# Vertical composition fluctuations in (Ga,In)(N,As) quantum wells grown on vicinal (1 1 1)B GaAs

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## Abstract

In this work, we present a detailed transmission electron microscopy analysis of the interfacial structure and composition uniformity of (Ga,In)(N,As) quantum wells grown by molecular beam epitaxy on vicinal GaAs(1 1 1)B substrates. *Vertical* composition fluctuations inside the (Ga,In)(N,As) quantum well are detected depending on the growth conditions, in particular the V/III flux ratio and the growth rate. This vertical composition fluctuation due to the phase separation tendency is in contrast to the (0 0 1) case, where the fluctuations proceed in the *lateral* direction. The specific character of the phase instabilities is discussed with respect to the spinodal decomposition of the (Ga,In)(N,As) alloy grown by step-flow on the misoriented (1 1 1)B substrates. The vertical composition fluctuations are explained by the formation of step bunches of alternating composition as a consequence of the different propagation velocity of steps with different atom terminations.

*Keywords:* A. Quantum wells; A. Semiconductors; B. Epitaxial growth; C. Electron microscopy; D. Luminescence

## 1. Introduction

In the last years, dilute (Ga,In)(N,As) nitrides have gained a great deal of interest for applications involving the important 1.3 and 1.55 μm telecom wavelengths. However, if incorporating 2–5% N, that is necessary to reach the 1.55 μm wavelength range, there are still serious difficulties in the growth of high quality (Ga,In)(N,As) quantum wells (QWs). Although overcoming the N solubility limit in (Ga,In)As by low-temperature growth, composition fluctuations and interface undulations are often detected in these QW structures, which deteriorate the optical response and limits further optoelectronic applications So far, most of the studies refer to (Ga,In)(N,As) grown on GaAs(0 0 1), while in general the epitaxial growth on (1 1 1)-oriented substrates (e.g, (Ga,In)As on GaAs(1 1 1)) is characterized by a delay in strain relaxation resulting in a larger critical thickness for misfit dislocation generation (Ga,In)(N,As) on GaAs(1 1 1) could allow the possibility of reaching longer emission wavelengths as it would be possible to grow thicker unrelaxed QWs with N content low enough to assure good optical properties. In addition, this orientation is particularly attractive because of the large piezoelectric field for strained heterostructures grown on it. Nevertheless, in general, the growth on (1 1 1)B GaAs is known to exhibit important difficulties and high-quality samples are obtained only when growing under very specific conditions. In this context, one of the requirements is the use of misoriented substrates which implies that the growth occurs via step-flow. As we show in the present paper, the step-flow growth mode will play a critical role concerning the morphological and phase instabilities of (Ga,In)(N,As) QWs grown on (1 1 1), which, in contrast to (0 0 1) (Ga,In)(N,As) QWs, exhibit pronounced vertical composition fluctuations.

## 2. Growth procedure and experimental setup

The samples were grown by molecular beam epitaxy (MBE) using a RIBER 32 system equipped with a valved cracker As cell and an Oxford Applied Research radio frequency nitrogen plasma cell to provide active N species. The N content was regulated by measuring the atomic N plasma emission at 425 nm using a standard optical emission detector (OED). The samples were grown on 1° toward misoriented GaAs(1 1 1)B substrates. After oxide removal, a buffer layer was grown for 30 min to flatten the growth surface. Then, the temperature was reduced to 420 °C to grow the 7 nm $Ga_{0.7}In_{0.3}N_{0.02}As_{0.98}$ QW. A 9 nm thick GaAs barrier layer was grown at the same temperature as the (Ga,In)(N,As) layer in order to avoid In segregation from the QW. Afterward, the temperature was risen back to 580 °C to grow a 100 nm GaAs cap layer. Growth rates between 0.5 and 1 μm/h were used for the QW Reflection high-energy electron diffraction (RHEED) was used to perform in situ observation of the growing surface. The RHEED pattern exhibits a streak-like appearance for all investigated samples, which evidences the two-dimensional (2D) growth mode based on step-flow.

