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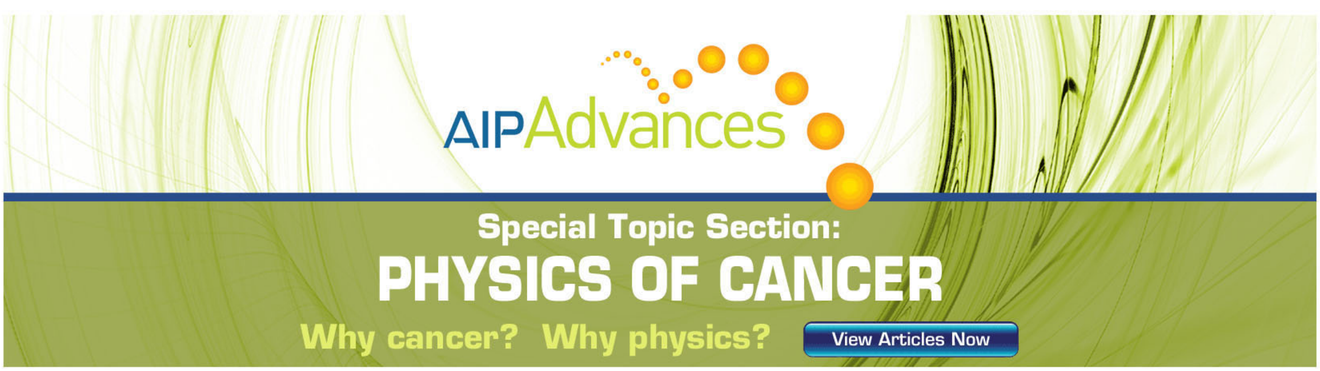

Nanoscale compositional fluctuations in multiple InGaAs/GaAs quantum wires

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An accurate analysis of nanoscale compositional fluctuations in InGaAs/GaAs quantum wires grown by metalorganic chemical vapor deposition on V-grooved substrates was performed by means of high-spatial-resolution transmission electron microscopy techniques. Small In fluctuations (2%–3% excess indium), spatially localized over approximately 5 nm, were detected and related to changes in the photoluminescence and photoluminescence excitation spectra. © *2000 American Institute of Physics.* [S0021-8979(00)07905-6]

I. INTRODUCTION

The effects of compositional disorder on the optical and electronic properties of semiconductor nanostructures are very important as they substantially limit the performances of optoelectronic devices.[1–3] The most important effects are the inhomogeneous broadening of the density of states due to the compositional fluctuations, resulting in the increase of the lasing threshold and in the decrease of the characteristic temperature T_0, and the redistribution of the oscillator strength over the broadened density of states, which reduces the strength of the optical nonlinearities of the nanostructures. In strained ternary alloy systems, like InGaAs/GaAs quantum dots and wires, the situation is even more complicated by the fluctuation of the strain field and by the consequent variation of the internal piezoelectric field, which make the control of the operation wavelength and of the transition probability quite difficult due to the Stark effect. Despite the strong impact of these effects on the optical properties of nanostructures, the assessment of compositional disorder in ternary alloy systems has been poorly addressed so far, primarily due to the paramount difficulty in the quantitative analysis of compositional fluctuations at the nanoscale. The indium distribution of InGaAs/GaAs quantum wires grown by MBE has been probed by cross sectional scanning tunneling microscopy, by averaging the counts of In atoms over few tens of cells, resulting in a rather smooth and broad In profile across the nanostructure.[4,5] In this work we use energy dispersive x-ray spectroscopy (EDX)[6] by means of a high-resolution scanning transmission electron microscope (STEM), to probe the In content across V-shaped quantum wires with subnanometer spatial resolution. The aim of the work is to measure the compositional homogeneity of vertically stacked quantum wires, which were already employed as active materials in electrically driven laser devices,[7] to quantitatively determine the fluctuation of the In composition (for different growth parameters) and its impact on the optical spectra. The samples are grown by metalorganic chemical vapor deposition (MOCVD). Small In fluctuations on the order of 2%–3% over approximately 5 nm are found to occur at the bottom of the wires depending on the III–V ratio adopted during the growth. The occurrence of compositional fluctuations is quantitatively correlated to the shift and broadening of the optical spectra, providing an exact determination of the effects of disorder on the optical spectra.

