

Structural properties of GaAsN/GaAs quantum wells studied at the atomic scale by cross-sectional scanning tunneling microscopy

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The nitrogen distribution in GaAsN/GaAs quantum wells (QWs) grown by molecular beam epitaxy is studied on the atomic scale by cross-sectional scanning tunneling microscopy. No nitrogen clustering is observed in the range of N contents studied (between 1.0% and 2.5%, as measured by counting the individual N atoms inside the QW). Nevertheless, the upper interface roughness increases with the amount of N. A residual N concentration in the GaAs barriers is found, which strongly increases with the amount of N in the QW. © 2008 American Institute of Physics. [DOI: 10.1063/1.2968213]

GaAsN and InGaAsN alloys have attracted much attention in the past few years due to the strong band gap reduction obtained when a small amount of N is added to GaAs or InGaAs. This makes them very good candidates for optoelectronic applications in the 1.3–1.55 μm range. Nevertheless, the optical emission of (In)GaAsN/GaAs quantum wells (QWs) showed typically a strong degradation when the N content is increased.^{1–3} This has been frequently attributed to different phenomena, such as N being incorporated in interstitial positions,^{4,5} compositional fluctuations in the alloy,^{6–8} or a rough top interface.⁸ All these have motivated a strong effort in the last years on the structural characterization of (In)GaAsN alloys, but only very few of these studies were performed using cross-sectional scanning tunneling microscopy (X-STM).^{9–11} This technique is very useful because it allows to image the cross section of a QW or bulk layer with atomic resolution and distinguish between the different atoms in the alloy. The distribution of N atoms in a metal-organic vapor phase epitaxy (MOVPE) grown GaAsN alloy with 1.7% N was studied by X-STM a few years ago.^{9,10} Three different N-related features on the (1–10) surface were found and no evidence of clustering was observed.^{9,10} Nevertheless, the N distribution homogeneity could depend on the amount of N in the alloy and in the growth conditions, which differ considerably between the MOVPE and molecular beam epitaxy (MBE) techniques. Therefore, further investigation is needed in order to extract a general conclusion.

In this work, we have used X-STM to study at the atomic scale the N distribution in MBE grown GaAsN/GaAs QWs with different N contents ranging between 1.0% and 2.5%. Structural properties with influence on the optical properties of the QWs are discussed, such as segregation, interface roughness, or the background N concentration in the barriers. N-related features which have not been predicted theoretically or observed experimentally are shown in high resolution images and their possible origin is discussed.

A sample containing a series of GaAsN QWs, separated by GaAs spacer layers and including AlAs as marker layers,

was grown by MBE using a VG V90 system. Nitrogen was provided using a plasma source with N flows of 0.1–0.6 SCCM (SCCM denotes cubic centimeter per minute at STP) and rf powers of 80–550 W. The GaAs growth rate was 0.5 ML/s and the substrate temperature was ~ 450 °C throughout. Starting with the lowest composition, three 15 nm GaAsN QWs of the same composition were grown, separated by 25 nm GaAs barriers. This group was separated from the next by 100 nm GaAs spacer layers during which the rf power and flow are adjusted to a low value and the N shutter is closed. A further group of three QWs of higher N composition is then grown. The sample contains three groups of three QWs of nominal compositions of approximately $(0.4 \pm 0.1)\%$, $(1.0 \pm 0.1)\%$, and $(2.5 \pm 0.3)\%$, with these values obtained from the calibration of N content against plasma cell conditions achieved by measuring the composition of thick (~ 0.6 μm) single GaAsN layers by x-ray diffraction.

The X-STM measurements were performed at room temperature on the [1 1 0] surface plane of *in situ* cleaved samples under UHV ($p < 4 \times 10^{-11}$ Torr) conditions. Polycrystalline tungsten tips prepared by electrochemical etching were used. All the images shown in this paper were obtained in constant current mode at negative voltage (filled states) so the group V elements (As and N) are directly imaged.

Figure 1 shows filled states images of QW1–QW3 [Figs. 1(a)–1(c), respectively]. Individual N atoms give rise to dark features which can be observed in these images (the different features will be discussed later). Also a few adsorbants and cleavage induced defects are observed, as labeled in the images by A and D, respectively. The contrast in the QWs is darker than in the barriers due to the presence of tensile strain since N decreases the lattice constant of GaAs. After cleavage, the tensile strained QWs relax inward giving rise to a dark contrast. The difference in contrast increases gradually from QW1 to QW2 and QW3, indicating an increased amount of N, as expected from the higher N flux.

