Dynamics of carrier-capture processes in $Ga_xIn_{1-x}As/GaAs$ near-surface quantum wells

J. Dreybrodt, F. Daiminger, J.P. Reithmaier, and A. Forchel
Technische Physik, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany
(Received 10 August 1994)

$Ga_xIn_{1-x}As/GaAs$ quantum wells with thin top barrier layers in the range of a few nanometers have been studied by time resolved photoluminescence spectroscopy. The excitonic lifetime is strongly influenced by a fast trapping mechanism of carriers into surface states. By varying the top barrier thickness the influence of the surface on the optical properties of quantum wells with different well thicknesses was investigated. We observe a simultaneous decrease of the photoluminescence intensity and lifetime below about 10 nm top barrier thickness. The onset of the decrease scales with the quantum well width and begins for thinner quantum wells at thicker top barrier layers. Calculations assuming electron capture times shorter than 1 ps into surface states located within a trapping layer of about 5 nm thickness reproduce the experimental results very well.

Optical transitions in near-surface quantum wells (QW's) offer the possibility to study influences of the surface on the QW eigenstates. The interaction between carriers confined within the well region and surface states can be controlled by the variation of the QW width and the thickness of the top barrier layer, respectively.[1,2] The wave function of narrow QW's with a high quantization energy penetrates deeply into the surrounding barrier material and may be therefore very sensitive to influences of the surface. In contrast, carriers in wide QW's are mainly confined within the active well region, resulting in a low sensitivity for surface related disturbances. Previous investigations[3] have shown that the energetic position of the photoluminescence (PL) signal of near-surface QW's is strongly influenced by the high vacuum potential of several eV. The emission line of a surface QW without any GaAs top barrier layer is shifted to higher energies due to an enhancement of the quantization energy. As a consequence of the high surface state density[4] changes in the dynamic behavior of the carriers are expected.

Near-surface QW's are well suited to investigate systematically the influence of the surface onto a limited volume of several nanometers thickness within a semiconductor. By changing the distance of the optically active well region to the surface the strength of this influence is controllable. PL spectroscopy detects the influence of surface related processes on the optical properties and allows conclusions about the recombination mechanism and the dynamics of carriers by time resolved measurements.

We have studied the optical properties of $Ga_xIn_{1-x}As/GaAs$ QW's as a function of the top barrier thickness by time resolved and continous wave (cw) PL spectroscopy. We observe a strong decrease in intensity and lifetime with reduced top barrier thickness. This demonstrates the strong influence of surface states on the radiative emission process of QW's for thin top barrier layers. Calculations of the lifetime assuming an ultrafast carrier capture within a trapping layer at the surface give a detailed understanding of the dominant recombination mechanism. In agreement with the data the model also predicts a saturation of the lifetime for very thin top barrier layers.

The samples were grown by molecular beam epitaxy (MBE) on [100] oriented substrates without any intentional doping. The structures consist of a 5 nm $Ga_{0.8}In_{0.2}As$ QW with 16 nm top barrier thickness and a 15 nm $Ga_{0.87}In_{0.13}As$ QW with 20 nm top barrier thickness, respectively. The growth temperature was 580 °C for the GaAs buffer and 520 °C for the $Ga_xIn_{1-x}As$ and the top barrier layer. The top barrier thickness was varied by a wet chemical etch process using a highly diluted H_2SO_4:H_2O_2:H_2O etchant (ratio 1:10:6000) with a GaAs etch rate of 0.25 nm/s. For further details, see Refs. 3 and 5. For the time resolved PL investigations a mode locked Ti:sapphire laser was used operating at a wavelength of 827 nm with a pulse width of 2 ps. The value of the excitation energy is below the GaAs barrier layers and carriers are only generated in the well region. The emission signal was dispersed by a 30 cm monochromator and detected by a streak camera with a time resolution of 20 ps. The peak excitation power was about 70 kW/cm^2. This corresponds to an estimated initial carrier density of 2×10^{10} cm^{-2}. The cw experiments were performed with the 514 nm line of an Ar ion laser and for detection a liquid nitrogen cooled charge coupled device camera was used. The average excitation density was about 10 W/cm^2. All samples were mounted in a cryostat and measured at a temperature of 2 K.

