Exciton properties in *p*-type GaAs/Al_xGa $_{1-x}$ As quantum wells in the high doping regime

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An experimental study of optical properties of acceptor-doped quantum wells is presented. We have studied the effects of acceptor doping at concentration levels varying from 10^{16} up to 10^{19} cm⁻³ using steady-state photoluminescence (PL) and PL excitation. Excitons can still be detected at high doping concentrations of 10^{19} cm⁻³, i.e., well above the degenerate limit in these quantum wells. They survive mostly due to the inefficiency of screening in the two-dimensional (2D) system. In addition to the dimensionality of the structure (2D or 3D), the quenching of excitons is found to depend on doping type (*n* or *p* type) and the position of the doping (well or barrier doped). We also report on hydrogen passivation effects on the same samples. As expected, there is a correlation between the results obtained, on the one hand, by decreasing the doping concentration and, on the other hand, increasing the passivation time. Their behavior follows the same directions, except for the unexpected increase in the bound exciton population with increasing passivation. [S0163-1829(96)07248-7]

I. INTRODUCTION

The properties of quantum well (QW) structures are strongly influenced by the presence of dopant impurities. So far, basic research has been focused on barrier-doped (BD) QW's, i.e., modulation-doped (MD) structures, with their potential for various technological applications, but also for the direct study of many-body effects. The properties of QW's doped within the well (WD) are significantly less studied, in particular for the case of *p*-type doping. For *n*-type WDQW structures, many-body effects, including carriers and excitonic effects, have recently been investigated for donor concentrations extending up to the degenerate limit.^{1,2} Olego et al.³ have investigated the temperature and holeconcentration dependence of the luminescence in p-type bulk GaAs. Sernelius⁴ has calculated the band-gap renormalization (BGR) in the high-hole-concentration regime for *p*-doped GaAs, including exchange and correlation effects on the electron-hole system together with the interaction with ionized impurities. Reynolds et al.⁵ have investigated the screening effects on hydrogenic donors in the presence of acceptors both in the barrier and in the well. Finally, Wagner et al.⁶ have studied the optical properties of the Fermi edge singularity for the corresponding acceptor doped WDQW's above the degenerate limit.

At a sufficiently high doping concentration, the impurity band will overlap with the free carrier continuum. This level corresponds to the metallic limit, i.e., an electronic phase transition from a semiconducting to a metallic behavior. The exchange correlation interactions, induced by the high carrier concentrations, give rise to a decrease of the fundamental band gap, i.e., the BGR. With increasing carrier concentration, there are two major counteracting effects affecting the absorption transition above the band gap: a blueshift due to the band filling up to the Fermi level, the "Burstein-Moss" shift, and on the other hand a redshift caused by the BGR. These band-gap shifts (of the fundamental absorption edge) depend on, e.g., the semiconductor material, the type of doping, and the carrier concentration. The Burstein-Moss shift and the shift caused by the BGR are of different sign, but of comparable magnitude. For *n*-type GaAs, the Fermi level shift dominates,^{7–12} while the reverse situation applies to *p*-type GaAs.^{3,7,8,11,13}

At a certain carrier concentration, the excitons are quenched. The principal mechanisms behind the quenching of the excitons are screening, short-range exchange and correlation, and phase-space filling by carriers, which result in a progressive decrease in exciton binding energy and eventually unbinding of the exciton state.¹⁴ The screening of 3D excitons is strong already at low doping concentrations and carrier densities ($\approx 10^{16}$ cm⁻³), while the corresponding screening effect in the 2D case is much weaker. The restriction on the movement of carriers due to the lower dimensionality inhibits their ability to screen. For the case of OW's, excitons are expected to survive all the way up to the degenerate limit.^{1,15} Consequently, a major difference between the 2D and 3D systems is the relatively stronger exciton recombination in optical spectra for the 2D case even at high carrier concentrations.

