Spectroscopic study of the effect of confinement on shallow acceptor states in GaAs/$Al_xGa_{1-x}As$ quantum wells

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Transitions from the ground state to excited states of the Be acceptor confined in GaAs/$Al_xGa_{1-x}As$ quantum wells (QW's) have been observed via two independent spectroscopic techniques: Two-hole transitions of the acceptor bound exciton (BE) observed in selective photoluminescence and resonant Raman scattering. The effect of confinement on the observed acceptor transitions has been investigated by varying the QW thicknesses in the range 50–138 Å. The results obtained are compared with recent theoretical predictions. An almost linear relationship was found between the binding energy of the acceptor BE and the observed acceptor transitions. This fact implies that a correspondence to Haynes's rule in bulk should be valid also for this QW system.

INTRODUCTION

The electronic structure and other properties of shallow impurities in bulk material are at the present fairly well understood, and countless papers, both theoretical and experimental, continue to be published on this subject. The corresponding information that can be found in the literature about impurities confined in quantum-well (QW) structures is, however, considerably more limited. Although the study of defects in QW's should not be, in principle, much more complicated than that for bulk material, it has, in practice, turned out to be more difficult than expected to transfer the techniques directly from bulk to QW's. Also, the quality of the QW material has been an important limiting factor for detailed studies of the defect properties. However, the recent improvement of QW-growth techniques, such as molecular-beam epitaxy (MBE) and metal organic chemical-vapor deposition (MOCVD), has contributed to progress in this field.

Pioneering experimental studies on the characterization of defects in QW's, using the techniques that have been well documented for bulk material for a long time, has not been reported until fairly recently. Examples of such are photoluminescence (PL),[1] Raman scattering,[2] and infrared[3] measurements. After this initial work, a number of reports have followed; nevertheless, the level of understanding of the properties of defects in QW's is considerably lower than the corresponding level for bulk material.

We recently reported the first observation of so-called two-hole transitions (THT's) via the acceptor bound exciton (BE) in selective PL (SPL) for a 70-Å-wide GaAs/$Al_xGa_{1-x}As$ QW.[4] When the BE recombines, there is a small probability that part of the recombination energy is transferred to the acceptor at which the exciton is bound. The acceptor hole is then left in an excited state after the recombination, resulting in a weak THT peak in addition to the principal BE in the luminescence spectrum. The energy separation between the observed THT peak and the principal BE line corresponds to the energy needed to excite the acceptor from its ground state to an excited state. We also observed resonant Raman scattering (RRS) originating from the same acceptor transitions in the same series of measurements. The fact that the same transitions can be observed with two independent techniques gives strong support for the proposed interpretation. This kind of observation gives us information not only about the ground state, but also about the excited states of the impurity, which, in turn, provide a more accurate and detailed picture of the electronic properties of the confined impurity than we can deduct from plain PL measurements. Our recently published report of the first observation of these transitions for a single-QW width[4] will be generalized in this paper to QW widths in the range 50–138 Å.

The introduction of an impurity into a perfect bulk semiconductor lattice gives rise to a potential at the vicinity of the impurity. This potential can, for shallow impurity levels, be treated as Coulomb-like to a first approximation, since short-range forces are of less importance for shallow states. Calculations using so-called effective-mass theory[5] (EMT) have been found to yield satisfactory accuracy for shallow impurity states in bulk material. EMT calculations result in scaled hydrogenic energy levels for the electrons (holes) bound to the donors (acceptors), which are found to be in good agreement with experimental results, at least for shallow states. The total binding energy of impurities have been very accurately determined in many cases by adding the binding energy of the excited state, calculated by EMT, to the experimental THT result of the energy separation between the ground and excited states.

Our knowledge of the energy levels for impurities confined in QW's is much more limited, and the situation is expected to be more complicated than for the bulk case. The symmetry for a point defect is reduced from T_d in bulk to D_{2d} in a QW. To calculate the energy levels, an extended Hamiltonian including additional terms

(e.g., for the potential energy of the barriers, which confines the carriers in the QW) has to be used. The original work on calculations of the energy levels of confined impurities was performed by Bastard using a variational method,[6] in which the impurity was assumed to be hydrogenic and the barriers were treated as infinite. The dependences of the impurity binding energy on the QW thickness as well as on the position of the impurity in the well were predicted. More realistic calculations, which also take the finite barrier heights into account, have been reported more recently by Masselink *et al.*[7,8] Our experimental results on transitions between the ground and excited states of the impurity for different QW widths will also be compared with theoretical predictions given by Masselink *et al.*[7]

EXPERIMENT

The samples used in this study were grown by MBE in a Varian Gen II system. The layers were grown on top of a semi-insulating GaAs(100) substrate having a 0.35-μm undoped GaAs buffer layer. The growth was performed under As_4-rich conditions and without interruption at the QW interfaces. The growth temperature was nominally 680 °C. Six samples with identical structure except for the QW width, $50 < L_z < 138$ Å, were used in this study. The final estimate of the QW widths was based on the energy positions of the free-exciton (FE) peaks in the PL spectra. In all cases the $Al_xGa_{1-x}As$ barriers were 150 Å wide and had a nominal Al composition of $x = 0.30$, but a variation of the order ± 0.02 between different growths was determined by measuring the PL of the $Al_xGa_{1-x}As$ layers. All samples investigated contained multiple-QW (MQW) structures with 50 periods of alternating layers of GaAs and $Al_xGa_{1-x}As$. The samples were doped with Be in the central 20% of the wells to a level of 1×10^{17} cm^{-3} in all cases.