Figure 1 shows the temporal evolution of the PL intensity for the 5 nm $Ga_{0.8}In_{0.2}As$ QW at a temperature of 2 K for different top barrier thicknesses. For large decay times the intensity decreases exponentially as can be seen from the semilogarithmic representation. The lifetimes and the corresponding top barrier thicknesses are given beneath the spectra. We observe a strong decrease in the lifetime with decreasing top barrier thickness. The lifetime is lowered from 220 ps for the unetched reference sample with a 16 nm thick top barrier layer down to 28 ps for the sample with 9 nm top barrier thickness.

We attribute the decrease of the lifetime with decreas-

0163-1829/95/51(7)/4657(4)/$06.00 ©1995 The American Physical Society

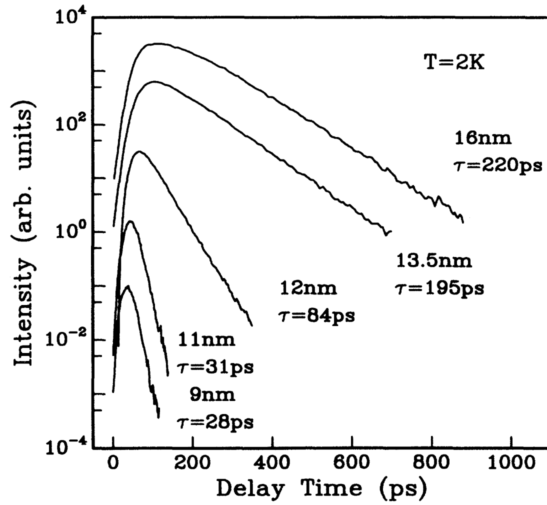

FIG. 1. Semilogarithmic plot of the decay time of a 5 nm $Ga_{0.8}In_{0.2}As$ QW for varying top barrier thickness ranging from 16 nm down to 9 nm. The lifetime τ is indicated beneath the spectra. Excitation was performed below the band gap of the GaAs barrier.

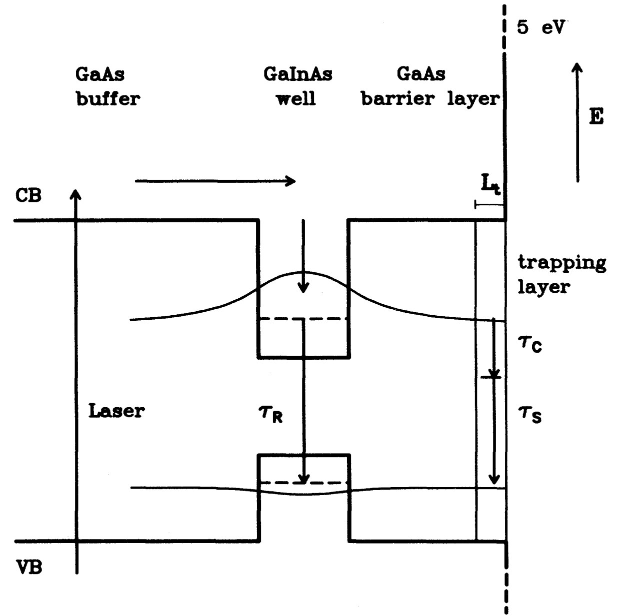

FIG. 2. Schematic picture of the dynamic processes and variables used in our model in the conduction and valence bands of near-surface QW's. Explanations in the text.

ing top barrier thickness to enhanced nonradiative recombination by surface states. The GaAs surface is characterized by a high density of midgap states on the order of 10^{11}–10^{13} $\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$.[6] By reducing the top barrier thickness the dominance of this nonradiative recombination channel increases and fewer carriers can contribute to the radiative QW emission.