The transmission electron microscopy (TEM) was carried out in a JEOL JEM 3010 microscope operating at 300 kV. Cross-sectional specimens were conventionally prepared including mechanical thinning and Ar-ion beam sputtering. The samples were studied in the two orthogonal projections. The images were acquired in real-time with a TV-rate or a 1k × 1k slow scan CCD camera and transferred to a computer for storage and further image processing. The morphology and composition of the layers were studied using (0 0 2) dark-field imaging conditions and by lattice structure-resolved high-resolution (HR) TEM. The (0 0 2) dark-field intensity depends on the difference in the atomic scattering factors of the group III and V elements and is thus sensitive to the chemical composition of the quaternary alloy

## 3. Results and discussion

Fig. 1(a) reveals a cross-sectional (0 0 2) dark-field micrograph of the $Ga_{0.7}In_{0.3}$ $N_{0.02}As_{0.98}$ QW grown with a growth rate of 1 μm/h and a V/III flux ratio of 6 Under the $\mathbf{g}_{002}$ imaging condition, which is obtained by tilting the sample 2–3° out of the $[\bar{1}10]$ zone axis, the QW appears in a uniform dark contrast reflecting a homogeneous alloy composition. The interface structure between the 7 nm thin QW and the GaAs barriers is rather smooth and abrupt in agreement with the HRTEM analysis (Fig. 1(b)). There are no indications found for a strain-induced surface roughening on the given length scale. This rather perfect 2D QW structure forms a basic requirement to achieve reasonable optical emission as it is shown by the photoluminescence (PL) spectrum in Fig. 1(c). Post-growth annealing improves drastically the PL intensity due to the reduction of point defects introduced during the low-temperature growth. Furthermore, room temperature laser emission based on these structures has recently been demonstrated Nevertheless, it is known that (Ga,In)(N,As) QWs grown on GaAs(0 0 1) with In concentrations larger than 20% and N concentrations larger than 2% exhibit lateral nanometer-sized composition fluctuations, as a result of the phase separation tendency In this context, little is known about the existence of phase instabilities in (1 1 1)-oriented (Ga,In)(N,As) samples and if any, how they manifest.

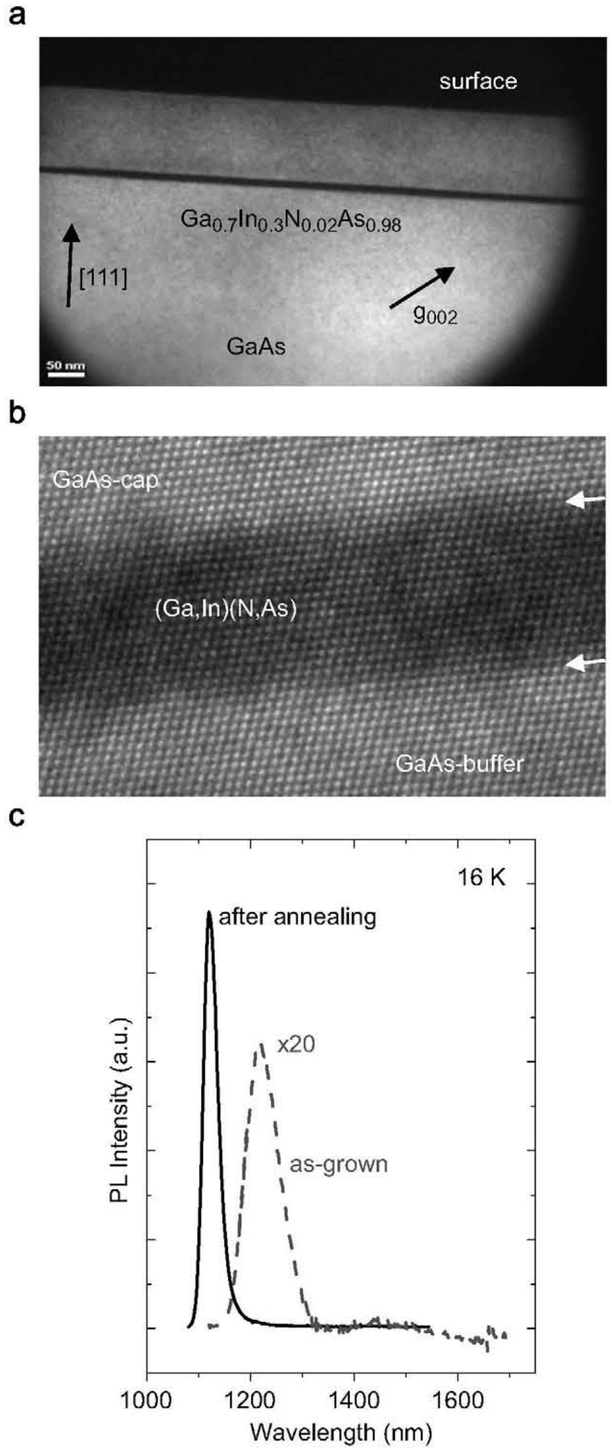

Fig. 1. (a) Cross-sectional dark-field TEM image ($\mathbf{g} = 0 0 2$) of a *perfect* 7 nm $Ga_{0.7}In_{0.3}N_{0.02}As_{0.98}$ QW. (b) High-resolution TEM image of the same QW. (c) The corresponding low-temperature PL spectra of the as-grown (dashed line) and annealed (solid line) sample.