For the PL measurements with above-band-gap excitation, an Ar-ion laser was used as the excitation source. The same Ar laser pumping a tunable dye laser with Styryl 8 or a Kr-ion laser pumping a dye laser with LD 700 was used for the SPL experiments. The two dye lasers could also be continuously tuned for the PL-excitation (PLE) measurements. The laser beam was focused on the sample to a diameter of the order 200 μm. The intensity of the laser excitation was kept at the lowest possible level to still get an acceptable signal-to-noise ratio. Sample luminescence was emitted perpendicular to the incident laser beam, and was focused on the slits of a 1m monochromator. The angle between the samples and the incident beam was always sufficiently far from 45° to avoid collecting reflected laser light in the monochromator. All measurements presented in this study were performed at 1.6 K. The PL signal from the monochromator was detected with a cooled GaAs photomultiplier tube.

LUMINESCENCE AT ABOVE-BAND-GAP EXCITATION

The same kinds of measurements were performed on all samples used, but we will limit the number of spectra shown in this paper to some representative cases of PL at above-band-gap excitation, SPL, and PLE.

The PL spectra measured with above-band-gap excitation show for all samples the FE as well as the acceptor BE. PL spectra for the two "extreme samples," the 50- and 138-Å-wide QW's, are shown in the Fig. 1. As can be seen in these figures, the FE dominates the PL spectrum and the BE is observed just as a weak shoulder for the narrow 50-Å QW [Fig. 1(a)], while the situation is almost the inverse for the wider QW [Fig. 1(b)]. This tendency, namely that the intensity ratio between the exciton peaks, I_{BE}/I_{FE}, decreases with decreasing QW width

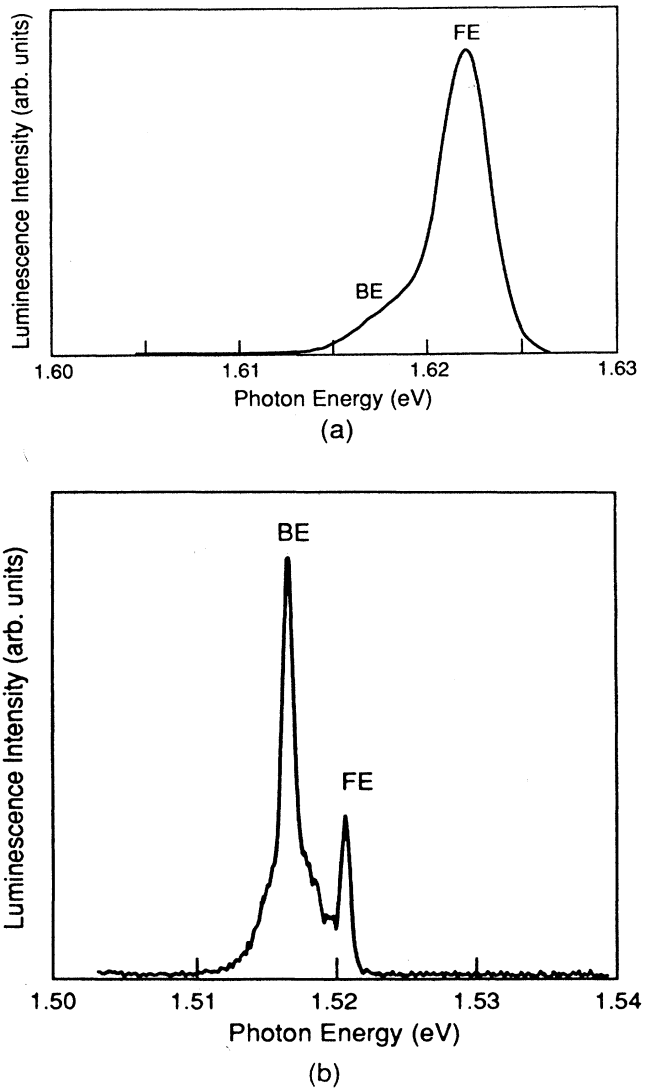

FIG. 1. PL spectra with above-band-gap excitation ($\lambda = 5145$ Å) measured at 1.6 K for two similar QW structures of different thicknesses, (a) 50 Å and (b) 138 Å. Both these samples are doped with Be in the central 20% of the wells to a level of $p = 1 \times 10^{17}$ cm^{-3}. The FE and BE are observed in both PL spectra, but at considerably different intensity ratios, I_{BE}/I_{FE}. The dependence of the intensity ratio, I_{BE}/I_{FE}, on the QW thickness is summarized in Fig. 2. No further luminescence originating from the QW's could be detected at this excitation, even at the highest possible detector sensitivity.

for otherwise identical samples, is obvious for the samples investigated, as shown in Fig. 2. This fact is mainly due to reduced FE lifetime with decreasing QW width, since the probability for the electron-hole pairs to recombine as a FE instead of getting captured by impurities will thus increase with decreasing QW width. In a recent paper,[9] an almost linear relationship between the FE decay time and the QW width was reported. It should also be pointed out that no further luminescence of extrinsic origin could be detected in any of these samples at this excitation.