To explain our results we have calculated the lifetime by taking into account the nonradiative recombination at the surface. The measured lifetime τ can be written as the sum of a QW and a surface term:[7]

$$\frac{1}{\tau}=\frac{1}{\tau_R}+\frac{1}{\tau_{\mathrm{NR}}}\,, \tag{1}$$

where τ_R is the lifetime for radiative carrier recombination in a QW with infinitely thick barriers without influences of the surface and τ_{NR} is the lifetime for nonradiative recombination by surface states.

Figure 2 shows a schematic diagram of the band structure for near-surface QW's with the important recombination processes. The QW is placed close to the surface and a finite top barrier thickness has to be considered, which separates the QW from the high vacuum potential of about 5 eV at the surface.[8] The samples are not intentionally doped. The Debye length is of the order of several 100 nm and much larger than the QW thicknesses we investigate. We have therefore assumed flatband conditions in the following evaluation.

The electron and hole wave functions of the QW penetrate into the surrounding barrier material. Due to the small distance of the QW to the surface there is a nonzero probability to find carriers at the surface. A capture into surface states is possible. The carrier-capture process by defects, acceptors, impurities, etc. can be characterized by a capture cross section.[9,10] The theory by Lax[11] describes the process as a capture into a potential trap followed by a relaxation through the bound states via phonon emission. Therefore it is reasonable to introduce a trapping layer with a thickness L_t describing the region where carriers are able to recombine nonradiatively via surface states. We distinguish between the capture time τ_C for carrier relaxation into a surface state and the overall nonradiative lifetime τ_S of the intermediate surface states. Due to the large number of surface states and the relatively low excitation density we cannot saturate surface states and change the lifetime τ_S. This was also confirmed by excitation density dependent measurements. Therefore the measured lifetime τ is only dependent of the capture time τ_C and the further relaxation process must not be taken into account.

Under the assumption of dominating nonradiative recombination at the surface we express the nonradiative lifetime τ_{NR} as the probability P to find carriers within the trapping layer with thickness L_t multiplied by the capture time τ_C and rewrite Eq. (1) to

$$\frac{1}{\tau}=\frac{1}{\tau_R}+P\frac{1}{\tau_C}\,. \tag{2}$$

The properties of the GaAs surface do not change in our experiments and therefore we consider τ_C as a constant value. In this model the measured lifetime is only varied via the probability P. P is the square of the wave function integrated over the trapping layer thickness L_t. The penetration of the wave function into the top barrier layer is determined by the QW parameters such as, e.g., QW width and indium content. For thin and shallow QW's the wave function penetrates deeply into the GaAs barriers, resulting in a high probability to find carriers within the trapping layer, while we get a low probability for wide and deep QW's. Therefore we expect that the 5 nm QW

is more sensitive to influences of the surface than the 15 nm QW.

We used in our calculations for the radiative lifetime τ_R the values of the unetched reference samples and as capture time τ_C 165 fs, which is on the time scale for electron–LO-phonon scattering processes.[12–14] The calculations of the probability are only performed for the electron wave function. This is reasonable because the electronic part of the excitonic wave function is dominating due to the light effective mass. The large hole mass causes a stronger localization of the hole wave function resulting in a much weaker sensitivity to surface effects.

Figure 3 shows a comparison of the measured lifetime at a temperature of 2 K with the calculations. The open dots and triangles represent the data for the 5 nm $Ga_{0.8}In_{0.2}As$ and 15 nm $Ga_{0.87}In_{0.13}As$ QW's, respectively. We observe a strong decrease of the lifetime for both etch series with decreasing top barrier thickness below a certain value. The onset of the decrease depends on the QW thickness and begins for the 15 nm thick QW at 9 nm top barrier thickness, while the decrease for the 5 nm QW starts at 13 nm top barrier thickness. The slope of the decrease itself is almost the same for both QW's. The solid lines represent calculations using Eq. (2). Taking for the trapping layer thickness L_t a value of 4.5 nm we get a remarkably good agreement with the experimental data. Our model fits the onset of the decrease of the lifetime as well as the slope for both QW's with the same set of parameters. The difference between both curves is only caused by different probabilities P of the electrons within the trapping layer. The slope is given by the exponential decrease of the wave function in the top barrier layer, which is for similar both QW samples. One sample has a narrow QW with high indium content and the other one a wide QW with low indium content, resulting in the same energetic difference between electron eigenstate and GaAs conduction band edge.

