0.53}\)As are given by

\[ m_{hh}^* = (\gamma_1^* - 2\gamma_2^*)^{-1} = 0.38 \]
\[ m_{lh}^* = (\gamma_1^* + 2\gamma_2^*)^{-1} = 0.052 \]

(3a)

(3b)

The effective heavy-hole mass \( m_{hh}^* = 0.38 \), according to the band-structure model, lies at the lower error limit of \( m_{hh}^* = 0.47 \pm 0.16 \), taken from the direct experimentally determined reduced effective mass. For the theoretical model calculations we have used the following effective masses for Ga\(_{0.47}\)In\(_{0.53}\)As:

\[ m_e^* = 0.041 \]
\[ m_{eh}^* = 0.38 \]
\[ m_{lh}^* = 0.052 \]

(4)

For the Al\(_{0.48}\)In\(_{0.52}\)As barrier material up to now only data for the band gap (\( E_g = 1.508 \text{ eV} \) at 4 K for the lattice-matched composition) from cathodoluminescence experiments\(^12\) and an extrapolation of the electron effective mass (\( m_e^* = 0.075 \)) from experiments on plasmon excitation in (Al\(_{0.49}\)Ga\(_{0.51}\))\(_{1-x}\)In\(_x\)\(_{0.53}\)As epitaxial layers\(^13\) have been reported. As a consequence of the higher band gap also the valence-band masses of Al\(_{0.48}\)In\(_{0.52}\)As are expected to be larger than in Ga\(_{0.47}\)In\(_{0.53}\)As. We assume the following values as band parameters for Al\(_{0.48}\)In\(_{0.52}\)As:

\[ m_e^* = 0.075 \]
\[ m_{hh}^* = 0.057 \]
\[ m_{lh}^* = 0.095 \]

(5)

B. Comparison of the experimental subband spacings with the theoretical models

The experimental subband spacings in Ga\(_{0.47}\)In\(_{0.53}\)As/Al\(_{0.48}\)In\(_{0.52}\)As MQWH's have been determined from optical subband transitions both in absorption and emission. The absorption spectra of three MQWH samples are shown in Fig. 1. Strong structures in the absorption spectrum are ascribed to electron–heavy-hole transitions, weaker structures to electron–light–hole transitions. For the determination of the higher-lying subband edges we have used the same exciton binding energies as for the
lowest subband edge. With increasing temperature the weaker structures in the absorption spectra show the same low-energy shift as the electron–heavy-hole transitions. Therefore, interference effects in the samples can be excluded for the explanation of these weaker structures in the absorption spectra. It is interesting to note that the red shift of the subband transitions with increasing temperature is constant irrespective of the well width and of the quantum number of the subband transition. We observed a constant red shift of 60 ± 5 meV for a temperature increase from 5 to 300 K. These results demonstrate that the band gaps of both Ga$_{0.47}$In$_{0.53}$As and Al$_{0.48}$In$_{0.52}$As have the same temperature dependence.

The energy shift of the subband transitions in Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As MQWH's with respect to the band gap of Ga$_{0.47}$In$_{0.53}$As are summarized in Fig. 2 as a function of the well width together with the results of the theoretical models. Open squares represent electron–heavy-hole transitions, solid squares electron–light-hole transitions. The results of luminescence experiments (crosses) were obtained from intrinsic $E_{1h}$ subband transitions of different MQWH's at 77 K. The dashed line gives the results of the parabolic single-band EFA, while the solid line represents the results of the coupled six-band EFA.

For the lowest subband transitions the results of the two theoretical models agree to within 5–10 meV. Therefore, only one line has been drawn for clarity. For the higher-lying transitions one can clearly see the energy reduction by taking the nonparabolicity of the conduction and the light-hole valence band into account, which gives a better description of the experimentally determined subband transitions. Nevertheless a discrepancy of about 10% remains between the experimental energy shifts and the results of the coupled six-band EFA.