Furthermore, the energy separation between the FE and BE, i.e., the binding energy of the BE, is found to be strongly dependent on the QW thickness. The BE binding energy increases with decreasing QW width in a way that will be further expounded on in the Discussion.

SELECTIVE PHOTOLUMINESCENCE

When the excitation energy is down-shifted to be resonant with or close to any of the FE states as observed in the PLE spectra (Fig. 3), the luminescence spectra change drastically compared to the case with above-band-gap excitation. New features appear in these SPL spectra, as shown in Fig. 4 for a 94-Å-wide QW. When the excitation is resonant with the heavy- or light-hole (hh or lh) state of the FE, at least four new features appear in the spectrum. The first and strongest peak, denoted FB in Fig. 4, occurs at ≈ 1.525 eV; this is the free-to-bound transition due to the recombination between free electrons and holes bound to the neutral Be acceptors. The FB peak is shifted by about 24 meV from the FE (at ≈ 1.549 eV). The binding energy of the FE has been determined by PLE measurements to be 10 meV for a 100-Å-wide QW.[10] This means that the energy separation between the $n=1$ electron and the $n=1$ hh state can be estimated to be 1.559 eV. The position of the FB peak is thus ≈ 34 meV below the "band gap," which should then correspond to the binding energy of the Be acceptor centered in a 94-Å-wide QW. This value is consistent with theoretical predictions,[7] as well as with earlier experimental reports.[11]

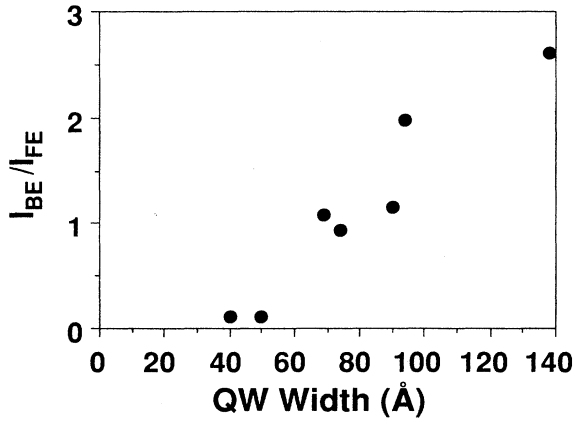

FIG. 2. PL intensity ratios, I_{BE}/I_{FE}, measured at 1.6 K with above-band-gap excitation for QW's of thicknesses in the range 50–138 Å.

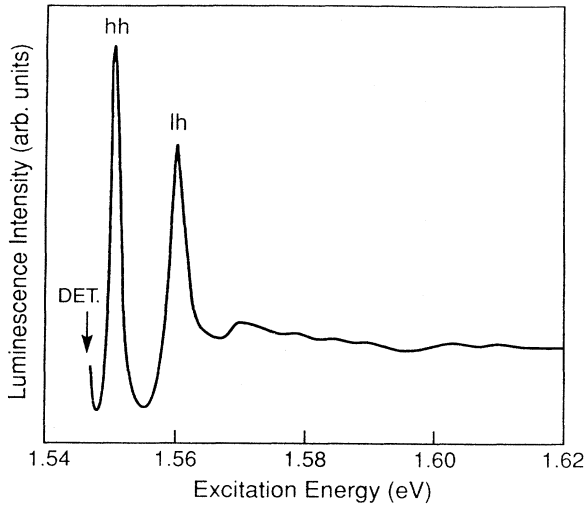

FIG. 3. PLE spectrum for a 94-Å-wide QW with the detection at the low-energy part of the FE peak as observed in PL. At this detection, only the FE-related states (the hh and lh states) can be observed.

The second peak, denoted A in Fig. 4, is interpreted as the first THT of the BE, at which the Be acceptor is excited from the $1s$ ground state to the $2s$ excited state. The energy separation between the BE and this peak, A, is $E(A^{1s-2s})=24.6\pm0.3$ meV. The intensities of peak A and the FB peak are both drastically reduced as the excitation is shifted off resonance with the hh or lh state of the FE and has reached 50% of the intensity within about ± 1 meV from the resonance position, which roughly corresponds to the half-width of the FE.

The third peak, B, separated by ≈ 31 meV from the BE, is much weaker than the peaks FB and A, and is not even detectable at nonresonant excitation. In addition to this problem, peak B overlaps with a broader feature, which can also be observed at excitation energies below the QW excitons (≤ 1.545 eV; see the lower spectrum in Fig. 4). This broad feature is most likely due to GaAs excitons. The interpretation of peak B is therefore less certain. Since there seems to be a general correlation between peaks A and B, as observed from many SPL measurements with slightly different excitation energies, we tentatively interpret peak B as a second THT. This interpretation is also supported by the measurements reported earlier on a narrower QW,[4] where a second weaker THT component was observed at slightly larger energy separation from the first THT.

