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Monolayer-scale optical investigation of segregation effects in semiconductor heterostructures

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An optical approach for the study of segregation effects on the interfaces of semiconductor heterostructures is implemented for InAs/GaAs. Pairs of identical $Ga_{1-y}Al_yAs$/GaAs quantum wells, in which an InAs monolayer is inserted at nominally symmetric positions in the well, are grown by molecular-beam epitaxy and studied by low-temperature photoluminescence. Such pairs of structures display marked band-gap differences, which highlight the asymmetric broadening of the InAs layer due to the surface segregation of indium atoms during the growth. Reliable information on the indium composition profile is gained on the monolayer scale. We greatly refine previous estimates of the broadening of the GaAs-on-InAs interface. We also demonstrate that the InAs-on-GaAs interface lies at its nominal position; this result gives a clear example of a kinetic freezing of segregation processes in semiconductor heterostructures, occurring here when InAs is deposited on GaAs.

Segregation effects at semiconductor heterojunctions constitute an ultimate limitation to the achievement of perfectly abrupt interfaces for high-control growth techniques such as molecular-beam epitaxy (MBE) or metalorganic chemical-vapor deposition (MOCVD).[1] Surface analysis studies of nominally 1-monolayer (ML) thick InAs quantum wells (QWs) in GaAs reveal, for instance, a surface segregation of In atoms, and their progressive incorporation in the GaAs matrix on a nanometer scale.[1] High-resolution electron microscopy (HREM) confirms for such structures a clear broadening of the GaAs-on-InAs interface.[2]

Optical studies display a strong ability to probe the *in-plane* interfacial perfection of QWs. Photoluminescence (PL) line splittings, for instance, reveal long-range fluctuations of the QW width by ML increments.[3] However, few PL studies have been devoted to the study of segregation-related interfacial gradings.[2,4] The electronic properties of a basic QW are in fact hardly sensitive to a smoothing of its composition profile. Interfacial effects are obviously weak for the larger QWs. This is also the case for the thinner QWs, since the wave functions of their first electron and hole levels extend widely in the barriers and thus vary slowly near the interfaces. Optical data on ultrathin (1-3 ML) InAs QWs in GaAs only allow us for instance to put a rough upper limit to the amplitude of segregation effects in this system.[2]

MOCVD-grown coupled InAs QWs in GaAs have recently been studied as a function of the spacing between QWs.[4] Though PL data are compatible with the assumption of perfectly sharp interfaces, little information is gained on the actual composition profile of the structure. The PL peak energy of the coupled wells indeed depends essentially on the spacing between the average positions of the indium atoms for both QWs. Segregation effects, which induce for both QWs a similar average drift of the In atoms from their nominal position, can therefore be neither easily ruled out nor precisely evaluated.

We present here, and implement in the case of InAs/GaAs, an optical technique for the study of segregation effects at semiconductor interfaces. We propose the study of the location of the In atoms with respect to a well-defined interface of a GaAs/$Ga_{1-y}Al_yAs$ QW. We grow for that purpose by MBE a pair of InAs/GaAs/$Ga_{1-y}Al_yAs$ QWs, s_1 and s_2, which are *nominally symmetric* with each other with respect to the center of the QW: 1-ML InAs is either deposited close to the first (in s_1) or to the second interface (in s_2), at the same given nominal distance a. Indium segregation, which entails an asymmetric broadening of the indium-containing layer, can lead to very large (tens of meV) differences, in the band gaps G_1 and G_2 of samples s_1 and s_2. In return, experimental measurements of G_2-G_1 for several pairs of samples, designed by varying the nominal position a of InAs, the barrier composition y or the well width w, allow us to gain information on the indium composition profile *on the monolayer scale.* We greatly refine previous estimates of the segregation amplitude obtained by surface analysis techniques and show that the first interface ("InAs" on GaAs) is essentially abrupt, and lies at its nominal location.

We have grown by MBE at 540 °C six pairs of QWs, whose nominal parameters (a,y,w) are listed in Table I. Hereafter we focus our description on the experimental results obtained for three pairs of InAs/GaAs/AlAs QWs ($y=1$, $w=28$ ML).