II. EXPERIMENT

$In_{0.1}Ga_{0.9}As$/GaAs quantum wires were grown by low pressure metalorganic vapor phase epitaxy on V-groove patterned GaAs substrates. The starting substrates were (100) oriented and were patterned by holographic lithography and wet chemical etching. The resulting grooves were aligned along the (01-1) direction and had (311)A-like sidewalls. The lateral periodicity of the pattern was 700 nm, whereas the groove depth was 150 nm. A 30 nm thick GaAs buffer layer followed by six InGaAs/GaAs well/barrier periods (5 nm/20 nm thickness, respectively) and 100 nm thick GaAs cap layer was then regrown by MOCVD. The self-organized growth of the InGaAs/GaAs wires in such grooves resulted in a weakly tapered quantum wire lying on the reconstructued (411) planes of the GaAs buffer layer. The wire thickness at the apex of the groove was about 6 nm, whereas the lateral extension of the ground level wave function confined

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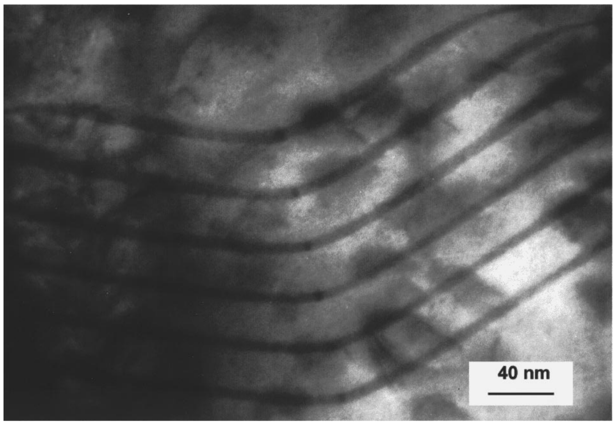

FIG. 1. Typical bright field image of multiple InGaAs/GaAs quantum wires. Note the darker contrast area at the apex of the wires.

at the bottom of the wire (which is taken as the empirical lateral extension of the wire) was on the order of 30 nm. The growth on (411) sidewalls allows a very efficient surface reconstruction on the wires, so that several wires can be vertically stacked with a reproducible thickness profile regardless of the barrier thickness. This is an important prerequisite for the investigation of the compositional homogeneity of vertically stacked wires presented in this work, which should not be influenced by the unintentional variation of the wire profile usually occurring in vertical arrays grown in grooves with (111) sidewalls. In fact, the wires commonly grown on (111) sidewalls[1] exhibit stronger tapering of the profile, i.e., stronger lateral confinement, but they need thick barriers to allow the surface reconstruction necessary for the vertical stacking of really identical wires.

The degree of compositional disorder in our samples is controlled by tuning the III/V ratio, which in turn affects the Ga and In mobility versus the As flux. Local compositional fluctuations are observed in nanostructures grown with high III/V ratio for both the well and the barrier, and originates from the different migration lengths of the group III species. In particular, for III/V ratio equal to 200 (like in Fig. 1), the reduced migration length of the group III species induces a preferential In incorporation on the (100) surface.[8] A reference quantum wire sample of similar profile and with negligible In fluctuation is otherwise obtained by reducing the III/V ratio down to about 100, while keeping the other growth parameters constant, as explained in detail in our previous paper.[8]

Single and vertically stacked wires, both grown with In fluctuations (high III/V ratio) or with homogeneous composition were therefore investigated by EDX spectroscopy. (0–11) cross sectional specimens were prepared for TEM studies by mechanical polishing down to $\sim$20 μm and then to electron transparency using 4 kV Ar^{++} ion mill. The ion current was limited to 0.25 mA/gun and samples were cooled at liquid nitrogen temperature to prevent them from damage due to the ion bombardment. A JEOL 4000 EX II operating at 400 kV accelerating voltage, with an interpretable resolution of 0.17 nm, was used for TEM observations. High spatial resolution chemical analysis was performed by using a Vacuum Generator's HB501 STEM equipped with a cold field emission gun and a LINK windowless EDX. An EMISCAN data acquisition system is interfaced to the microscope both for digital image and spectral acquisition. The EMISCAN system can also be used to acquire and process position resolved lines of EDX spectra with nanometer resolution. TEM observations were performed in the [0–11] zone axis in order to observe the wires perpendicular to the patterning direction and with the wire axis parallel to the electron beam direction, in order to clearly visualize the wire sidewalls and its apex region.