In this paper we present experimental results from an optical study of acceptor-doped QW's, where the acceptor concentration is varied from 10^{16} up to 10^{19} cm⁻³. We also report on hydrogen passivation effects on the same samples. Furthermore, the quenching of excitons has been investigated and compared with corresponding results found in the

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literature for bulk and n-type QW structures (WDQW and BDQW) and p-type BDQW's.

II. SAMPLES AND EXPERIMENTAL TECHNIQUES

The samples used in this study were grown by molecular beam epitaxy (MBE) at a temperature of nominally 680°C without interruptions at the QW interfaces. The layers were grown on top of a semi-insulating GaAs (100) substrate with a 0.35- μ m undoped GaAs buffer layer. The Al_xGa_{1-x}As barriers were 150 Å wide with a nominal Al composition of x=0.3. The wells had a width of 150 Å and were doped with Be in the central 20% of the well, at a concentration varying from 3×10^{16} up to 1×10^{19} cm⁻³. The hole concentrations in the QW structures were obtained by Hall measurements.

For the photoluminescence (PL) and PL excitation (PLE) measurements, an Ar⁺-ion laser was used to pump a tunable titanium-doped sapphire solid-state laser. The emitted light from the samples was focused on the slits of a 1-m double-grating monochromator and detected with a dry-ice-cooled GaAs photomultiplier. For the polarization-dependent measurements, we have employed the photoelastic modulation technique.¹⁶ All optical measurements presented were performed at 1.5 K.

Post-growth hydrogen passivation was accomplished at around 190 °C, inside a quartz reactor with a remote dc hydrogen plasma at a pressure of 2.0 mTorr. The passivation time was varied from 30 min to 6 h. The samples were placed ~ 15 cm away from the hydrogen discharge region to avoid damage due to ionic impact.

III. EXPERIMENTAL RESULTS

A. Increasing doping concentration

Figure 1 displays the development of the PL spectra with increasing acceptor concentration. As can be seen in Fig. 1, the excitonic peaks, the acceptor-bound exciton (BE), and the heavy-hole (hh) state of the free exciton (FE) are redshifted and broadened as the acceptor concentration increases. At lower energies, we observe the free-to-bound emission (electronic transition from the conduction band to the acceptor level inside the gap) and two-hole-transition.¹⁷ Above 2×10^{18} cm⁻³, the BE's start to overlap with the bulk GaAs luminescence. For the same doping concentration, 2×10^{18} cm⁻³, the light-hole (lh) state of the FE can be observed even at low temperatures, as illustrated separately in Fig. 2. The intensity of the FE_{hb} decreases continuously with increasing acceptor concentration, while the BE, on the other hand, gains intensity. The development of the PLE for different acceptor concentrations exhibits the same trends as observed in PL: increasing BE population, and broadening and redshifting of the excitonic transitions. The energy separation between FE_{1h} and FE_{hh} in PLE decreases with increasing acceptor concentration, i.e., the opposite effect to what was observed for PL (Fig. 3).

As illustrated in Fig. 2, not only the FE_{hh}, but also the FE_{lh} can be monitored in PL. It should be pointed out that the energy position of the FE_{lh} is approximately the same in PLE and PL (inset of Fig. 2) for a WDQW structure $(2 \times 10^{18} \text{ acceptors per cm}^3)$. It was found that there is no equilibrium lh population for all analyzed samples, and the



FIG. 1. PL spectra at different doping concentrations. The acceptor-BE dominate even at low doping concentrations. The FE_{hh} intensity decreases continuously with increasing doping. The spectrum at the doping concentration of 2×10^{18} cm⁻³ is shown separately in Fig. 2.