We will now discuss the theoretical description of the subband structure in the Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As material system by showing how much the theoretical results change if the parameters which enter the model calculations are varied within the experimental error. In the

![Image of Absorption Spectra](image)

**FIG. 1.** Absorption spectra of three Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As MQWH's with different well widths $L_z$ at 5 K. The arrows indicate experimentally determined subband transitions.

![Image of Energy Shift](image)

**FIG. 2.** Energy shift of the subband transitions of a Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As MQWH with respect to the Ga$_{0.47}$In$_{0.53}$As band gap as a function of the well width. The experimentally determined values from absorption (open squares, electron–heavy-hole transitions; solid squares, electron–light-hole transitions) and luminescence experiments (crosses) are compared to results of theoretical models (dashed line, parabolic single-band envelope function approximation; solid line, coupled six-band envelope-function approximation).
following we will concentrate on the valence-band structure. The difference in energy between respective electron–heavy-hole and electron–light-hole transitions gives the energy separation of light- and heavy-hole subbands of the same quantum number. This energy difference is plotted in Fig. 3 as a function of the well width together with the theoretical model calculations. Also for the valence-subband structure the coupled six-band EFA (solid line) describes the experimental results better than the parabolic single-band EFA. The error bars of the theoretical curves in the Figs. 2 and 3 result from the error of the band-offset determination by the C-V method of ±50 meV. However, any conclusion from the better description of the valence-subband transitions that the valence-band offset can be determined to be \( \Delta E_v = 150 \) meV is misleading. The reason for this misinterpretation is that this apparent decrease in the valence-band offset yields an increase in the conduction-band offset, which results in a high-energy shift of the electron subband energies and thus a high-energy shift of the electron to heavy-hole subband transitions. This behavior would increase the discrepancy between experiment and theory for these transitions (see Fig. 2), leading to a description of the whole subband structure which is worse than for the case of \( \Delta E_v = 200 \) meV.

In contrast, Weiner et al.\(^2\) have tried to fit the subband transitions of MQWH’s of about 10 nm well width by decreasing the conduction-band offset to a value of \( \Delta E_c = 440 \) meV. In this way they were able to shift the theoretical values of the electron subbands to lower energies and thus to describe the position of the electron-to-heavy-hole subband transitions quite accurately. On the other hand, this fit yielded a worse description of the electron-to-light-hole transitions. In this context we have to keep in mind that in this material system the carrier masses have only been measured for the bulk Ga\(_{0.47}\)In\(_{0.53}\)As material and that the heavy-hole mass is determined very unprecisely. For the Al\(_{0.48}\)In\(_{0.52}\)As barrier material only an extrapolation and reasonable assumptions, respectively, are available up to now. These uncertain carrier masses do strongly influence the results of the theoretical models. Furthermore, as we will see in the next section, the coupling of the valence bands for \( k_z \neq 0 \) leads to completely different hole masses for the in-plane motion than predicted by the simple theoretical model. It is assumed that this coupling also alters the hole masses for the motion perpendicular to the quantum-well planes and thus alters the energy position of the quantized subband levels.

This discussion clearly shows that the band offset is only one parameter which determines the theoretical subband structure in MQWH. The other important parameters are the carrier effective masses and their behavior as a function of the 2D character of the respective MQWH. Taking all these uncertainties into account, the coupled six-band EFA gives a satisfactory description of the subband structure in the Ga\(_{0.47}\)In\(_{0.53}\)As/Al\(_{0.48}\)In\(_{0.52}\)As MQWH (see Figs. 2 and 3). It should be noted that there is up to now no experimental evidence which would unambiguously require a change in the conduction-band offset of \( \Delta E_c = 500 \) meV as determined by C-V measurements for this material system.