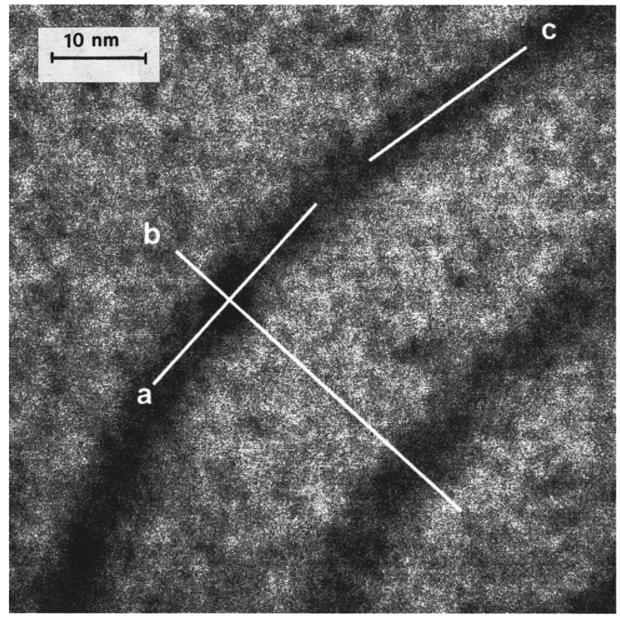

FIG. 2. STEM image of the first two wires. The lines a, b, and c marked on the picture represent the regions where the line scans were performed.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the bright field image of the stacked quantum wires grown with the III/V ratio equal to 200. The wires exhibit reduced tapering and an opening angle of 139 $\pm 3°$, as expected for wires grown with (411) sidewalls.[7] Both the crystallographic planes and the profile remain unchanged during the growth, showing that the quantum wire structure preserves its shape during the growth until total planarization takes place. In fact, the extension of the (411) crystallographic planes decreases during the growth, determining an enlargement of the reconstructed (100) surfaces between adjacent grooves. In the image a contrast increase at the apex of every groove is evident. This contrast variation occurs in a region of about 4.7 ± 0.7 nm, and is confined at the (100) facet which develops at the bottom of the grooves. The compositional fluctuation occurs in the region where most of the electron and hole wave functions are confined, and therefore represents a substantial perturbation for the carrier confinement. The quantitative analysis of the compositional fluctuation was carried out by means of position resolved EDX experiments by scanning a probe with a FWHM of about 2 nm across the InGaAs quantum wire profile. The EMISCAN system was used to acquire several EDX line scans along the directions *a, b,* and *c* marked in Fig. 2. The

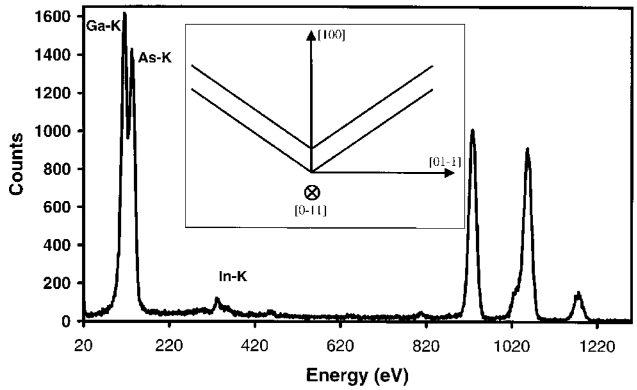

FIG. 3. Typical EDX spectrum for the InGaAs quantum wire. (Inset) Scheme of the crystallographic directions.

typical EDX spectrum from one of the quantum wires, showing characteristic x-ray lines from In, Ga, and As, is exemplified in Fig. 3. Figure 4 summarizes the spatially resolved compositional analysis of the wires along the three directions. The line scan of Fig. 4(a) is taken across the precipitate along the [01-1] direction (see inset of Fig. 3 for the crystallographic directions) and shows an In signal equal to 3.25 $\times 10^2$, corresponding to the nominal In concentration of about 10% in the InGaAs wire. The position resolved EDX data show that the In concentration increases by approximately 2.3% in the precipitate ($x = 12.3\%$ at the apex of the wire), following an approximately Gaussian distribution of width around 5 nm.

