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Optical properties of $Ga_{0.8}In_{0.2}As/GaAs$ surface quantum wells

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We have investigated the photoluminescence of $Ga_{0.8}In_{0.2}As$ quantum wells where the top barrier is defined by the surface of $Ga_{0.8}In_{0.2}As$ layers. The spectra of surface quantum wells are compared to the emission of $GaAs/Ga_{0.8}In_{0.2}As/GaAs$ quantum wells with varying GaAs top barrier thicknesses. Due to the increase of the confinement potential in the surface quantum wells we observe a significant blueshift of the emission line (of about 20 meV) compared to the emission line of quantum wells with a thick semiconductor barrier. The experimentally observed energy shift and line broadening for surface quantum wells as well as the onset of the blueshift for quantum wells with thin top barrier layers can be modeled by assuming a 5-eV electron affinity. For quantum wells with top barrier thicknesses below 10 nm we observe a decrease of the emission intensity due to nonradiative recombination at the surface.

Two-dimensional systems such as quantum wells (QW's) have been intensely studied during the last two decades.[1,2] Almost all results were obtained on QW's in which the well and both barrier layers consist of a semiconductor. However, confinement may also be obtained if the barrier is given by the transition between a semiconductor and the vacuum or a surface oxide. In this case a very large discontinuity (typically on the order of several eV) may be realized, given approximately by the electron affinity of the semiconductor. As a consequence in surface QW's a strong increase of the confinement compared to semiconductor barrier structures is expected. Therefore, a wide variety of basic QW properties should change strongly if a surface QW is formed, e.g., by removing the top barrier layer of a QW by selective chemical etching. This includes a blueshift of the emission energy and a change of the relevant recombination mechanisms.

The understanding of the physical properties of surface QW's is furthermore of interest for the modeling of lateral quantization effects in etched quantum wires and dots. In these structures the lateral barriers are defined by open surfaces[3,4] and in a first approximation the confinement potential should be equivalent to the energy discontinuity realized at the surface of the active layers in surface QW's. Up to now surface quantum wells have been studied mainly in conjunction with passivation effects.[5,6] For $GaAs/Al_{0.3}Ga_{0.7}As$ surface quantum wells Moison *et al.*[7] have observed a rather unexpected shift of the emission line to longer wavelengths compared to structures with thick cap layers. The redshift of the emission was attributed by these authors to an interaction of carriers with surface states.

We have studied the optical properties of molecular-beam-epitaxy (MBE) grown $Ga_{0.8}In_{0.2}As/GaAs$ QW's as a function of the top barrier thickness. In comparison to $Ga_{0.8}In_{0.2}As$ QW's with a thick semiconductor top barrier layer the surface QW emission occurs at significantly higher energy. By a simple model calculation the increase of the quantization can be attributed to the replacement of the rather small energy discontinuity between the semiconductor and the barrier material (on the order of 0.1 eV) by the large electron affinity (about 5 eV) of the material. The influence of the surface is already significant for nonzero top barrier thicknesses. We observe the onset of a blueshift at top barrier thicknesses of about 3 nm. The photoluminescence (PL) linewidth increases with decreasing top barrier thickness. The line broadening for surface QW's is consistent with potential fluctuations at the surface corresponding to thickness variations of several monolayers. Furthermore the emission intensity of the samples decreases strongly for top barrier thicknesses below 10 nm, due to nonradiative recombination at the surface.

The samples were grown by MBE on [100] orientated GaAs substrates without any intentional doping. The samples consist of 5-nm $Ga_{0.8}In_{0.2}As$ QW's on a 600-nm GaAs buffer. The GaAs top barrier thickness varies from 16 nm down to 0 nm for the surface QW. The growth temperature of 580 °C used for the GaAs buffer was reduced to 520 °C for the growth of $Ga_{0.8}In_{0.2}As$ and the GaAs top barrier. The growth rate was 0.25 nm/s.