relatively high FE_{lh} intensity in the PL spectrum, obtained at high excitation intensity or at higher temperatures, implies that the Fermi level is fairly close to the lh band. At low intensity excitation, the temperature required to populate the lh band is about 40 K, based on the fact that we can estimate that the Fermi level is approximately 3 and 5 meV from the lh band. The Stoke's shift of the FE_{lh} for any of the samples is very small and mainly due to localization effects at the interfaces. For the FE_{hh}, on the other hand, the Stoke's shifts increase with increasing hole concentration (Fig. 3). The polarization-dependent PLE spectrum (inset of Fig. 2) con-



FIG. 2. PL spectrum of a sample with a doping concentration of 2×10^{18} cm⁻³ (above the degenerate limit). A polarized PLE spectrum is depicted in the inset. At such a doping concentration, besides the normal FE_{hh} and the acceptor BE, the FE_{lh} is also observed.



FIG. 3. The calculated difference in energy position of the FE_{hh} between PLE and PL, is compared to experiment. It is seen that the filling of the hh subband starts at moderate hole concentrations. The experimental difference in energy position between FE_{lh} and FE_{hh} in PL and PLE is also shown in the figure.

firms the lh and hh characteristics of the FE's as compared with the corresponding unpolarized PLE measurements. The diamagnetic shifts rate of the FE_{hh} and FE_{lh} have been experimentally estimated, 3.5×10^{-5} and 2.0×10^{-5} eV/T², respectively, i.e., a quadratic dependence as expected for excitonic transitions.

B. Increasing passivation time

It is well known that a hydrogen treatment of bulk samples passivates both shallow dopants and deep centers due to the formation of hydrogen-impurity complexes and a saturation of the dangling bonds.¹⁸ In QW's, hydrogen interacts both with the impurities, causing passivation, and with the interface.¹⁹ Accordingly, an increasing passivation level provided by, e.g., a prolonged hydrogenation time ($\tau_{\rm H}$) has an effect that is similar to an efficient reduction of the acceptor concentration. We can also, in this case, draw conclusions about the efficiency of the hydrogenation process in passivating impurities and the interface degradation. Figure 4



FIG. 4. Normalized PL spectra for a sample with intermediate acceptor concentration $(2 \times 10^{17} \text{ acceptors per cm}^3)$ exposed to different passivation times $(\tau_{\rm H})$; both FE_{hh} and the BE peaks are blue-shifted as the $\tau_{\rm H}$ increases. The FE/BE intensity ratio decreases with increasing $\tau_{\rm H}$.

shows PL spectra for a sample with an intermediate acceptor concentration $(2 \times 10^{17} \text{ acceptors per cm}^3)$ exposed at various times $\tau_{\rm H}$. Earlier studies¹⁹ have shown that the major effect of hydrogenation of samples with intermediate acceptor concentration at moderate $\tau_{\rm H}$ (less than 1.5 h) is impurity passivation, while interface degradation, presumably due to the enhanced Ga-Al intermixing, is observed for prolonged $(\geq 2.5 \text{ h})$ treatment. As expected, both the FE and BE peaks are blueshifted as the $\tau_{\rm H}$ increases. This tendency is consistent with what is observed for decreasing acceptor concentration (Fig. 1). Furthermore, an increasing energy separation between the FE $_{lh}$ and the FE $_{hh}$ is observed in PLE, as well as a decreasing in FE $_{\rm hh}$ Stoke's shift as a function of increasing $\tau_{\rm H}$. In Fig. 4, the normalized PL spectra are plotted. It turns out that the FE/BE PL intensity ratio decreases with increasing $\tau_{\rm H}$. This effect might appear surprising since the BE population is expected to decrease when more acceptors are passivated. This topic will be further exploited in the next section.