The PL spectra displayed in Fig. 1 have been obtained at 4 K on two multiple QW structures, S_1 and S_2. S_1 contains three s_1 QWs obtained for different positions of the

TABLE I. Structural parameters and experimental band-gap difference G_2-G_1 of the pairs of InAs/GaAs/$Ga_{1-y}Al_yAs$ QW samples, nominally symmetric of each other.

Barrier composition y	Well width w (ML)	Position a of InAs (ML)	G_2-G_1 (meV)
1	28	3	29
1	28	5	24
1	28	7	17
0.3	28	3	21
0.3	28	7	9
0.3	56	6	12

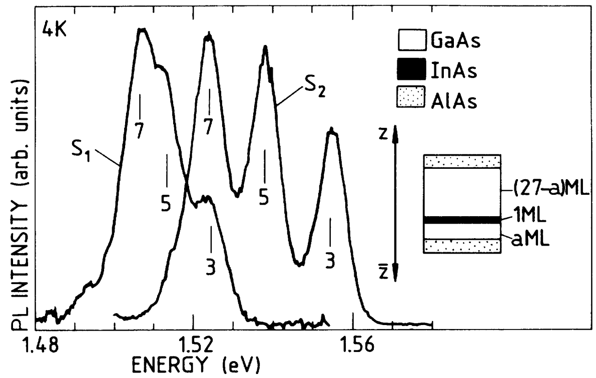

FIG. 1. PL spectra of InAs/GaAs/AlAs multi-QWs S_1 and S_2; the PL peaks are labeled by the value of a in ML. The structure of one given QW ($a=3$, 5, or 7 ML) is shown in the inset. The growth direction is z for S_1 and $\bar{z}$ for S_2.

InAs ML ($a=3$, 5, and 7 ML), close to the first grown interface. S_2 contains the corresponding, nominally symmetric, s_2 QWs. We easily attribute each of the three (intrinsic[5]) PL peaks to a given value of a, since the band-gap energy of InAs/GaAs/$Ga_{1-y}Al_yAs$ QWs decreases monotonically when the location of InAs varies from the edge to the center of the well.[5] The PL peak energy is clearly lower in a s_1 than in a s_2 QW, for each value of a. Band-gap differences G_2-G_1 as large as 29 meV are observed for $a=3$ ML.

The nonequivalence of s_1 and s_2-type QWs cannot stem from an asymmetry of the GaAs/$Ga_{1-y}Al_yAs$ interfaces themselves, though GaAs-on-$Ga_{1-y}Al_yAs$ interfaces are known to be rougher than reversed ones.[3,6] This effect alone would indeed lead to G_2-G_1 values in the 0.1-meV range for a reasonable broadening of the GaAs-on-$Ga_{1-y}Al_yAs$ interface over 2–4 ML.

Fluctuations of the QW's parameters are also unlikely to explain such large and reproducible discrepancies in the position of the PL peak. The observed behavior is, on the contrary, easily understood as soon as In segregation is invoked: In atoms are (on average) moved away from the first grown interface, and brought closer to the second one. As a result, the PL peak is displaced toward lower energies for s_1 QWs, and higher energies for s_2 QWs, with respect to its expected energy for the nominal composition profile.

For a quantitative discussion of our results, we first model the In composition profile and then calculate G_2-G_1 for each pair of QWs. We now detail our major assumptions.

(i) We use a simple one-dimensional equilibrium model[1] to calculate the In composition profile. We assume that during the completion of each deposited ML ("surface" layer s), an equilibrium is reached for the surface exchange reaction (1),

$$\text{In (in } b) + \text{Ga (in } s) \leftrightarrow \text{In (in } s) + \text{Ga (in } b)\,, \qquad (1)$$

where b designates the last complete ("bulk") ML. Apart from the entropy and elastic energy terms, the free energy of layers $s+b$ includes a phenomenological "chemical" energy term E_s, which accounts for the propensity of In atoms for being segregated in ML s. E_s is gained when a single In atom in a GaAs matrix undergoes reaction (1). The following mass-action law is then derived for (1):