The assignment of the broad feature, C, is even less certain. The peak disappears at excitations below the BE (≈ 1.545 eV) in the same manner as the peaks A and B, which strongly supports its relationship with the investigated QW. The width of this feature indicates that it should be related to a transition to a continuum. The en-

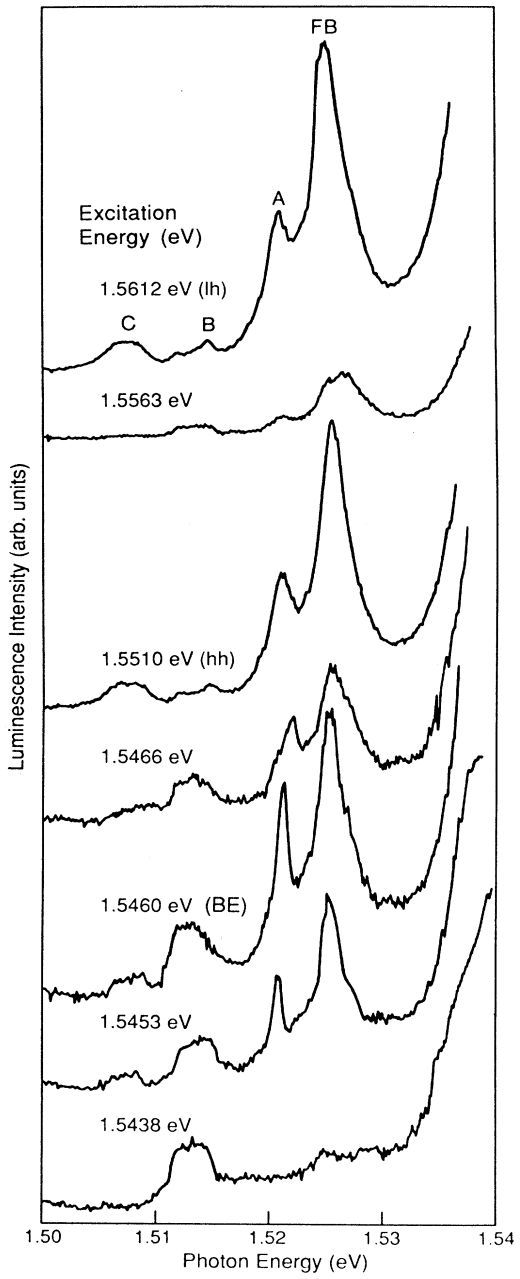

FIG. 4. SPL spectra measured on the same 94-Å-wide QW as shown in Fig. 3. When the excitation energy is lowered below the band gap, several new features appear in the spectrum compared with above-band-gap excitation. These new features are significantly enhanced upon excitation resonant with the FE or BE states, as described in detail in the text. The peak labeled FB originates from the recombination between a quantized $n=1$ electron and a hole from the neutral Be acceptor. Two narrow lines at slightly lower energy (A and B) appear upon below-band-gap excitation and are strikingly enhanced, when either the lh or hh state of the FE is resonantly excited. These peaks are interpreted ast the THT's of the BE. Peak A is observed also at excitation close to or resonant with the BE (as observed in PL), but shifts with the excitation energy in such a way that the energy separation between this peak and the excitation energy is constant, which is characteristic for RRS.

ergy separation, ≈ 38 meV, from the BE is in poor agreement with the predicted acceptor binding energies for both Γ_6 or Γ_7 symmetry.[7] Considering the fact that the transition interpreted as the transition from the $1s(\Gamma_6)$ ground state to the $2s(\Gamma_7)$ excited state (peak B) is about 6 meV below the theoretically predicted transition energy[7] implies that the binding energies should also be reduced correspondingly. The observed energy separation of 7 meV between peaks B and C could likely be the separation between the $2s$ state and the continuum for Γ_7 symmetry. This energy separation is in reasonable agreement with the observations for the Γ_6 acceptor, where the corresponding energy difference between the transition from the $1s(\Gamma_6)$ ground state to the continuum (FB) and the observed transition $1s(\Gamma_6)-2s(\Gamma_6)$ (THT) is found to be ≈ 9 meV. The reason why the corresponding continuum for Γ_6 symmetry is not observed in the SPL spectra is now known.

When the excitation is shifted to even lower energies, resonant with or close to the BE as observed in PL (1.546 eV), the same peaks as described above appear (except for the weak peak B), as shown in the lower part of Fig. 4, but at a reduced intensity level. These peaks are rendered undetectable at excitation energies below ≈ 1.544 eV (the lowest spectrum in Fig. 4). Further, it should be noted that when the excitation energy is slightly off resonance (from the BE), the main component of peak A shifts from its original position. This component shifts with the excitation energy in a way that maintains the separation between this peak and the excitation energy, 24.8 ± 0.3 meV. Such a behavior is characteristic for Raman-active transitions. This means that the THT peak (A) at an energy of E(BE)-$E(A^{1s-2s})$ dominates the SPL spectra at excitation energies in the range of the FE states as observed in PLE, while the RRS peak at an energy of E(laser)-$E(A^{1s-2s})$ is the strongest when the excitation energy is close to the BE, as observed in PL.