Figure 4(b) shows the line scan across two precipitates belonging to different wires [line scan (b)]. The zero signal here corresponds to the GaAs barriers, where no In is present. The peaks in the In integrated counts arise from the areas with darker contrast. In this case we find that the In content at the apex of the upper wire is slightly less than that measured in the bottom wire, as it increases by only 1.9% with respect to the sidewalls ($x = 1.19$ at the apex of the second wire). This finding is consistent with the qualitative analysis of the TEM image of Fig. 2, where the contrast of the precipitate in the upper wire is slightly lighter than that of the lower wire. This suggests that the preferential In incorporation at the apex of the wires reduces with increasing regrowth, i.e., with increasing planarization of the structure. Overall we thus expect that the In precipitation causes an almost continuous compositional modulation on the order of 2%–3% excess In, either laterally, following the Gaussian profile of the precipitate, or vertically, due to the small differences in the actual In content at the apex of different wires in the stack. The resulting chemical gradient provides an unexpected confinement mechanism which has to be taken into account in modeling the nanostructure.

It is important to note that the line scan experiments along the (411) sidewalls shown in Fig. 4(c) [line scan (c) in Fig. 2] reveal excellent compositional uniformity and no preferential In incorporation in the other regions of the nanostructure. Similar homogeneity is observed in the reference sample.

Qualitatively, the effect of the compositional fluctuation is immediately seen in the photoluminescence (PL) and PL

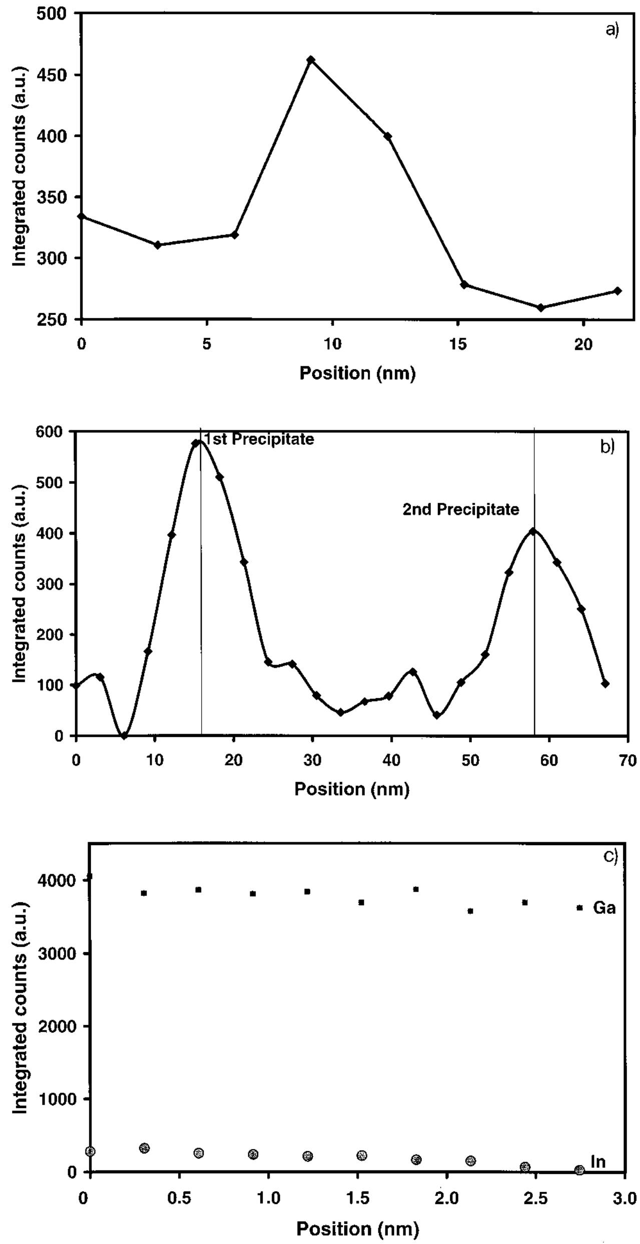

FIG. 4. Line scan experiments across precipitate on [100] direction (a), along the growth direction across two precipitates (b), and along the sidewall far from the precipitate.

excitation (PLE) spectra of the quantum wires (Fig. 5). The PLE spectrum exhibits a featureless exponential onset and no resonance in the wire region. The lateral (411) quantum well and the GaAs absorption onset are seen at 1.498 and 1.517 eV, respectively. The occurrence of In incorporation at the apex of the wire results in the broadened density of states below 1.48 eV. Moreover the spectral broadening of the PL amounts to about approximately 15 meV. On the contrary, the reference sample (inset of Fig. 5) exhibits a sharper ground level resonance of linewidth 5 meV, and a sharper density of states as expected for a nanostructure of better compositional homogeneity.[8]