We used two methods to vary the top barrier thickness. First the GaAs top barrier (thickness 16 nm) of a $GaAs/Ga_{0.8}In_{0.2}As/GaAs$ QW was gradually removed by wet chemical etching. This allows us to study the influence of the top barrier thickness on an existing layer structure. Furthermore the variation of the surface QW emission due to etching of the QW layer itself can be investigated by this technique.[5] For the etching a highly diluted sulfuric acid/hydrogen peroxide solution was used (H_2SO_4:H_2O_2:H_2O=1:10:6000. GaAs etch rate at 25 °C 0.25 nm/min). In order to obtain the resulting etch depth the samples were half side covered by an organic resist mask. After the etching and the mask removal the etch depth was determined by a surface profiler (resolution: 0.5 nm). A second set of samples was grown with different top barrier layers (16–0 nm) and was investigated without further processing.

For the luminescence experiments the samples were mounted in a *L*He cryostate and excited with the 514-nm line of an Ar laser. The excitation density was about 10 W/cm^2. The PL signal was dispersed by a 32-cm monochromator and detected by a liquid-nitrogen-cooled

charge coupled device camera.

Figure 1 displays the measured PL spectra of the etched samples. The spectrum of the unetched reference sample with 16-nm top barrier thickness is shown at the top. With decreasing top barrier thickness a distinct PL line shift to higher energies is observed. After complete removal of the 16-nm top barrier layer we obtain the PL spectrum of a surface QW (labeled with ~0 nm), which shows an energy shift of about 35 meV as well as a significant line broadening compared to the reference emission. Further etching leads to a reduction of the $Ga_{0.8}In_{0.2}As$ layer thickness and yields a $Ga_{0.8}In_{0.2}As$ emission energy shift almost up to the GaAs barrier edge (spectrum at the bottom). For etch depths larger than 20 nm only the three-dimensional GaAs signal is detectable.

The second method of direct growth of samples was used to obtain well-defined top barrier layers with thicknesses in the range below 5 nm. Figure 2 shows the PL spectra for as-grown samples with top barriers of 16, 3, 1, and 0 nm. We observe a blueshift already for the sample with 3-nm top barrier layer thickness. The surface QW (spectrum at the bottom) has a well-defined $Ga_{0.8}In_{0.2}As$ surface, which permits a precise determination of the blueshift due to the change of the top barrier discontinuity. The emission of the surface QW shows an energetic shift of about 24 meV in comparison to the QW with 16-nm top barrier thickness (spectrum at the top). This demonstrates clearly the large influence of the high surface potential on the transition energy.

In Fig. 3 the experimentally observed transition energies of the etched (dots) and as-grown samples (triangles) are compared. Both data sets show a similar shift to higher energies beginning approximately below 5-nm top barrier thickness. The deviation between the two sets of data is mainly caused by inaccuracies of the thickness measurements, particularly for the etched samples. The

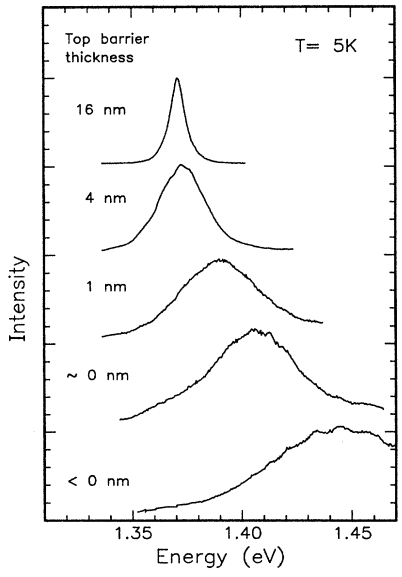

FIG. 1. 5-K PL spectra from a 5-nm $Ga_{0.8}In_{0.2}As/GaAs$ QW with different GaAs top barrier thicknesses. The barrier thickness is given at each spectrum on the left-hand side.

