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Near-surface GaAs/$Ga_{0.7}Al_{0.3}As$ quantum wells: Interaction with the surface states

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We report a study by ultra-high-vacuum photoluminescence of the interaction of surface and near-surface GaAs/$Ga_{0.7}Al_{0.3}As$ quantum wells with the free surface. For surface-barrier thicknesses below 150 Å, strong redshifts (up to 40 meV) and intensity decreases (up to $\frac{1}{1000}$) of the quantum-well peak are observed, revealing the coupling of the confined states with surface states located near the band edges. While demonstrating quantum wells to be promising surface probes, this observation opens a way to untangling confinement and interface effects on electron states in low-dimensional systems such as clusters and one-dimensional–zero-dimensional nanostructures.

In recent years, the physics of electron states which was previously restricted to quasi-infinite crystals has moved to study more complex systems for which states are confined inside a spatial zone, often called the "well," of finite size along at least one direction. In such systems, the medium surrounding the well must form a "barrier" which prevents well wave functions from extending much outside it. Whatever the nature of this barrier, the vacuum or a selected material, the discontinuity of atomic bonding at the well/barrier interface most often generates interface states, which are in a sense unwanted confined states. If they are numerous enough and extend far enough into the well, they may strongly interact with confined states and bias them. One of the only cases where this bias has been clearly avoided is the GaAs(well)/$Ga_{0.7}Al_{0.3}As$(barrier) system, due to the quasiperfect crystal matching between well and barrier and thus the extremely low-interface state density.[1] The opposite extreme is attained by self-supported ultrasmall clusters, whose surface and bulk are intricate enough to be nearly indistinguishable. A wide range of systems of interest lies between those extreme cases of sensitivity to interface states, for instance, the presently much-debated engraved quantum wires and boxes,[2] in which the proximity of the surface may bias the expected one- or zero-dimension confinement properties.

To our knowledge, the general problem of the interaction between states confined in a well and the well/barrier interface states has not been treated as such on a quantitative basis up to now. For this case study, we have chosen one of the best-defined well/barrier systems, GaAs/$Ga_{0.7}Al_{0.3}As$, in which well/barrier interface states are negligible, and made it interact with the surface states of these materials, whose surfaces again rank among the best defined. This is achieved by building planar structures in which the two-dimensional quantum well (QW) is confined on one side by a quasi-infinite barrier and on the other by either the vacuum barrier (interaction of confined states with surface states of the QW material) or only a very thin variable barrier layer (interaction with surface states of the barrier material located at a variable distance). These interactions, which have not been observed previously except in a preliminary manner,[3] are conversely of fundamental interest to surface physics, because the well-known QW can be used to probe the surface; such probing of local properties by structural perturbations is known to yield otherwise unattainable information like the spatial extension of localized wave functions.[4] The surface/well interaction is detected here by photoluminescence (PL) inside the growth-analysis ultra-high-vacuum system in order to keep clean surfaces. As the QW draws nearer to the surface, we observe drastic changes in the energy position and intensity of the PL originating from the QW, which can be unambiguously attributed to the coupling of QW confined states with surface states.

Sample growth by molecular-beam epitaxy and PL are performed in connected ultra-high-vacuum chambers. Single GaAs QW's of thickness L_w confined on one side by a thick $Ga_{0.7}Al_{0.3}As$ barrier and on the other by a $Ga_{0.7}Al_{0.3}As$ barrier whose thickness L_b is varied from 0 to 1000 Å are grown at 600 °C under an As pressure of 10^{-5} Torr on (100)GaAs substrates (see Fig. 1). Growth rates (≈ 1 Å/s), QW thickness, and barrier composition

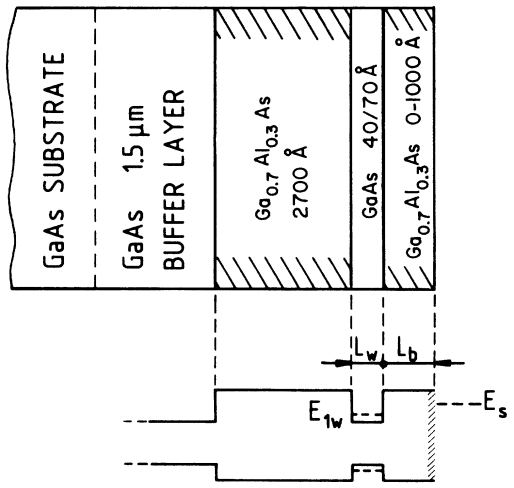

FIG. 1. Schematic drawing of the sample structures and of their conduction and valence bands; E_{1w} is the lowest confined electron state and E_s the coupled surface state.