Fig. 2 represents two (0 0 2) dark-field TEM micrographs of QWs, where the N to As partial pressure ratio was increased by about 20% (a) and the growth rate was reduced from 1 to 0.5 μm/h while maintaining the same V/III flux ratio of 6 (b). In these cases, the dark contrast of the QWs is non-uniform and thin bright contrast lines of about 20–100 nm length parallel to the QW become visible in combination with well-defined steps at the second interface (marked by arrows in Fig. 2(a)). These contrast variations directly indicate composition fluctuations, which, however proceed in the vertical direction of the QW, i.e., they differ from the corresponding (0 0 1) case. The reduction of the growth rate from 1 to 0.5 μm/h results in extreme composition fluctuations of the (Ga,In)(N,As) alloy as seen in Fig. 2(b), rather characterized by very thin decomposed lamellae. This phase decomposition additionally causes nanotwins and stacking faults parallel to the (1 1 1) growth surface, which are finally responsible for the structural deterioration of the GaAs cap layer that is produced by a high density of extended defects.

Associated with these vertical fluctuations, the interface between the (Ga,In)(N,As) QW and the GaAs cap layer presents steps of several monolayers height and terraces with lateral dimension varying between 100 and ~200 nm, larger than the ideal terrace width generated by the 1° miscut angle (19 nm). The observed step bunching, i.e., the accumulation of atomic steps during the step-flow growth, is understandable if a "two-step system" is taken into account that is characterized by different step flow rates and Schwoebel barriers.

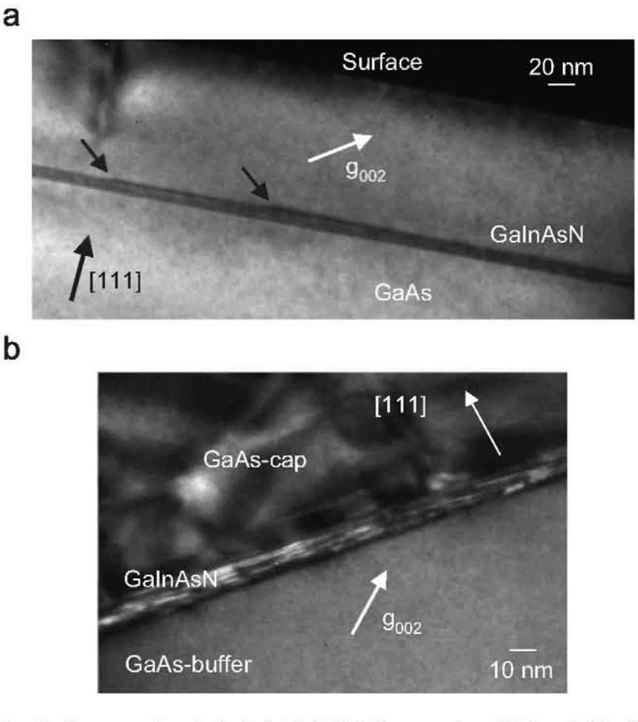

Fig. 2. Cross-sectional dark-field TEM images ($\mathbf{g} = 0\,0\,2$) of (Ga,In)(N,As) QWs grown (a) increasing the N to As ratio and (b) reducing the growth rate from 1 to 0.5 μm/h. Notice the presence of step bunching at the second interface (a), as well as the bright contrast lines parallel to the QW ((b) and also (a)).

As we will discuss in the following, this step bunching can be regarded as a consequence of the spinodal decomposition process during the step flow growth of metastable systems on vicinal surfaces As proposed theoretically by Tersoff spinodal decomposition manifests itself in thermodynamically unstable semiconductor alloys, which are epitaxially grown under step-flow conditions. Based on this model, the decomposition takes place by the formation of step bunches of alternating composition as a consequence of the different propagation velocity of steps with different atom terminations, which provide preferred sinks for the respective constituents. In our concrete case, the N adatom attachment at the steps will favor Ga next neighbors resulting in a layer of preferred Ga–N bond configuration, whereas, As terminated steps favor In atoms generating monolayers of preferred In–As configuration (cf., Fig. 3(a)). Such bonding configurations are driven by maximizing the cohesive bond energy and neglecting the strain contribution Consequently, steps with different atom configuration will grow with different propagation rate depending on the complex growth kinetics, creating step-bunches with In-rich and N-rich layers (see Fig. 3(b)). The final size and dimension of the decomposed area depends on the competition between thermodynamics (cohesive energy) and kinetics that is strongly influenced by the growth rate as well as the actual V/III flux ratio, as demonstrated by our experimental results in Fig. 2.