IV. DISCUSSION

A. Increasing doping concentration

The redshift of the FE's, observed in PL (Fig. 1), with increasing acceptor concentration is explained in terms of BGR, due to the interactions between the carriers, the exchange-correlation effect. We have performed theoretical calculations taking these interactions into account, with details described elsewhere.²⁰ Figure 5(a) shows the theoretical prediction for the renormalization of the electron (e), hh, and lh subbands (relative to the bottom of the conduction and valence bands, respectively), partly at k=0 and partly at the Fermi level $(k=k_F)$, with increasing hole concentration. This plot shows that the filling of the hh subband starts at moderate hole concentrations, $\approx 2 \times 10^{17}$ cm⁻³. The calculated shift of the FE_{hh} is compared to experiment in Fig. 3. At k=0 the BGR is slightly stronger for the hh band compared to the lh band all the way up to high hole concentration [Fig. 5(b)]. With increasing filling of the hh band, the separation between FE_{lh} at k=0 (the lh band is empty) and FE_{hh} at $k = k_F$ decreases. Figure 3 shows these effects observed experimentally as illustrated by the energy separation between FE_{lh} in PL (k=0) and FE_{hh} in PLE ($k=k_F$).

B. Increasing passivation time

The reduced FE/BE intensity ratio with increasing acceptor concentration can be understood in terms of an increasing FE capture at impurities. We have, up to now, observed similar trends when the acceptor concentration is reduced as when more acceptors are passivated due to longer $\tau_{\rm H}$. We have for instance observed energy shifts of the FE and BE, the FE_{hh} Stoke's shift, the energy separation between FE_{lh} and FE_{hh}, and finally the linewidth, which are consistent with an efficient acceptor concentration reduction. Following this principle, increasing $\tau_{\rm H}$ would give rise to an increasing FE/BE intensity ratio since more acceptors are passivated and are accordingly not available for FE capture. We observe experimentally the opposite effect, however. One possible explanation for the decreasing FE/BE intensity ratio would be that we have an absolute increase of the BE population. In



FIG. 5. (a) Theoretically predicted renormalization of electron energy (relative to the bottom of the conduction band at low doping), hh and lh energy levels (relative to the bottom of the valence band at low doping), partly at k=0 (open markers), and partly at the Fermi level (solid markers) with increasing hole concentration. (b) The band-gap renormalization for the hh, at k=0 and $k=k_F$, and for the lh at k=0.

fact, we do observe this tendency in our experimental results. The hydrogen passivation of the impurities results in a smoothing of the fluctuation potential caused by the impurities. This effect also gives rise to a narrowing of the BE line (Fig. 4). As a consequence, the FE mobility should improve considerably, which in turn would result in an enhanced capture rate at nonpassivated impurities. It should be recalled that the hydrogenation process was estimated to passivate up to 50% of all impurities for moderate doping concentrations.¹⁹

C. Quenching of excitons: *n*- and *p*-type bulk and WDQW GaAs

In *n*-type doped GaAs, excitons are quenched already at doping concentrations of $\approx 10^{16}$ cm⁻³, i.e., well below the metallic limit, due to a strong screening of the electron-hole interaction.²¹ For *p*-type GaAs,³ excitons were still detected at hole concentrations as high as 1.7×10^{17} cm⁻³, i.e., one order of magnitude higher than for *n*-type GaAs. In QW structures, excitons survive to considerably higher carrier concentrations. It has earlier been found that in *n*-type WDQW structures, excitons survive all the way up to the degenerate limit¹ (3×10^{18} cm⁻³ or 1.5×10^{12} cm⁻²). For *p*-type WDQW's, we can confirm the same tendency and state that they survive up to hole concentrations as high as 1×10^{19} cm⁻³ (3×10^{12} cm⁻²), as seen in Fig. 6. For comparison, another PLE spectrum for a hole concentration of



FIG. 6. PLE spectra for doping concentrations above the degenerate limit. For the sample with 5×10^{18} acceptors per cm³, the BE, n=1 related FE_{hh} and FE_{lh} are well defined. The n=2 related FE_{hh} can also be observed. Also in the sample with 1×10^{19} acceptors per cm³, the cited excitons are clearly seen.