are checked by oscillations of *in situ* 10-keV reflection high-energy electron diffraction (RHEED) and *ex situ* PL. All layers are nominally undoped, with a residual doping level $N_a - N_d < 10^{16}$ cm^{-3}. The buffer layer, the bottom barrier, and the QW are grown in a single step. In most cases, the growth is then interrupted and the sample is allowed to cool to 300 °C under the full As flux, then to about room temperature under the residual As pressure, and finally to ≈ 180 K under vacuum by liquid-nitrogen circulation in the sample holder. PL is excited by the 514.5-nm line of an Ar^+ ion laser at a density of 100 W/cm^2. The sample may also be analyzed by various surface techniques such as low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and x-ray or ultraviolet photoemission spectroscopy (XPS or UPS). It displays highly contrasted $c4\times4$ RHEED and LEED patterns and sharp UPS features,[5] while XPS and AES reveal no contamination. After analysis, it is brought back to the growth chamber for initial or additional growth of the top barrier. The minimum time needed for a growth-analysis cycle is 40 min. At the end of the *in situ* cycles, the structure is covered by a thin (50 Å) GaAs cap layer and analyzed by *ex situ* PL at 10 K.

We have first checked the effect of growth interruption and thermal cycling on the sample quality. On two samples grown under similar conditions, except that one is grown without interruption, while the top barrier of the other is built in three cycles, *ex situ* PL spectra and integrated intensities are found to be nearly the same, including the impurity peaks. Moreover, we find no significant influence of the number of cycles used to grow the top barrier of a structure on its *in situ* PL spectrum. This favorable result may be partly attributed to the structure of the $c4\times4$ surface, whose As adlayer[6] is flashed off at the beginning of each growth, probably along with any species adsorbed during the analysis, thus leaving a clean surface for epitaxy.

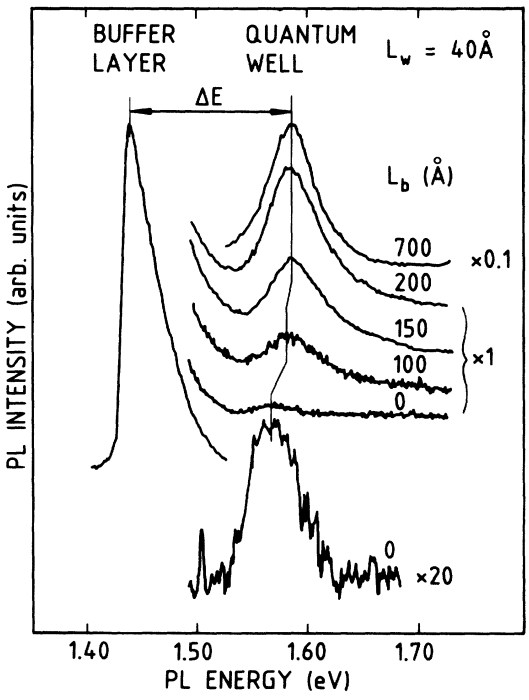

FIG. 2. Typical series of PL spectra obtained *in situ* at 180 K for $L_w = 40$ Å and various L_b values.

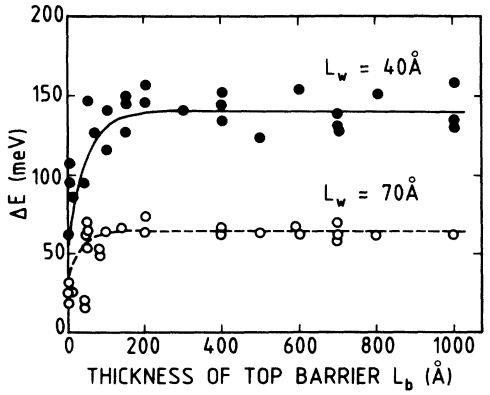

FIG. 3. Variation of ΔE with L_b for $L_w = 40$ Å (solid circles) and 70 Å (open circles). Lines are obtained from the model for $E_s = 20$ meV below the conduction-band edge of the barrier and $L_s = 80$ Å.

Figure 2 shows a typical series of *in situ* PL spectra which involve mostly two peaks originating from the buffer layer and the QW. The high-energy tail of the former is a straight exponential, which allows us to extract small (0.1%) contributions from the QW superimposed on it. In all structures, the shape of the QW peak remains essentially the same (width ≤ 35 meV). Figures 3 and 4 show the variation with L_b of the energy difference between the two peaks, ΔE, and of their intensity ratio, R, obtained on many samples with L_w values equal to 40 or 70 Å. For $L_b \geq 300$ Å, no significant evolution is observed; in this respect, the QW does not "feel" the surface any more. Below this thickness R is drastically reduced, by up to a thousandth for zero thickness, which makes PL analysis more difficult, as commonly observed on near-surface engraved microstructures. We show here that the quality of the surface is not the only cause of such a decrease since we deal, all along, with similar near-perfect surfaces. Simultaneously, ΔE is significantly lowered.