A quantitative account of these experimental results is obtained by using the profile of the In distribution determined in Fig. 4, and by modeling the potential of the wires

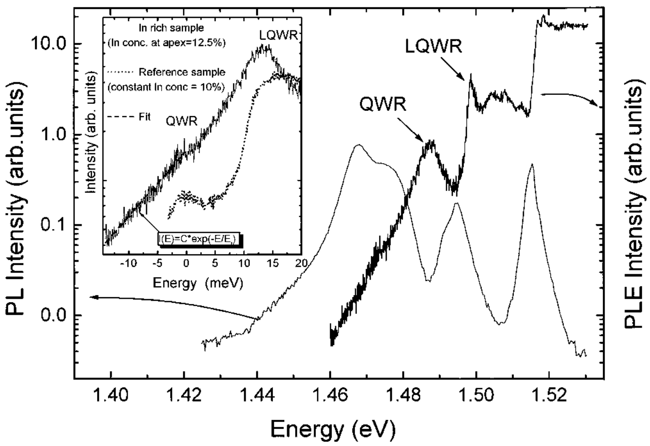

FIG. 5. Photoluminescence and photoluminescence excitation spectra of the quantum wires. The inset shows an enlargement of the low-energy tail for the quantum wire sample with precipitate (continuous line) and for a reference quantum wire without precipitate (dotted line). The dashed line represents a best fit to an Urbach-like dependence.

following our previous work. The quantum wire confining potential is obtained from the resulting two-dimensional (2D) map of the local energy gap and band offsets across the nanostructure (the parameters for the InGaAs alloy are calculated by linear interpolation between the constituting binary compounds). Our potential is thus represented by the bent $In_{0.10}Ga_{0.90}As$ quantum well with (411) sidewalls, with a local minimum at the apex corresponding to the In-enriched region, according to the concentration and spatial extension observed by the EDX analysis. The wave functions are assumed to be factorized in a plane wave along the wire axis and an envelope function which is the solution of a 2D Schroedinger equation for this potential.[9] In the absence of In-enrichement at the apex, we find a very weak confinement that originates primarily from the bending of the quantum well, whereas the weak tapering of the profile does not influence appreciably the carrier wave functions [as opposed to the usual V-grooved wires with (111) sidewalls and stronger tapering]. The corresponding calculated energy states do not account for the observed optical spectra. On the contrary, the observed spectral features are well reproduced (arrows in Fig. 5) if the In-enrichement at the apex is included in the potential profile.

The existence of In fluctuations at the apex of the groove causes a local reduction of the energy gap, which is partially compensated by the increased confinement induced by the local potential minimum at the apex and by the lighter effective masses of carriers in the In-rich region. Taking the variation of the In content through the stacked wires and along the lateral direction determined above, we calculate a corresponding maximum fluctuation in the ground level of about $E_0 = 11$ MeV with respect to the ideally homogeneous sample. This is expected to generate a tail in the density of states which can be modeled as an Urbach's-type tail, $I(E) = Ce^{-E/E_t}$, with the tailing parameter $E_t = E_0$. Indeed, this equation is found to give a good fit to the experimental data in the low-energy tail of the PLE spectrum of Fig. 5 (see dashed curve in the inset[10]), with a best-fit value $E_t = 10.7$ meV.

IV. CONCLUSIONS

In conclusion, we have performed a quantitative investigation of compositional fluctuations in V-shaped InGaAs/GaAs quantum wires, showing the existence of strongly localized In-rich clusters at the apex of the wires. The resulting chemical modulation strongly affects the optical spectra, whose spectral broadening is quantitatively explained by the presence of the In fluctuations. Clusters localized at the bottom of the wire and extending over about 5 nm, with In content in excess of about 2% with respect to the nominal composition, are found to cause a spectral broadening on the order of 11 meV, which smears out completely the one-dimensional features in the optical spectra.

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[10] In the inset, energy zero corresponds to the ground level of the quantum wires. This is because the wires grown with variable III–V ratio and without In precipitates have slightly different average In content (though with identical profile), resulting in a rigid shift of the ground level.