The SPL spectra for the narrower 69-Å-wide QW are fairly similar to the corresponding spectra for the 91-Å-wide QW shown above. A synopsis of SPL spectra for the 69-Å QW with excitation energies ranging from 1.576 to 1.588 eV is shown in Fig. 5. The excitation energy (1.588 eV) used in the lower spectrum in this figure corresponds to the hh state of the FE as observed in PLE. At this excitation energy the FB peak entirely dominates the SPL spectrum. This enhancement of the FB upon excitation resonant with any of the FE states has been observed and reported elsewhere.[12] A multistep process, involving an excitonic Auger recombination, has been proposed to give rise to this enhancement.[12] When the excitation energy is shifted slightly off resonance, the relative intensity of the FB peak is reduced, and the two additional peaks, $P1$ and $P2$, are better resolved. These two peaks are interpreted as the THT's of the BE. The separation between the $P1$ and $P2$ peaks and the BE is 28.5 and 37.0 meV, respectively, which then corresponds to the energy separation between the ground state and the excited states of the Be acceptor confined in a 69-Å-wide QW. Upon further down shift of the excitation energy, three new, sharp lines, $R1-R3$, appear, which have in common the fact that they shift with excitation energy in

such a way that the separation between these peaks and the dye-laser excitation remains constant. The observed transition energies, 29.0 and 36.5 meV for $R1$ and $R2$, respectively, are consistent with the acceptor excitations as deduced from the THT peaks. Furthermore, the $R1$ and $R2$ lines reach maximum intensity upon excitation resonant with the BE (1.579 eV) as observed in PL. These lines are therefore interpreted as due to electronic Raman scattering corresponding to the same acceptor transitions as observed for the THT's.[4] In conclusion, the same transition, from the ground state to the excited states of the confined Be acceptor, can thus be observed with two independent techniques, THT's of the BE observed in SPL and RRS, at very similar transition energies.

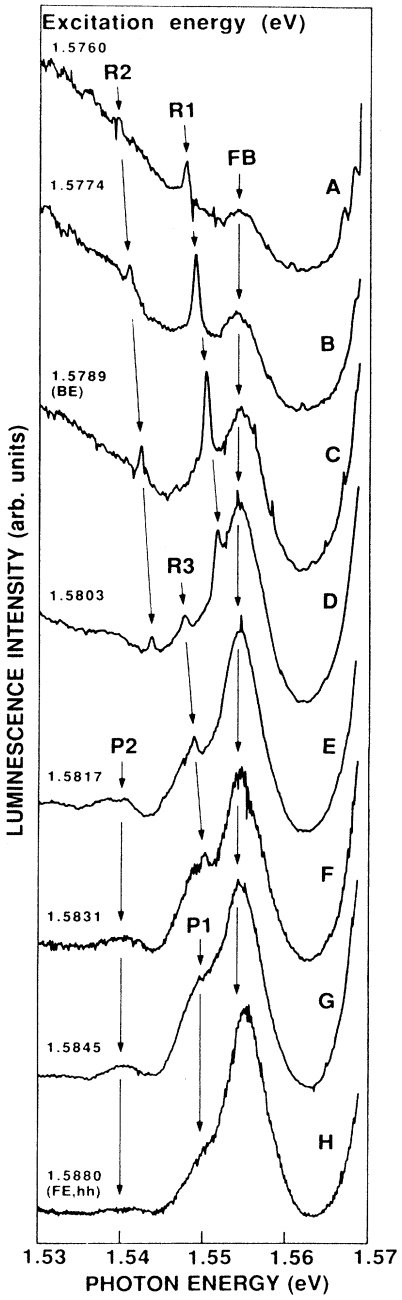

FIG. 5. Synopsis of SPL spectra for a 69-Å-wide QW with excitation energies ranging from 1.576 to 1.588 eV, where 1.588 eV corresponds to the hh state of the FE as observed in PLE and 1.579 eV is the position of the BE in PL. The conditions at which these SPL spectra and the corresponding spectra for the 94-Å-wide QW (Fig. 4) are measured are thus similar, and the observed features are consistently very similar, as expounded on in more detail in the text.

PHOTOLUMINESCENCE EXCITATION

PLE spectra for undoped as well as doped QW's are usually totally dominated by the intrinsic FE states. In fact, no structure related to impurities in PLE has been reported up to now. A typical PLE spectrum of a 71-Å-wide QW is shown in Fig. 6, in which the FB transition is detected (the lower spectrum). The hh and lh states of the FE are the strongest peaks in this spectrum. In addition, two weaker peaks at about 10 meV above each of these states can be observed. These peaks are usually observed in PLE spectra and are due to the exciton excited states.[10]

If we instead detect the THT peak, a new peak appears in the PLE spectrum at about 4 meV below the hh state of the FE (the upper spectrum in Fig. 6). The energy separation is the same as observed between the BE and FE in