Another important factor affecting the growth kinetics and thus the spinodal decomposition process is given by the step density. Lowering the step density should increasingly suppress the decomposition trend. We have grown two samples of nominally the same structure and composition (7 nm $Ga_{0.75}In_{0.25}N_{0.02}As_{0.98}$ QW) under

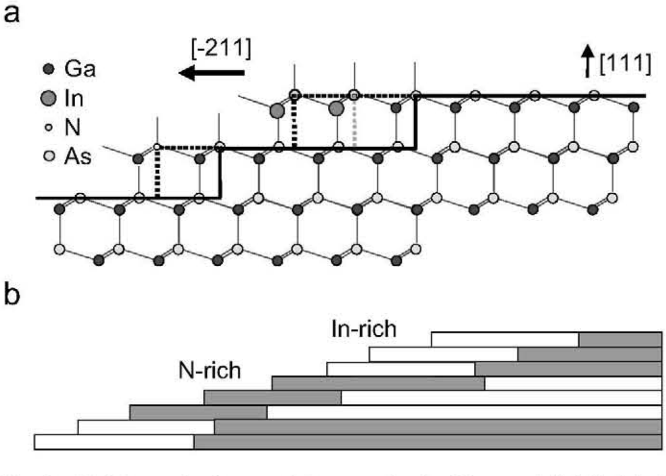

Fig. 3. (a) Schematic picture of the steps in the 1° toward $[\bar{2}\,1\,1]$ vicinal GaAs(1 1 1)B surface showing the possible atom terminations (As-terminated or N-terminated). (b) Steps with different atom configuration will grow with different propagation rate creating step-bunches with In-rich and N-rich layers.

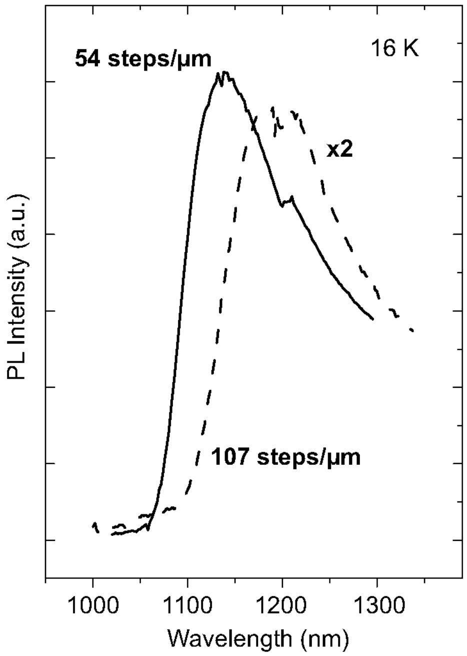

Fig. 4. Low-temperature PL spectra of two nominally identical (Ga,In)(N,As) QW samples grown on different misoriented substrates, with 1° (solid line) and 2° (dashed line) miscut.

identical growth conditions but on substrates with different misorientation: 1° and 2° toward corresponding to 54 and 107 steps/µm, respectively. In fact, the QW grown on the (1 1 1) surface with smaller miscut angle reflects a higher PL efficiency, as expected (Fig. 4). This result is ascribed to a reduced level of decomposition. A more direct proof of this correlation by means of a detailed structural analysis is presently undertaken.

## 4. Summary

A TEM analysis of (Ga,In)(N,As) QWs grown on GaAs(1 1 1)B misoriented substrates reveals the existence of vertical composition fluctuations inside the QW depending on the growth conditions. In particular, these phase instabilities are critically affected by the N to As ratio as well as by the growth rate. The observed step-bunching and bright contrast lines can be regarded as a consequence of the spinodal decomposition process during the step flow of metastable systems on vicinal surfaces as theoretically suggested by Tersoff. The decomposition takes place by the formation of step bunches of alternating composition because of the different propagation velocity of steps with different atom termination, in our case As-terminated and N-terminated steps, which generates layers of preferred In–As and Ga–N bond configurations, respectively. The observed vertical composition fluctuations are in contrast to the case of (Ga,In)(N,As) QWs grown on on-axis (0 0 1) GaAs substrates, where the phase separation tendency leads to lateral composition fluctuations.

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