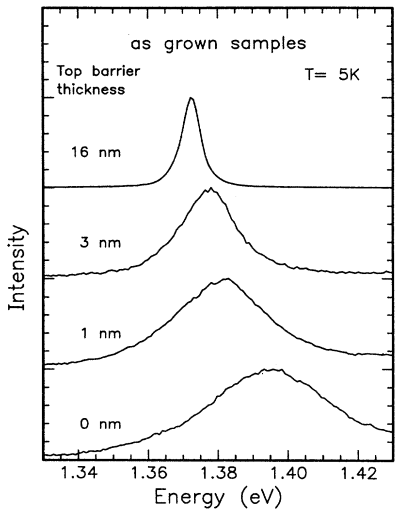

FIG. 2. 5-K PL spectra from as-grown 5-nm $Ga_{0.8}In_{0.2}As/GaAs$ QW's with top barrier thicknesses of 16, 3, 1, and 0 nm.

observed blueshifts can be described quantitatively by a simple confinement model. The inset of Fig. 3 schematically describes the conduction band. We use a rectangular square well with the usual effective masses and semiconductor band offsets.[8] The effects of the strained $Ga_{0.8}In_{0.2}As$ layer on effective mass and band gap are included in the calculations. Less well known is the situation for the surface potential. The semiconductor surface is separated from the vacuum by several nm thick oxide layers.[9,10] Ultraviolet photoemission spectroscopy measurements[11] and theoretical calculations[12] have given a vacuum potential around 5–6 eV. This value is only slightly lowered by an oxide layer at the surface.[13] Our experiments are not sensitive to the exact value of the discontinuity. We assume 5 eV for the conduction-band offset. Furthermore for simplicity an infinite discontinui-

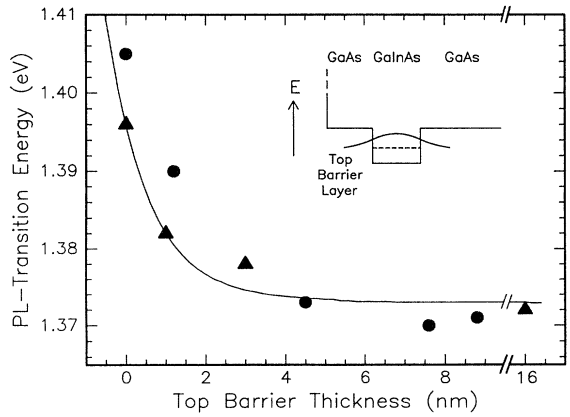

FIG. 3. PL transition energies for etched (dots) and as-grown samples (triangles) as a function of the top barrier thickness. The solid line represents a quantum-mechanical calculation assuming a finite GaAs top barrier thickness with a 5-eV vacuum potential at the surface. An exciton binding energy of 8 meV has been assumed in the calculation. The schematic band diagram in the inset describes the situation in the conduction band.

ty is assumed for the valence band at the surface. The effective electron mass in the vacuum and oxide layer is set equal to the free-electron mass. An exciton binding energy of 8 meV is taken into account.[14] The solid line in Fig. 3 represents the calculated transition energy for the lowest transition (e1-hh1) of a 5-nm $Ga_{0.8}In_{0.2}As$ QW as a function of the top barrier thickness. The agreement between experiment and calculation is rather good, particularly for the as-grown samples. The model quantitatively explains the maximum blueshift for a surface QW as well as the significant increase of the transition energy for thin top barrier thicknesses (below about 5 nm).

Previous experiments on $GaAs/Al_{0.3}Ga_{0.7}As$ and $InP/Ga_{0.8}In_{0.2}P$ QW's showed a redshift of the emission instead of the presently observed blueshift.[6,7] This was partially attributed to an interaction of carriers with surface states resulting in an energy lowering or band bending near the surface. Our results imply a different situation for $Ga_{0.8}In_{0.2}As/GaAs$ QW's. In the present system the good agreement between the experimentally observed blueshift and the model calculations indicates that surface traps or band bending[15,16] do not play a significant role for the eigenstates in the surface QW's.