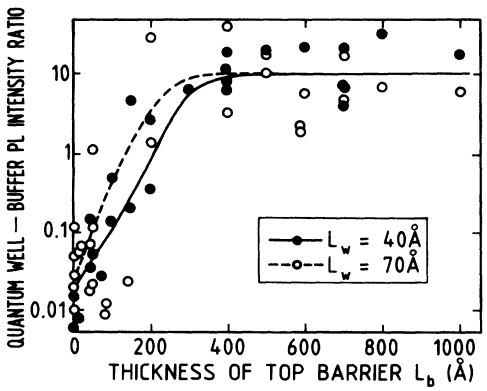

FIG. 4. Variation of R with L_b for $L_w = 40$ Å (solid circles) and 70 Å (open circles). Lines are obtained from the model for $\tau_{(\infty)}/\tau_s = 500$.

This redshift, already reported for InP/InGaAsP QW's,[2] may deeply bias the interpretation of PL shifts in surface or near-surface microstructures since it is opposite in sign to that expected from dimensional reduction.

The influence of the free surface on nearby QW's is *a priori* complex, and we tried to simplify it by minimizing effects[2] due to the space-charge field originating from the Fermi-level pinning at the surface.[5] With a worst-case unwanted doping of 10^{16} cm^{-3}, this field is only 40 kV/cm at the surface in the dark, a value probably reduced by photovoltage effect during PL. From both calculations and experiments,[7] the resulting redshift of ΔE due to the Stark effect is much smaller (<5 meV for the surface QW) than that observed and it vanishes with increasing L_b much more slowly (interaction distance >1000 Å). Only very-high-doping levels ($\approx 10^{19}$ cm^{-3})—completely unrealistic considering the PL spectra—would correspond to the observed interaction distance but in that case the predicted Stark shift would be enormous. Moreover, this shift is predicted[7] to increase with increasing L_w, in opposition to the observed behavior. Similarly, the decrease of R is too large and the corresponding interaction distance is too small to originate from the carrier depletion due to the built-in field or to surface recombination (tenfold depletion over ≥ 500 Å for a worst-case velocity of 10^7 cm/s). Thus we can safely neglect field effects. In view of the small interaction distance, the observed QW surface coupling is most likely a quantum coupling. The first-basis modeling of the surface as an abrupt termination of the structure with a quasi-infinite potential barrier clearly disagrees with experimental data: As in separate-confinement heterostructures, the carrier confinement would increase as the QW draws nearer to the surface. This type of interaction is therefore screened by the electronic structure of the surface itself.

Within surface-state bands, only states located in the zone center at Γ near the lowest QW states can couple efficiently with them. For electron states, we consider the interaction between the lowest QW confined state $|\psi_{1w}\rangle$ at energy E_{1w} and a single surface state $|\psi_s\rangle$ at E_s, leading to a coupled state $|\psi'\rangle$ at E'. Together with a similar term for holes, $E'-E_{1w}$ contributes to the shift of ΔE. In a preliminary approach, we calculate $|\psi'\rangle$ and E' by usual first-order perturbation theory, with a surface potential localized at the surface, a square QW potential (-0.25 eV), and the simplest description of the wave functions: an exponential with a decay length L_s for $|\psi_s\rangle$ and a sinusoid truncated to the QW width for $|\psi_{1w}\rangle$. A similar calculation performed for near-valence-band surface states and confined hole states gives a smaller contribution to the shift of ΔE, all else being equal, due to the smaller well potential for holes. At the temperature of our experiment, excitons in bulk QW's are dissociated due to their low binding energy (≈ 8 meV). While several experiments and calculations suggest that excitons localized at surfaces could be more strongly bound than in the bulk,[8] the binding energy, localization, and equilibrium with bulk excitons of these two-dimensional excitons remain debated. In the case we consider, the confined exciton is partly delocalized towards the surface as the QW draws nearer to it, which rather suggests a decrease of its binding energy, with a possible increase only for very short L_b values (≤ 10 Å).[9] Although further effort is obviously needed, we neglect here excitonic effects and we consider only the effect of the surface-QW coupling.