The lifetime of the e-h pairs is directly connected with the PL intensity. Figure 4 displays the integrated PL intensities as a function of the top barrier thickness for the 5 nm and 15 nm thick QW's. The intensities are normalized to the unetched reference samples. We observe for the range of 5–20 nm top barrier thickness a similar behavior as for the lifetime. The intensity strongly decreases for both sets of samples below a certain value of the top barrier thickness. The onset again scales with the QW width. While we are limited for the time resolved experiments to top barrier thicknesses above 5 nm, the QW emission is detectable even when we begin to reduce the $Ga_xIn_{1-x}As$ well layer itself. Below 5 nm top barrier thickness we obtain a low constant intensity. The total decrease is about three orders of magnitude. The intensity in the constant regime at low intensity is half an order of magnitude higher for the 15 nm QW than for the 5 nm QW.

The integrated PL intensity I_{PL} is connected with the lifetime τ by[15]

$$I_{PL} = c_e n \frac{\tau}{\tau_R}, \quad (3)$$

where c_e is the experimental efficiency and n is the number of carrier pairs photogenerated by the laser. Under the assumption that the radiative lifetime τ_R of the QW does not change with the top barrier thickness, the PL intensity is proportional to the measured lifetime. This allows us to apply our model for the lifetimes to the intensity dependence. The solid lines in Fig. 4 represent calculations correspondingly based on the same parameters as used for the calculations in Fig. 3. The model

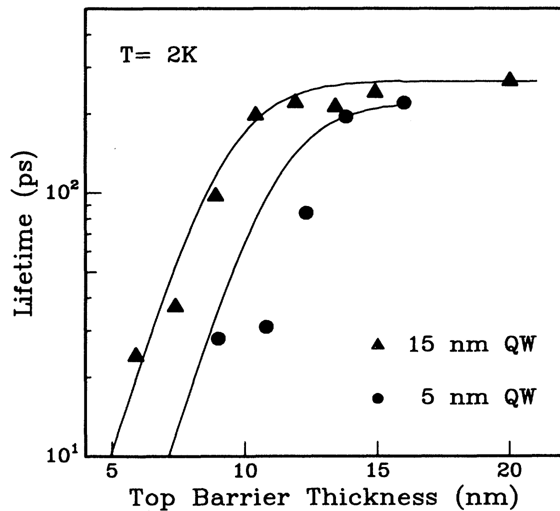

FIG. 3. Lifetime as a function of the top barrier thickness for 5 nm and 15 nm wide QW's. The solid lines represent calculations assuming nonradiative recombination within a 4.5 nm trapping layer at the surface determined by the occupation probability of this layer by the electrons.

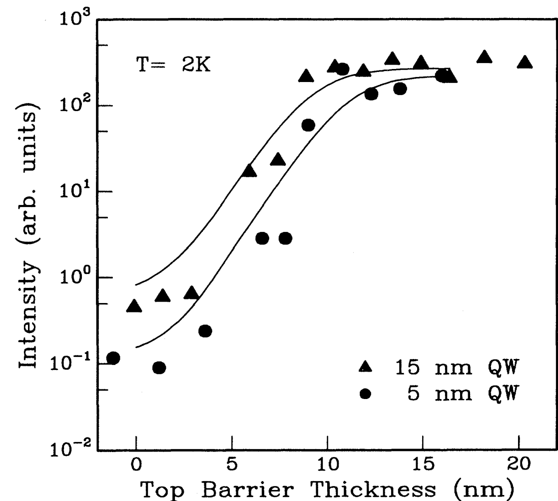

FIG. 4. Integrated intensity vs top barrier thickness for QW's of 5 nm and 15 nm well width. The solid lines correspond to the same set of parameters used for the calculations plotted in Fig. 3. Note that the saturation of the intensity for very thin top barriers predicted by the model is in agreement with the measured data. Negative values of the top barrier thickness belong to QW's with partially etched $Ga_xIn_{1-x}As$ layers.

describes the observed low constant intensity below 5 nm top barrier thickness and the difference between the 5 nm and 15 nm QW's.