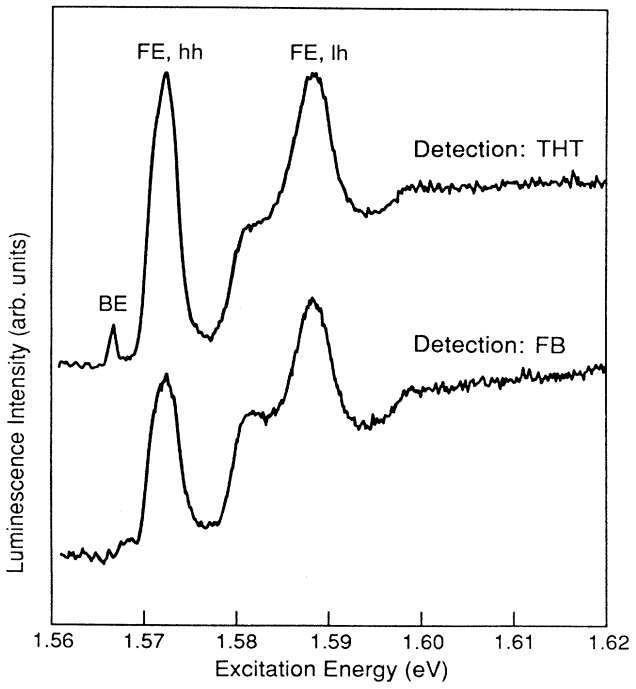

FIG. 6. PLE spectra for a 71-Å-wide QW, when the FB (the lower spectrum) and the THT (the upper spectrum) are detected. When the FB is detected, only the FE states, mainly the hh and lh states, are observed. If this PLE spectrum is compared to the spectrum in which the THT is detected instead, the appearance of the BE in the latter PLE spectrum is obvious.

PL for this sample. This new peak is thus interpreted as the BE and is, as mentioned above, observed for the first time in a PLE spectrum. The fact that we can observe the BE, when the THT is detected, is expected, since the THT can be considered as a generalized form of BE recombination. That is, the acceptor is left in an excited state after the recombination as a THT instead of in the ground state as is the case for normal BE recombination. The PLE spectrum, when the BE itself is detected, is, as expected, similar to the PLE spectrum, when instead the THT is detected. Thus, the fact that the BE is observed in PLE only, when either the BE or the THT is detected, is strong support for our interpretation of the THT's.

SUMMARY OF THE RESULTS

The experimental results corresponding to transitions from the ground state to excited states of the confined Be acceptor for the investigated samples are summarized in Fig. 7. The transition energies provided from the THT as well as the RRS experiments are shown in this figure. The data points at lowest transition energies correspond to the stronger THT (RRS) peaks, e.g., peak A in Fig. 4 and $P1$ ($R1$) in Fig. 5, while the transitions at higher energies correspond to the weaker peaks in the SPL spectra, e.g., peak B in Fig. 4 and $P2$ ($R2$) in Fig. 5. As can be seen, the observed transition energies are very similar for the two techniques used. The solid lines in Fig. 7 correspond to the theoretical predictions by Masselink *et al.*[7] for the Be-acceptor transitions $1s(\Gamma_6)$-$2s(\Gamma_6)$ and $1s(\Gamma_6)$-$2s(\Gamma_7)$, respectively [using the same central-cell correction (1 meV) as in bulk material].

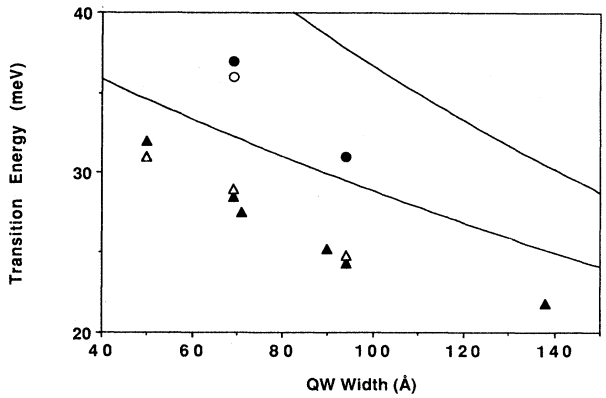

FIG. 7. Experimental results from the THT (solid symbols) and RRS (open symbols) measurements for the two observed transitions (triangles and circles, respectively) summarized for the samples investigated with QW widths in the range 50–138 Å. The solid line corresponds to the theoretical prediction by Masselink *et al.* (Ref. 7) for the Be-acceptor transitions $1s(\Gamma_6)$-$2s(\Gamma_6)$ and $1s(\Gamma_6)$-$2s(\Gamma_7)$, respectively. A central-cell correction of 1 meV, corresponding to the difference in binding energy of the $1s$ ground state between the Be acceptor and an EM-like acceptor in bulk, has been used.