From a simple visual inspection, no significant N clustering or composition modulation was found in any of the QWs, i.e., the N distribution in GaAsN/GaAs QWs appears to be close to random for N contents below 2.5%. This is in

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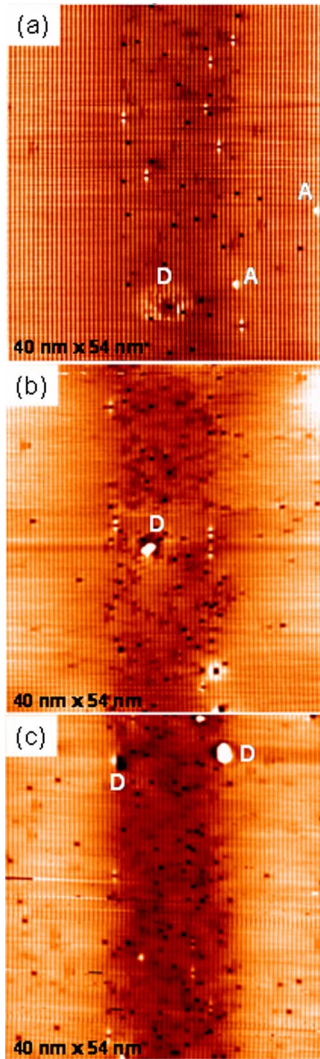


FIG. 1. (Color online) Filled states images taken at -3.0 V of QW1 (a), QW2 (b), and QW3 (c). The QWs appear darker than the GaAs barriers due to the tensile strain. Some adsorbants and cleavage induce defects are labeled as A and D, respectively.

agreement with what was found for MOVPE grown GaAsN alloys with 1.7% N.^{9,10} The short and long range compositional fluctuations observed in GaInNAs/GaAs QWs with similar N contents are not present in this case.^{7,8}

Figure 2 shows a high resolution filled states image of all the different N-related features found. The darkest spots labeled A are N_{As} substitutional impurities in the surface plane (first atomic layer).^{9,12} Similar features with a reduced contrast indicate substitutional N in the third and fifth planes below the surface (labeled B and C, respectively). The different intensity profiles shown in the inset of Fig. 2 with two asymmetric minima are reproducibly found for these three N-related features. The features indicated by D are N atoms on the second plane. At that position, the smaller N atom induces a considerable shift of the closest As atoms toward the N in the $[001]$ direction, as recently predicted by means of density-functional theory in Ref. 12. The As atoms on the other side of the impurity are also slightly shifted.¹² Therefore, N on the second plane gives rise to a broader feature, as shown in Fig. 2. This is strongly supported by a statistical analysis, which shows that these features appear in the same proportion than those corresponding to N on the first and

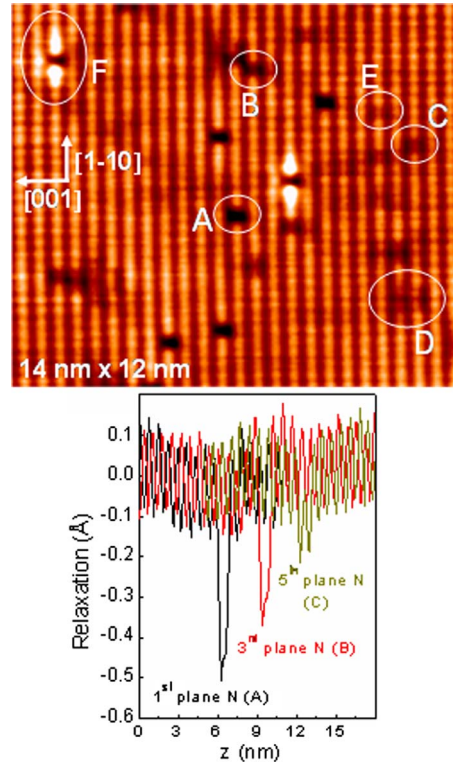


FIG. 2. (Color online) High resolution filled states image showing all the different N-related features found. The inset shows the height profile across the features A, B, and C (N in the first, third and fifth planes, respectively).

third planes. After counting the A, B, and D features found in a 15×50 nm² region in each QW, a similar total number is obtained for the three: 161, 170, and 165 for A, B, and D, respectively. The E features are very weak and probably correspond to N atoms in the fourth plane (the contrast induced by N on the second plane is already only ~ 0.2 Å, so very weak features are expected for N on the fourth plane). The F features are unidentified but they are certainly N-related since they only appear in N containing samples and have also been observed also in other GaAsN and InGaAsN samples that we have studied. Moreover, they seem to be present in the MOVPE grown GaAsN layer in Ref. 9 (although not mentioned in the text), and they were observed by another group.¹³ They are present in a much smaller proportion, approximately six times less than the other N features per atomic layer (only 27 were found in the region described above). They are not related to N pairs since N pair features are found to appear just as the addition of two single N features. Therefore, we suggest that they could represent N atoms at the surface, originated from the segregation of the interstitial N in the first atomic planes to the cleaved surface. This explains the fact that all the other features observed in the first atomic planes are related to substitutional N.