$$\ln\left[\frac{x_s(1-x_b)}{x_b(1-x_s)}\right] = \frac{E_s}{kT} - \frac{c^3\Delta^2(x_s-x_b)}{2kT} \times [J + \tfrac{3}{2}\,\delta J(x_s+x_b)]\,, \qquad (2)$$

where x_s and x_b are the In compositions of layers s and b, c is the cubic lattice constant of the GaAs substrate, and Δ ($\Delta=7\%$) is the lattice mismatch between InAs and GaAs. J and $J+\delta J$ designate the $C_{11}+C_{12}-2C_{12}^2/C_{11}$ elastic constant of GaAs (12.33×10^{10} Pa) and InAs (7.93×10^{10} Pa), respectively; a linear dependence of this constant with x is assumed for $In_xGa_{1-x}As$. Finally, previous extensive surface analysis studies of the surface composition of (InGa)As and of the composition profile of GaAs-on-InAs interfaces have yielded an estimate of E_s ($E_s=0.15\pm0.1$ eV).[1]

(ii) We suppose that the In distribution is homogeneous enough in the plane of the QW to allow a one-dimensional envelope function calculation. HREM studies[2] only reveal in-plane fluctuations of the In mole fraction of limited amplitude, which occur at a much lower scale (4 nm) than the exciton Bohr radius. InAs monolayers embedded in GaAs, and InAs/GaAs/$Ga_{1-y}Al_yAs$ QWs display therefore a perfect bidimensional character as far as optical studies are concerned.[5,7]

(iii) We calculate for each ML the band gap of $In_xGa_{1-x}As$ when the hydrostatic part of the strain it experiences is taken into account, and assume that the conduction-band discontinuity between GaAs and strained $In_xGa_{1-x}As$ is a constant part R of the band-gap difference between these hydrostatically strained materials.[8] For $In_{0.15}Ga_{0.85}As$/GaAs, $R=0.89$,[8] so that we retain this value over the whole range of compositions of interest here ($0\le x\le0.3$ typically). As demonstrated below, our conclusions do not rely on a specific choice of R.

(iv) We assume that the exciton binding energies are identical for a given value of a for s_1 and s_2 QWs.

As displayed in Fig. 2, this simple model clearly underestimates G_2-G_1, for the three pairs of InAs/GaAs/AlAs QWs, and over the whole range of relevant values for E_s. A breakdown of hypotheses (ii)–(iv) is not likely to explain this clear irrelevancy. We therefore correct the first assumption, concerning the composition profile itself.

We now suppose that no exchange reactions occur when InAs is deposited on GaAs. (Such reactions exist in an equilibrium model since exchange reactions reduce the elastic energy and increase the entropy of the surface bilayer $s+b$.) The physical origin of such a kinetic freezing of the exchange process will be discussed later. We assume, moreover, that during the subsequent deposition of GaAs on top of InAs, In segregation can be described as previously by the law of mass action (2). As shown in the insets in Fig. 2, the In composition profile is the same in this "limited" equilibrium model than in the previous "full" equilibrium model, but displaced of 1 ML in the growth direction z. Estimates of G_2-G_1 are larger for