Figure 4 displays the variation of the half-widths of the PL spectra [full width at half maximum (FWHM)] versus the top barrier thickness. The data for the etch series are shown as dots and for the as-grown samples as triangles. We observe a continuous increase of the FWHM with decreasing top barrier thickness. For a surface QW the FWHM is more than four times larger than for the QW with 16-nm thick top barrier layers. The FWHM of the emission of QW structures is, in general, determined by the interface roughness of the active layer. For the samples with thin top barrier layers investigated here, one must also take into account the effect of the surface roughness. To estimate this influence, we have calculated the FWHM assuming one monolayer fluctuation for the $Ga_{0.8}In_{0.2}As$ layer and ± 1.2-nm surface roughness. Both contributions were treated as independent and added with their quadratical weights. The solid line in Fig. 4 represents the calculation of the FWHM with the values mentioned above. The agreement is good for thin and wide top barriers, while there is a deviation for top barrier thicknesses between 3 and 10 nm. We conclude from this that the FWHM for surface QW's with top barriers of several nm thicknesses is mainly determined by the surface roughness.

A comparison between etched and as-grown samples shows comparable values for the FWHM variation. This indicates a similar quality of etched and as-grown surfaces. The residual roughness may result from fluctuations caused by the uncontrolled formation of an oxide layer at the surface.

The inset in Fig. 4 displays the integrated PL intensities normalized to an unetched reference sample. For top barrier layer thicknesses down to 12 nm the PL intensity remains constant, indicating no influence from the surface. If the top barrier layer is reduced from about 10 nm to 0 nm, we observe a strong decrease in intensity by about three orders of magnitude. For etched surface QW's (top barrier thickness below 0 nm in the inset of Fig. 4) we do not observe any further decrease of the emission intensity. The strong decrease is due to nonradiative recombination[17] by midgap states[18] at the surface. A similar behavior of the emission intensity was also observed by Moison *et al.*[7] and Sandroff *et al.*[19]

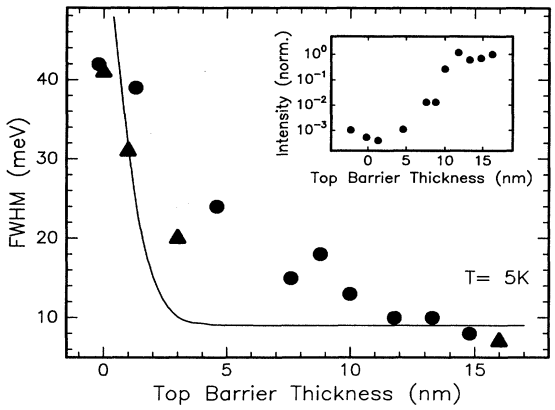

FIG. 4. PL half-widths (FWHM) vs top carrier thickness for a 5-nm $Ga_{0.8}In_{0.2}As/GaAs$ QW (dots for etched samples, triangles for as-grown samples). The inset shows the dependence of the integrated PL intensity on the top barrier thickness.

In summary our investigations have shown that the proximity of the surface strongly influences the energy states in $Ga_{0.8}In_{0.2}As/GaAs$ surface QW's. Even for QW's with thin top barrier thicknesses an influence of the surface must be taken into account. We observe with decreasing top barrier layer thickness a strong PL line shift to higher energies. This behavior can be modeled quantitatively by assuming a rectangular well with a 5-eV potential at the surface. In addition to the shift to higher energies the surface potential leads to an emission line broadening, which can be related to monolayer thickness fluctuations of the QW and a residual roughness of the surface. The roughness of the surface may be caused by an oxide layer with an estimated thickness fluctuation of about ± 1 nm. Furthermore an intensity decrease of three orders of magnitude is observed for surface QW's with top barrier thicknesses below 10 nm, which can be attributed to surface recombination of carriers.

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