C. Determination of the carrier effective masses for in-plane motion

In order to determine the carrier effective masses for the in-plane motion in Ga\(_{0.47}\)In\(_{0.53}\)As/Al\(_{0.48}\)In\(_{0.52}\)As MQWH’s we have evaluated the magnetooabsorption experiments, yielding the reduced carrier masses [see Eq. (5) of the preceding paper\(^4\)]. In addition, we measured the electron effective mass by temperature-dependent Shubnikov–de Haas (SdH) and cyclotron-resonance (CR) experiments. For the latter measurements 50-period \( n \)-type modulation-doped Al\(_{0.48}\)In\(_{0.52}\)As/Ga\(_{0.47}\)In\(_{0.53}\)As MQWH’s were grown with well thicknesses of 8.2 and 3.4 nm, as determined by double-crystal x-ray diffraction. The advantages of using such narrow quantum wells for the SdH measurements is, first of all, the investigation of MQWH’s which really reach the quasi-2D limit, and second, that band-bending effects at the two interfaces of the quantum well can be neglected. Therefore, the real-space band edges of the modulation-doped MQWH’s are rectangular, similar to the case of the undoped MQWH. The disadvantage of the small well width is the decrease in mobility of the carriers due to scattering at the two nearby interfaces. At 5 K we observe a mobility of 8000 cm\(^2\)/V sec with a carrier concentration of \( n = 4.2 \times 10^{11} \) cm\(^{-2}\) per quantum well in the 8.2-nm MQWH and a mobility of 3300 cm\(^2\)/V sec with \( n = 3.6 \times 10^{11} \) cm\(^{-2}\) in the 3.4-nm MQWH, respectively. The carrier concentrations determined by Hall and SdH measurements coincide to within 5%.

As an example for the evaluation of the reduced carrier
mass from the magnetoabsorption measurements, the slopes of the Landau-level fan of a 8.0-nm MQWH are plotted in Fig. 4 as a function of the Landau quantum number $N$. Using the relation of the transition energy $\Delta E_N$ between Landau levels, given by Eq. (5) in the preceding paper, we can determine the electron–heavy-hole reduced effective mass for this MQWH to be $\mu_{eh}^* = 0.051$.

For low magnetic fields $B$ the SdH oscillations show a sinusoidal variation as a function of $1/B$ with a temperature-dependent amplitude $A_{\text{SdH}}$:

$$A_{\text{SdH}} = \frac{2\pi^2 k_B T / \hbar \omega_c}{\sinh(2\pi^2 k_B T / \hbar \omega_c)}.$$  

(6)

From the ratio of the SdH amplitudes at different temperatures we can determine the effective mass $m_{\text{SdH}}^*$. Figure 5 shows SdH oscillations of an 8.2-nm MQWH for two different orientations of the magnetic field and for different temperatures (upper part, $B$ parallel; lower part, $B$ perpendicular to the well layers) on the same scale. The anisotropy of the SdH oscillations proves the existence of a 2D carrier system in the $xy$ plane. With increasing temperature we observe a decrease in the SdH oscillations. From these measurements we deduce an effective electron mass of $m_{\text{SdH}}^* = 0.049 \pm 0.005$ for the 8.2-nm MQWH and of $m_{\text{SdH}}^* = 0.053 \pm 0.005$ for the 3.4-nm MQWH, respectively. The error bars represent the standard deviation of $m_{\text{SdH}}^*$ as a result of the averaging procedure by evaluating the amplitude ratios at various sets of two temperatures.

The results of the determination of the carrier effective masses for in-plane motion are summarized in Fig. 6. The reduced effective carrier masses, obtained from magnetoabsorption measurements, are almost identical to the electron effective masses, obtained from SdH and CR measurements. They are much higher than the assumed theoretical value of $\mu_{eh}^* = 0.025$, taking the bulk value of $m_{\text{SdH}}^* = 0.041$ and $m_{\text{SdH}}^* = (\gamma 1^L + \gamma 2^L)^{-1} = 0.066$. This enhancement is caused by the increased electron mass due to the nonparabolicity of the Ga$_{0.47}$In$_{0.53}$As conduction band and the much higher heavy-hole mass. This observation is consistent with the result of a 15-nm MQWH re-

FIG. 4. Slope of the Landau level fan as a function of the Landau quantum number $N$ for a Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As MQWH with $L_z = 8$ nm.