 5×10^{18} cm⁻³ (1.5×10^{12} cm⁻²) is also shown in the figure. The BGR in *p*-type QW structures is stronger than the filling effect of the bands, in contrast to *n*-type QW structures, which is attributed to the difference in effective mass between the electrons and hh's. Our theoretical results show that for *p*-type QW's the BGR effects start at a hole concentration of $\approx 2 \times 10^{17}$ cm⁻³ (Fig. 5). In *n*-type WDQW's, excitons are quenched mostly due to the filling of the conduction band.¹ The larger effective mass for the holes in *p*-type structures leads to the survival of excitons to much higher hole concentrations.

D. Quenching of excitons: *n*- and *p*-type WDQW's and BDQW's

It has been observed that the mechanisms responsible for exciton quenching in n-type QW's are less effective in WDQW's in comparison with BDQW structures. The limit for excitonic quenching was found to be above 1.5×10^{12} cm⁻² $(3 \times 10^{18} \text{ cm}^{-3})$ and $4 \times 10^{11} \text{ cm}^{-2}$ for WDQW's (Refs. 1 and 2) and BDQW's,²² respectively. To the best of our knowledge, no report on quenching of excitons in p-type BDQW's has been presented so far. We have, however, no reason to believe that the behavior in *p*-type structures should be different. The reason for the different efficiency of the quenching mechanism is not completely understood, but one should take some facts into consideration. The high doping will give rise to a distortion of the density of states close to the band edge.²³ As a result, the corresponding occupancy in **k** space can be very different for WDQW's in comparison with the BD structures with the result that the formation of exciton states is not blocked at the same limit.¹ Based on this idea, the limit for exciton survival will be larger for p than for n-type structures due to the difference in binding energy of acceptors and donors. The experimental results, for bulk and WDQW's, presented here, are consistent with this assertion. Reynolds et al.⁵ studied the screening effect on the donor binding energy for structures similar to what have been analyzed here. The donor binding energy was observed to decrease when the Be

dopants were moved from the center of the QW to the barrier. The screening effect of the free holes on the bound electrons decreases due to presence of ionized acceptors inside the QW. Such evidence implies that for our system the presence of ionized acceptors inside the well can also affect the screening effect of free holes on the excitons. The screening effect, as for the donor binding energy, on excitons is reduced by the presence of acceptors inside the well. Summarizing, the presence of dopants inside the well affects the principal mechanisms responsible for quenching of excitons: the filling of the bands as well as the screening caused by the carriers, giving advantages to these structures in keeping excitons at higher hole concentrations.

For a 90-Å-wide BDQW with a hole concentration of 5.3×10^{11} cm⁻², the FE_{hh} is observed in PLE only at high temperatures (43 K).²⁴ This particular case has nothing to do with the topic of quenching of excitons as discussed above since the FE_{hh} is still observed in PL at low temperatures. Conversely, this effect is not observed for WDQW's. In our samples, for example, the FE_{hh} is still observed up to 3×10^{12} cm⁻² (Fig. 6). In this particular case, we are dealing with the formation of excitons with both electrons and holes at $k \neq 0$. In BDQW's, the electrons at high **k** would relax to the bottom of the conduction band before finding a hole to

from an exciton; this effect can only benefit excitons at k=0, observed only in PL. As a result of the higher mobility in BDQW's, the probability of such an electron (k=+k) to find a hole (k=-k) decreases drastically. WDQW's, on the contrary, have an array of dopants in the well, deteriorating the mobility and causing carrier localization due to fluctuations at the impurity potential. These circumstances would favor the formation of excitons at k=0.

V. CONCLUSION

We have studied the effects of acceptor concentration up to the degenerate limit using steady-state photoluminescence (PL) and PL excitation (PLE). The same samples were hydrogen passivated, and the luminescence results are compared with PL results obtained with increasing acceptor concentration. We also discuss the topic of quenching of excitons by comparing results obtained in n- and p-type bulk BDQW and WDQW structures.

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