We explain the low constant PL intensity by a shift of the trapping layer into the active QW region. In this case the slope of the curve is no longer determined by the exponential tail of the wave function. The trapping layer shifts to the maximum of the wave function, resulting in almost constant occupation probabilities for electrons in the layer. The start of the saturation of the PL intensity at top barriers of around 5 nm thickness confirms the choice of a 4.5 nm thick trapping layer in the calculations.

In summary, we have investigated the influence of the surface on the excitonic lifetime and intensity in $Ga_xIn_{1-x}As/GaAs$ QW's. We observe a strong decrease of the lifetime and PL intensity below approximately 10 nm thick top barriers. The onset of the decrease scales with the QW width and occurs for a 15 nm wide QW at significantly thinner top barrier layers than for a QW with 5 nm thickness. Calculations assuming nonradiative recombination within a 4.5 nm thick trapping layer at the surface with ultrafast capture times of 165 fs are in very good agreement with our data. The dominating parameter is the occupation probability of the trapping layer by the electrons. The model predicts a saturation of the lifetime and the related emission intensity for top barrier thicknesses less than 5 nm. This effect is observed in the PL investigations and can be understood by a shift of the trapping layer into the active QW region itself, resulting in an almost constant probability for nonradiative recombination by surface states.

We acknowledge valuable discussions with F. Faller concerning the growth of the MBE samples. The work was financially supported by the Deutsche Forschungsgemeinschaft.

[1] J.M. Moison, K. Elcess, F. Houzay, J.Y. Marzin, J.M. Gerard, F. Barthe, and M. Bensoussan, Phys. Rev. B **41**, 12 945 (1990).
[2] Y.L. Chang, I.H. Tan, Y.H. Zhang, J. Merz, E. Hu, A. Frova, and E. Emiliani, Appl. Phys. Lett. **62**, 2697 (1993).
[3] J. Dreybrodt, A. Forchel, and J.P. Reithmaier, Phys. Rev. B **41**, 14 741 (1993).
[4] E. Yablonovitch, R. Bhat, C.E. Zah, T.J. Gmitter, and M.A. Koza, Appl. Phys. Lett. **60**, 371 (1992).
[5] J. Dreybrodt, F. Faller, A. Forchel, and J.P. Reithmaier, Mater. Sci. Eng. B **21**, 198 (1993).
[6] T. Sawada, K. Numata, S. Tohdoh, T. Saitoh, and H. Hasegawa, Jpn. J. Appl. Phys. **32**, 511 (1993).
[7] W. Shockley, *Electrons and Holes in Semiconductors* (van Nostrand, New York, 1950), p. 318.
[8] J.M. Moison, C. Guille, M. Van Rompay, F. Barthe, F. Houzay, and M. Bensoussan, Phys. Rev. B **39**, 1772 (1989).
[9] D. Bimberg, H. Münzel, A. Steckenborn, and J. Christen, Phys. Rev. B **31**, 7788 (1985).
[10] C.I. Harris, B. Monemar, P.O. Holtz, H. Kalt, M. Sundaram, J.L. Merz, and A.C. Gossard, Surf. Sci. **305**, 230 (1994).
[11] M. Lax, Phys. Rev. **119**, 1502 (1960).
[12] P.W.M. Blom, C. Smit, J.E.M. Haverkort, and J.H. Wolter, Phys. Rev. B **47**, 2072 (1993).
[13] J.A. Kash, J.C. Tsang, and J.M. Hvam, Phys. Rev. Lett. **54**, 2151 (1985).
[14] M.C. Tatham, J.F. Ryan, and C.T. Foxon, Phys. Rev. Lett. **63**, 1637 (1989).
[15] M. Gurioli, J. Martinez-Pastor, M. Colocci, C. Deparis, B. Chastaingt, and J. Massies, Phys. Rev. B **46**, 6922 (1992).