FIG. 5. Magnetoresistance measurements of a modulation-doped Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As MQWH ($L_z = 8.2$ nm) for two different orientations of the magnetic field with respect to the well layers at various temperatures.

FIG. 6. Carrier effective masses of a Ga$_{0.47}$In$_{0.53}$As/Al$_{0.48}$In$_{0.52}$As MQWH as a function of the well width.
cently reported by Rogers et al.\textsuperscript{5} The precision of the determination of the electron effective mass by SdH measurements is not high enough to allow a distinct evaluation of the heavy-hole mass in these Ga\textsubscript{0.47}In\textsubscript{0.53}As/Al\textsubscript{0.48}In\textsubscript{0.52}As MQWH's. It is interesting to note that a calculation of the in-plane dispersion of the conduction band (coupled six-band envelope function approximation, axial model\textsuperscript{6}) yields an electron effective mass of $m^*_e = 0.049$ for an 8-nm MQWH. This value is identical to the experimentally measured electron mass. Therefore, we can conclude that the coupled six-band EFA describes the nonparabolicity of the conduction band accurately.

As in the case of the GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As MQWH system,\textsuperscript{14} these results demonstrate the influence of the coupling behavior of all valence subband levels. It should be pointed out that the coupling yielding a high mass for the top-most valence subband in MQWH's can also be deduced from the observation of the increase of the exciton binding energy and oscillator strength, presented in the preceding paper.\textsuperscript{6} Thus these three independent measurements give a consistent picture of the behavior of the carrier effective masses in MQWH.

III. CONCLUSION

The complete subband structure of a Ga\textsubscript{0.47}In\textsubscript{0.53}As/Al\textsubscript{0.48}In\textsubscript{0.52}As MQWH has been determined by absorption and photoluminescence experiments. With increasing temperature all subband transitions show the same temperature dependence independent of the well width of the respective sample, thus indicating the similar temperature dependence of the band edge of the Ga\textsubscript{0.47}In\textsubscript{0.53}As well and the Al\textsubscript{0.48}In\textsubscript{0.52}As barrier material. When the temperature is increased from 5 to 300 K the observed red shift of all the subband transitions amounts to 60±5 meV. The theoretical description of the subband structure requires the consideration of the nonparabolicity of the conduction as well as all the valence subbands. Because of the uncertainties in the carrier masses of Ga\textsubscript{0.47}In\textsubscript{0.53}As valence subbands and especially in the Al\textsubscript{0.48}In\textsubscript{0.52}As barrier material, where up to now only an extrapolation of the electron effective mass and reasonable assumptions of the valence subbands are available, there is as yet no experimental evidence for a change of the band offset in this material system ($\Delta E_c = 0.5\pm0.05$ eV), as determined by C-V measurements in the literature. Based on the present knowledge of these parameters for the Ga\textsubscript{0.47}In\textsubscript{0.53}As/Al\textsubscript{0.48}In\textsubscript{0.52}As material system, the theoretical subband transition energies (coupled six-band EFA) overestimate the experimental ones by about 10%.

The large increase in both the binding energy as well as the oscillator strength of the exciton for well widths of about 4 nm is consistent with the observed increase in the reduced carrier effective mass as determined by magnetoabsorption experiments. From a comparison with measured electron effective masses we conclude that the reduced effective mass is almost identical to the electron effective mass. This leads to a mass for the highest valence subband which is much larger than predicted theoretically by the assumption of a completely decoupled heavy-hole valence subband for $k \parallel = 0$. These results are consistent with data reported for the GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As material system in the literature and demonstrate the complicated coupling behavior of the valence subbands also in Ga\textsubscript{0.47}In\textsubscript{0.53}As/Al\textsubscript{0.48}In\textsubscript{0.52}As MQWH's.

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