The shift of ΔE may then be obtained from the shift of electron and hole levels, and approximated by $E'-E_{1w}$. Fitting the $\Delta E(L_b)$ data for both QW widths with E_s and L_s as free parameters (Fig. 3) yields $E_s=20\pm 10$ meV below the bottom of the conduction band of the $Ga_{0.7}Al_{0.3}As$ barrier, i.e., 230 meV above that of GaAs, and $L_s=80\pm 15$ Å. $R(L_b,L_w)$ is proportional to the ratio of the radiative recombination rate in the QW to the total recombination rate, which also involves a constant nonradiative term and a variable term due to tunnel recombination to gap surface states through the surface-QW coupling, taken as proportional to the weight of the surface state in $|\psi'\rangle$. Using the E_s and L_s values obtained from the ΔE data, $R(L_b,L_w)$ is then obtained with a single adjustable parameter, the ratio of the total recombination rate for deeply buried QW's ($1/\tau_\infty$) to the surface-related rate for a surface QW ($1/\tau_s$). A fair fit to experimental data (see Fig. 4) is obtained for a value of this ratio equal to 500. Since τ_∞ lies in the nanosecond range, τ_s lies in the picosecond range. The crude model of interaction between QW confined states and surface states then fits both experimental peak shifts and intensity variations. It may be noted that while the scatter of intensity data does not depend significantly on L_b and seems related to the quality of the layers, the scatter on energy data increases with decreasing L_b, which could be attributed to a scatter of the surface-state energy. Comparison with our model, which predicts this high sensitivity to E_s of energies and the comparatively smaller one on intensities, indicates an E_s scatter of ± 8 meV.

The evaluation of the parameters extracted from the fit (E_s, L_s, and τ_s) is made difficult by the lack of theoretical or experimental studies of the surface states of (100)$Ga_{0.7}Al_{0.3}As$. However, from our AES-XPS analysis of surface segregation,[10] the surface of $Ga_{0.7}Al_{0.3}As$ is Ga-rich ($\approx Ga_{0.9}Al_{0.1}As$), i.e., is nearly GaAs. Furthermore, the occupied surface states of $Ga_{0.7}Al_{0.3}As$ and GaAs detected by UPS (Ref. 6) are nearly the same, so that we may consider the surface to be GaAs always. This explains the continuity of PL data between $L_b=0$ and $L_b>0$, where the surface material switches *a priori* from GaAs to $Ga_{0.7}Al_{0.3}As$. On the $c(4\times 4)$ (100)GaAs surface, empty and occupied surface bands which on (110) lie well (≈ 0.5 eV) outside the band gap at Γ (Ref. 11) are brought towards the band edges by the reconstruction,[12] with their tails pinning the Fermi level near midgap, but their mean position and *a fortiori* their dispersion is not well known. Nevertheless, the location of surface states ≈ 0.2 eV away from the band edges at Γ is quite reasonable. Concerning the wave-function extension, our 80 Å estimation, which is probably optimistic due to some crude approximations such as the truncation of the QW wave function may be compared to the tunneling length $\hbar/\sqrt{2m_eE_s}$ which is ≈ 50 Å for the unperturbed surface state. As a comparison with other near-band-edge electron levels, the extension of the three-dimensional wave function for a shallow impurity, the

effective Bohr radius, is ≈ 75 Å. Finally, the τ_s value of 1 ps corresponds to a surface recombination velocity of about 10^5 cm/s, in the commonly observed range for the kind of surface—i.e., not the cleaved surface whose band gap is free of surface states—and the doping levels we consider.[13]

In summary, we have performed an extended study by *in situ* photoluminescence of the interaction of electron states confined in a well with interface states, originating here respectively from surface or near-surface GaAs/$Ga_{0.7}Al_{0.3}As$ quantum wells and from the free surface of the structure. The large redshift and intensity decrease of the quantum-well peak may be both attributed to a strong coupling of its confined states with surface states located near the band-gap edges and extending ≈ 80 Å inside the bulk. Probing surface states with nearby quantum wells and optical methods is shown here to be a powerful technique in view of the high resolution and selectivity of these methods, which are potentially considerably higher than that of more usual surface techniques. Conversely, from the point of view of semiconductor microstructures, our result points to a possibly deep modification of confined states in near-surface structures such as quantum wires or dots. More generally, it shows that, at least in well-selected cases, one can untangle the effects on electronic structure of the spatial confinement and of the presence of interface states at the confinement interface, even though their magnitudes are similar. The extension of this approach to two-dimension or three-dimension confinement is under way in our laboratory.

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[1]See, for instance, G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Editions de Physique, Les Ulis, 1988).

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