Once the different N features are identified, the amount of N in the QWs can be measured by directly counting the individual N atoms, for example, those on the first plane. The N concentration profile along the growth direction across the three QWs (those in the middle of each MQW group) is shown in Fig. 3. Each profile is the average of three different ones made in 50×50 nm² images. From these profiles, a QW thickness of 15 ± 1 nm is found in the three cases, in very good agreement with the nominal value. By integrating the profile area, average amounts of N of $(1.0 \pm 0.2)\%$,

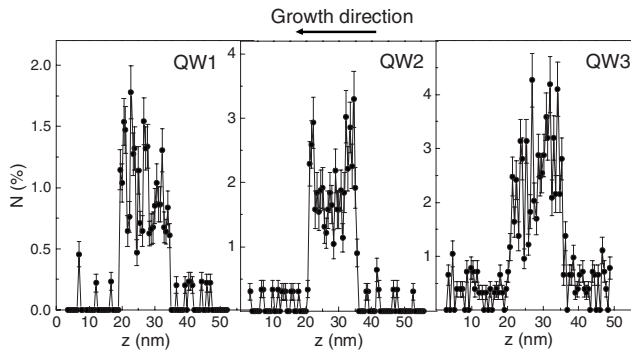


FIG. 3. N content as a function of the distance in the growth direction across the three different QWs. The N concentration is obtained by counting the individual N atoms on the first surface plane.

($1.8 \pm 0.4\%$), and ($2.5 \pm 0.5\%$) are found for QW1, QW2, and QW3, respectively. The relative differences between the measured N content and the nominal one are 150%, 80%, and 0% for QW1, QW2, and QW3, respectively. The difference is very big for low N contents and decreases strongly when the N content increases. This could indicate a lack of reproducibility in controlling very small amounts of N, or a problem with the calibration coming from the x-ray measurements of bulk samples with low N contents. The N distribution in the growth direction does not show a clear or reproducible behavior. While QW2 shows higher N accumulation at the interfaces, the N content seems to slightly increase from bottom to top in QW1 and it seems to decrease in QW3. A higher N accumulation at the interfaces, as found in MBE grown InGaAsN/GaAs QWs with similar N contents,¹⁴ is therefore not necessarily present in GaAsN/GaAs QWs.

As seen in Fig. 3, the interfaces are quite abrupt, and no significant N carryover is observed in the upper interface. Nevertheless, the upper interface becomes less abrupt when the N content is increased. The slope of the N profile at the upper interface decreases slightly from QW1 to QW2 (from 2.07 to 1.97 nm^{-1} , respectively) and more significantly to QW3 (1.24 nm^{-1}). This means that the upper interface roughness increases with the N content, in agreement with what was observed in InGaAsN QWs.¹⁴ The roughness can be quantified to be $\pm 1 \text{ ML}$ for 1.0% N, $\pm 2 \text{ ML}$ for 1.8% N, and $\pm 4 \text{ ML}$ for 2.5% N. The increase in roughness seems to become more relevant for N contents above $\sim 2\%$. This may be one of the reasons why the optical properties of GaAsN QWs are significantly degraded when the N content is increased.

A residual concentration of N in the GaAs barriers, coming probably from a N background in the growth chamber,

can clearly be observed in Fig. 1 and can be quantified from the N concentration profiles shown in Fig. 3. The average N contents in the barriers are ($0.05 \pm 0.01\%$), ($0.09 \pm 0.02\%$), and ($0.40 \pm 0.06\%$) for QW1, QW2, and QW3, respectively. The concentration of N outside the QW increases with the amount of N in the QW. This is very important because N-induced defects in the barriers could be one of the main reasons determining the degradation of the performance of InGaAsN/GaAs QW lasers compared to their InGaAs/GaAs counterparts.¹⁵ Moreover, for GaAsN/GaAs QWs with N contents higher than 2.5% , the amount of N in the barriers ($\sim 0.5\%$) is enough to significantly affect the band gap of GaAs, modifying the carrier confinement in the QW and the PL emission wavelength and efficiency.

In conclusion, the structural properties of GaAsN/GaAs QWs with N contents between 1.0% and 2.5% were studied at the atomic scale by X-STM. Six different N-related features were found, some of them still unidentified. No significant N clustering is observed in that range of compositions. Nevertheless, the upper interface roughness increases with the N content in the QW, as well as the residual N concentration in the GaAs barriers.

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