TWO-HOLE TRANSITIONS

The THT's can be treated as a generalized form of BE recombination, where the acceptor is left in the ground state at the principal BE recombination and in an excited state for the THT case. THT's can be observed because the wave functions of the hole states in the BE contain a superposition of contributions from the excited states of the same parity as the ground state. The probability for THT's to occur decreases with increasing acceptor binding energy, since the ground state is lowered in energy relative to the excited states because of the stronger central-cell potential for deeper acceptors. The transition probability for the BE decay is proportional to[13]

$$\int\int \phi_{\rm imp}(r_a)\phi(r_a,r_e,r_h)e^{iqr_h}dr_a dr_h \approx \int\int \phi_{\rm imp}(r_a)\phi(r_a,r_e,r_h)dr_a dr_h + iq\int\int \phi_{\rm imp}(r_a)\phi(r_a,r_e,r_h)r_h dr_a dr_h \ . \quad (1)$$

$\phi_{\rm imp}(r_a)$ is the wave function of the impurity after the recombination and $\phi(r_a,r_e,r_h)$ is the BE wave function, where r_a,r_e,r_h are the spatial coordinates of the electronic particles, two holes, and an electron, forming the acceptor BE. The electron must have the same spatial coordinate, r_e, as the hole, r_h, at the instant of recombination, and the emitted photon has a small but finite wave vector, q. The first term on the right-hand side in Eq. (1) corresponds to transitions to the impurity ground state or to excited states of same parity as the ground state. The next term represents parity-forbidden transitions such as transitions to p-like excited states. Thus, there is a small, but non-negligible, probability for transitions to other than s-like excited states. In fact, intensity ratios of up to 20% for the THT peaks originating from transitions to p-like versus s-like states have been reported for donors in bulk ZnTe.[14] The s-like states will, however, by far, dominate the THT's. Accordingly, it seems to be unlikely, that we, in the case of QW's with relatively weak THT peaks, should be able to observe anything but transitions to s-like states.

DISCUSSION

The theoretical analysis of electronic structure is considerably more complicated for the case of acceptors than for donors due to the more complex nature of the valence band. For the case of a shallow acceptor of T_d symmetry introduced in bulk GaAs, the contribution from several valence bands has to be included in the acceptor wave function. These valence-band states are, however, degenerate at $k=0$ in the absence of spin-orbit interaction, with a sixfold degeneracy. That degeneracy is deduced from the coupling of the p-like band with the spin-$\frac{1}{2}$ hole. In T_d symmetry, the p-like band transforms like Γ_5 and

the spin-$\frac{1}{2}$ hole as Γ_6. According to group theory, this spin-orbit coupling will give rise to $\Gamma_5 \times \Gamma_6 = \Gamma_7 + \Gamma_8$. The sixfold-degenerate band is then split into the fourfold-degenerate Γ_8 band and the twofold-degenerate Γ_7 band, corresponding to the split-off band. The upper Γ_8 band will split further into two Kramers doublets, the twofold-degenerate heavy-hole and the twofold degenerate light-hole bands for $k \neq 0$.

If the acceptor is introduced into a QW instead of bulk, the symmetry is reduced from T_d to D_{2d} since the material has a preferred direction. If the same coupling as for the bulk case between the p-like valence band and the spin-$\frac{1}{2}$ hole is performed for this lower symmetry,[7,8] it is found that the resulting bands will transform like $\Gamma_6 + \Gamma_7^1 + \Gamma_7^2$, where Γ_7^2 corresponds to the split-off band. This means that the fourfold-degenerate Γ_8 band in T_d symmetry splits into two twofold-degenerate bands, Γ_6 and Γ_7, in D_{2d} symmetry. The binding energies for an effective-mass-like acceptor of Γ_6 and Γ_7 symmetry, respectively, have been calculated by Masselink *et al.*[7,8] using the variational method. The resulting energy levels for the case of a Be acceptor of each symmetry in the center of a GaAs QW confined by $Al_{0.3}Ga_{0.7}As$ barriers as a function of QW thickness is shown in Fig. 7. The same central-cell potential V_c used for bulk GaAs, corresponding to the difference in chemical shift between the Be acceptor and an effective-mass-like (EM-like) acceptor, $V_c = 1$ meV, has been used for all QW thicknesses.

The experimental results from the THT and RRS experiments are also given in Fig. 7. Some points regarding this figure merit comment. First, the interpretation of the lower-energy transition as the $1s(\Gamma_6)$-$2s(\Gamma_6)$ acceptor transition is supported by several experiments, including (1) the correlation between the transition energies derived from the THT and RRS experiments, (2) the similar temperature dependence for the BE, THT, and RRS peaks,[4] (3) the appearance of the BE in the PLE spectrum when the THT is detected, and (4) the position of the FB band in PL also provides rough guidance. The same strong arguments cannot be applied to the second transition [tentatively interpreted as the $1s(\Gamma_6)$-$2s(\Gamma_7)$ acceptor transition], since it is much weaker and, in addition, not observed for all samples investigated. The interpretation of this transition is therefore less certain than for the first. Secondly, it should be emphasized that the spectroscopic techniques used in this investigation, THT and RRS, are very accurate methods for the determination of transition energies with an uncertainty better than ± 1 meV. However, as can be seen in Fig. 7, the experimental results are consistently at 3–4 meV (i.e., about 10–15 %) lower energy than the theoretical predictions. A minor deviation towards lower energies (of the order 1 meV) has been observed for the FB band in the PL observed by not only us, but also by others.[1,7] It should be noted, however, that if the calculated total binding energy for the Be acceptor[7,8] minus the same binding energy for the $2s$ state as for bulk GaAs (8 meV) is used, better agreement with the experimental results can be achieved. The deviation is then found to be less than 2 meV. In fact, the very close agreement between the two different techniques (RRS and THT) for which this transition is observed suggests that the experimentally determined energies are the correct ones, providing theorists with very accurate data points for further calculations.