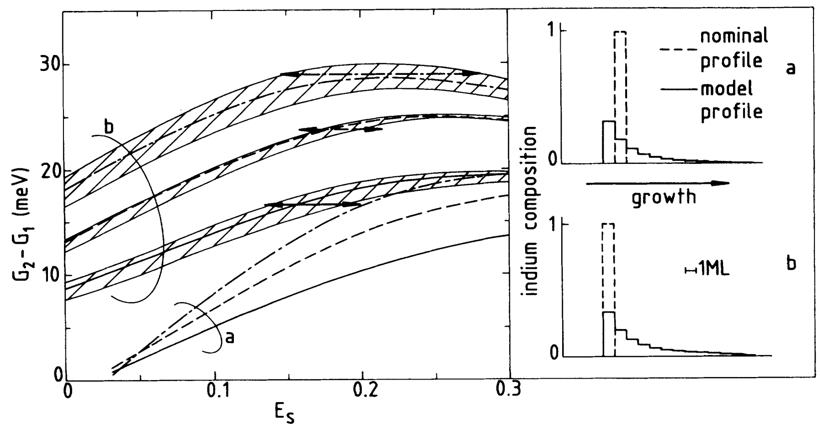

FIG. 2. Theoretical estimates of the band-gap energy difference G_2-G_1 for the pairs of InAs/GaAs/AlAs QWs as a function of E_s ($R=0.89$); $a=3$ (—-—-), 5 (---), or 7 (——) ML. The two sets of curves are obtained (a) if the segregation process reaches its equilibrium for each deposited ML ("full" equilibrium model) and (b) if exchange processes only occur at the GaAs-on-InAs interface ("limited" equilibrium model). In case (b), the dashed areas correspond to the $0.7 \leq R \leq 1$ offset range; the horizontal arrows mark the experimental values of G_2-G_1 and display the typical domain of agreement. The insets show the model composition profiles for 1-ML InAs in GaAs obtained under assumptions (a) and (b).

the limited equilibrium model than for the full one, since the average drift of In atoms along z is increased by 1 ML. For $R=0.89$, a fair agreement can be simultaneously obtained for $a=3$, 5, and 7 ML as shown in Fig. 2. The dashed areas correspond to a very broad range of values of the offset coefficient R $(0.7 < R \leq 1)$. Obviously, the observed agreement is neither fortuitous nor R dependent. Owing to the typical uncertainty on the determination of the PL peak energies (± 0.5 meV) and the maximum possible fluctuations of the InAs content from QW to QW (0.04 ML),[7] E_s lies in the 0.15–0.20 eV range.

Our approach thus displays a clear ability to probe on the monolayer scale details of the In composition profile. We now confirm that the position of the first interface and the typical extent of the indium distribution (i.e., E_s) can be extracted independently from our experimental data. Let us label l the last ML containing GaAs before InAs deposition. By varying its composition x_l between 0 and its expectation x_l^{eq} in the full equilibrium model, we can study how uncomplete the exchange process (1) is at the InAs-on-GaAs interface. Figure 3 displays in a (E_s, x_l) diagram the standard deviation σ of the theoretical estimates to our six experimental values of G_2-G_1. We also plot the dependence of x_l on E_s for a full equilibrium scheme; it is clearly irrelevant since σ is then always larger than 5.5 meV. The best fit ($\sigma \approx 1.2$ meV) is on the contrary obtained for $x_l=0$, i.e., if no exchange reactions take place when InAs is deposited on GaAs. This result constitutes the first clear example of a kinetic freezing of the segregation process (here for 1-ML InAs on GaAs), though previous Raman scattering studies of GaAs/AlAs samples had already suggested that kinetics might play a role for low growth temperatures.[6] Finally, our previous estimate of E_s $(0.15 \leq E_s \leq 0.20$ eV) is confirmed when our six experimental results are taken into account.

Finally, we deduce from our data a range of composition profiles for a nominal InAs ML in GaAs (Fig. 4). The first interface is abrupt and located at its nominal position ($x_l=0$). The average position of the indium atoms in the structure is drifted by 3 ML (4.5 ML) for $E_s=0.15$ eV (0.2 eV). The first three ML have an In composition larger than 10%; HREM, which is essentially insensitive

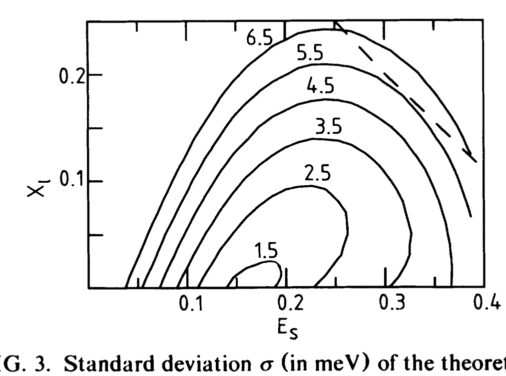

FIG. 3. Standard deviation σ (in meV) of the theoretical estimate of G_2-G_1 to its experimental value (calculated for the six pairs of QW of Table I) as a function of E_s and x_l. x_l is the In composition of the last (nominally In-free) ML deposited before InAs. The dashed line indicates the dependence of x_l on E_s if the exchange process at the InAs-on-GaAs interface reaches its equilibrium.