The energy separation between the FE and BE, i.e., the binding energy of the BE, is, as mentioned above, dependent on the QW thickness. Further, the QW thickness is related to the acceptor transition energies according to Fig. 7. Based on this information, it is possible to plot the dependence of the BE binding energy on the $1s(\Gamma_6)$-$2s(\Gamma_6)$ transition energy of the acceptor binding the exciton. This dependence is shown in Fig. 8. We have chosen to plot the experimentally determined $1s(\Gamma_6)$-$2s(\Gamma_6)$ transition energies instead of the total binding energies on the abscissa, since the total binding energies involve effective-mass estimates of the binding energies for the excited states and are therefore less accurate. The point at lowest energy [E(BE) = 2.9 meV] corresponds to bulk GaAs.[15] Furthermore, the points at highest energies are determined from PLE measurements,[12] since the BE peak is just observed as a shoulder on the low-energy side of the FE in PL for narrow QW's doped at this level (Fig. 1). The dependence of the BE binding energy on the acceptor transition energy seems to be almost linear from Fig. 8. Such a linear relationship is found to be valid for many shallow impurities (donors as well as acceptors) in bulk semiconductors with an indirect band gap e.g., Si and GaP, as well as for materials with a direct band gap such as CdS and ZnSe, but notably not for e.g., acceptors in the direct-band-gap semiconductor GaAs.[16] This linear relationship is usually referred to as Haynes's rule,[17]

$$E(\mathrm{BE}) = a + bE(A)\,, \tag{2}$$

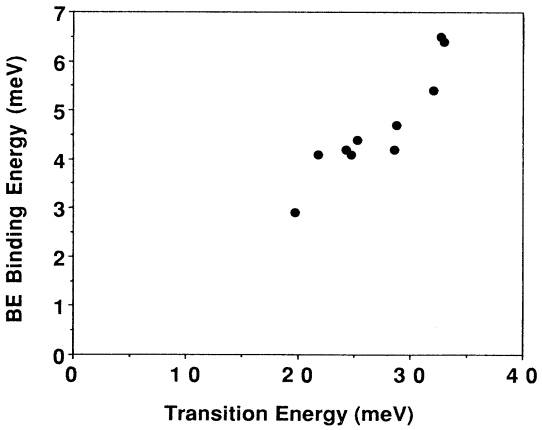

FIG. 8. Dependence of the BE binding energy on the transition energy for the $1s(\Gamma_6)$-$2s(\Gamma_6)$ transition for the Be acceptor, which binds the exciton. The transition energies are deduced from THT experiments. The point at lowest energy [E(BE) = 2.9 meV] corresponds to bulk GaAs. As can be seen in this figure, there seems to be an almost linear relationship between the acceptor transition energy and the BE binding energy. This implies that a correspondence to Haynes's rule in the bulk should also be valid for this QW system.

where $E(A)$ corresponds to the binding energy of the acceptor ground state. This simple monotonic trend has been explained in terms of an expression derived from first-order perturbation theory. For the case of shallow impurities, for which we can assume that the central-cell correction is small, i.e., minor deviation from EM-like states, it can be shown that[18]

$$E(\mathrm{BE})=\{[E(\mathrm{BE})]_{\mathrm{EM}}-[E(A)]_{\mathrm{EM}}\delta\rho_c/\rho_c\}+(\delta\rho_c/\rho_c)E(A)\,, \tag{3}$$

where ρ_c is the electronic charge in the impurity central cell and $\delta\rho_c$ is the increased charge, when the BE is present, and $[E(A)]_{\mathrm{EM}}$ is the EM-like binding energy of the impurity. The value of the constant term, a, can be either positive or negative, depending on the terms $\delta\rho_c/\rho_c$ and $[E(\mathrm{BE})]_{\mathrm{EM}}/[E(A)]_{\mathrm{EM}}$, both of which are functions of ρ. The estimated values for the a and b terms in Eq. (2) are $a\approx -3$ meV [including a constant factor of 8 meV for the binding energy of the $2s(\Gamma_6)$ state] and $b\approx 0.22$.

SUMMARY

We have in this study investigated the energy levels for the Be acceptor confined in GaAs/$Al_xGa_{1-x}As$ QW's using spectroscopic techniques: THT's of the BE observed in SPL and RRS. The derived results from these two independent techniques agree within 1 meV, which is indicative of the accuracy of these experiments. Two transitions interpreted as the transitions from the $1s(\Gamma_6)$ ground state to the excited states, $2s(\Gamma_6)$ and tentatively $2s(\Gamma_7)$, respectively, have been observed for the Be acceptor confined in the central part of QW's with thicknesses in the range 50–138 Å. The experimental results on these transition energies are found to be, consequently, at 10–15 % lower energy than theoretically predicted.

Also, the dependence of the binding energy of the excitons bound at the confined acceptors on the observed acceptor transition energies was studied and an almost linear relationship between these quantities was found. The linear dependence is similar to what is found for different impurities in some bulk material and is usually referred to as Haynes's rule. The difference is that in this study we are dealing with the same acceptor, whose binding energy is varied by a different degree of confinement related to the thickness of the QW.

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