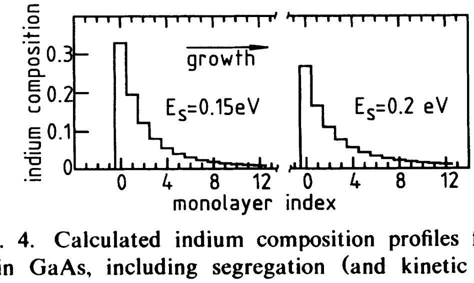

FIG. 4. Calculated indium composition profiles for 1-ML InAs in GaAs, including segregation (and kinetic freezing) effects. 0 labels the nominal position of the InAs ML. $E_s=0.15$ and 0.2 eV correspond to extreme values of our uncertainty range on E_s.

to lower In mole fractions, attributes therefore a 3–4 ML thickness to a nominal InAs ML in GaAs.[2]

We thus observe a breakdown of the equilibrium model for the InAs-on-GaAs interfacial bilayer *alone*, which seems particularly striking at first sight. It might, however, be related to the very different surface morphologies of GaAs and InGaAs. The surface of GaAs has large terraces and few steps under usual growth conditions, whereas a short-scale roughness appears on the opposite as soon as the growth of InGaAs is initiated on GaAs.[9] Since exchange processes at steps or kinks have a lower activation energy (i.e., less bonds have to be broken), the flatness of the GaAs surface can possibly lead to a kinetic freezing of the segregation process.

To conclude, our optical study of InAs/GaAs/$Ga_{1-y}Al_yAs$ QWs confirms and refines previous estimates of the efficiency of the surface segregation of In in GaAs ($0.15 \leq E_s \leq 0.20$ eV). By probing the position of an InAs-on-GaAs interface on the monolayer scale, we demonstrate that an off-equilibrium surface is obtained when 1-ML InAs is deposited on GaAs. On the one hand, our precise estimate of the In segregation efficiency allows one to alleviate its impact on the electronic properties of heterostructures containing thin InAs layers (a change of their nominal position can compensate the average drift of In atoms, for instance). On the other hand, our results suggest that kinetics might be used to suppress completely or at least to limit the segregation process: Growth conditions improving the surface flatness of InGaAs, or low growth temperatures, might therefore be implemented. Finally, our experimental framework clearly allows us to test precisely any technique, based for instance on a thermal desorption of the segregated atoms[10] or on a kinetic freezing, and aiming at a reduction of segregation effects on semiconductor heterojunctions.

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[1]J. M. Moison, C. Guille, F. Houzay, F. Barthe, and M. Van Rompay, Phys. Rev. B **40**, 6149 (1989), and references therein.

[2]C. d'Anterroches, J. M. Gerard, and J. Y. Marzin, in *Evaluation of Advanced Semiconductor Materials by Electron Microscopy*, edited by D. Cherns, NATO Advanced Study Institutes Ser. B, Vol. 203 (Plenum, New York, 1989), p. 47.

[3]B. Deveaud, A. Regreny, J. Y. Emery, and A. Chomette, J. Appl. Phys. **59**, 1633 (1986).

[4]M. Sato and Y. Horikoshi, J. Appl. Phys. **66**, 851 (1989).

[5]J. Y. Marzin and J. M. Gerard, Phys. Rev. Lett. **62**, 2172 (1989).

[6]B. Jusserand, F. Mollot, J. M. Moison, and G. Le Roux, Appl. Phys. Lett. **57**, 560 (1990).

[7]J. M. Gerard and J. Y. Marzin, Appl. Phys. Lett. **53**, 568 (1988).

[8]J. Y. Marzin, M. N. Charasse, and B. Sermage, Phys. Rev. B **31**, 8298 (1985).

[9]P. R. Berger, K. Chang, P. K. Bhattacharya, and J. Singh, J. Vac. Sci. Technol. B **5**, 1182 (1987).

[10]O. Brandt, L. Tapfer, R. Cingolani, K. Ploog, M. Hohenstein, and F. Phillipp, Phys. Rev. B **41**, 12599 (1990).