Strain assisted inter-diffusion in GaN/AIN quantum dots

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The structural and optical properties of high temperature-annealed superlattices of GaN quantum dots embedded in AlN barrier have been studied by a combination of X-ray techniques (reciprocal space mapping, multiwavelength anomalous diffraction, and diffraction anomalous fine structure), high resolution transmission electron microscopy, and photoluminescence spectroscopy. Taking advantage of the disentangling of the chemical and structural information provided by the simultaneous use of X-ray absorption and diffraction data obtained in a synchrotron environment, we provide quantitative determination of strain and composition for each different region of the nanostructures. Eventually, it is shown that strain driven dot/barrier intermixing is present, mostly on top of the dots. These observations have been confirmed by high resolution electron microscopy. A blue shift of photoluminescence peak has been furthermore observed and assigned to GaN/AlN intermixing suggesting a new path for engineering the emission wavelength of such heterostructures. © 2013 American Institute of Physics.

I. INTRODUCTION

Semiconductor quantum dots (QDs) have been a subject of continuous interest for several decades due to their remarkable structural and optical properties. Such nano-objects are generally grown either by molecular beam epitaxy (MBE) or by metalorganic chemical vapor deposition (MOCVD), using the Stranski-Krastanow (SK) growth mode during which pseudomorphic deposition of dot-forming material on a mismatched substrate is followed by three-dimensional (3D) island formation above a critical thickness of some monolayers. This growth mode has been extensively used to grow self-assembled InAs,16 InGaAs,33 SiGe,48 GaN,11 and InGaN1 QDs. In the case of InAs, InGaAs, and SiGe, interdiffusion with barrier material surrounding QDs is commonly observed and has been found to contribute to elastic energy minimization process.4,5,56 By contrast, in the case of III-nitride QDs, interdiffusion has been found to play a minor role. This is spectacularly true in the case of GaN QDs embedded in AlN barrier material. High resolution transmission electron microscopy (HRTEM) studies of stacking of GaN QDs embedded in AlN have revealed no significant interdiffusion. Nevertheless, a detailed study has established that capped dots were slightly smaller than uncapped ones, due to the conversion of one GaN monolayer into AlN, which has been assigned to a Ga/Al exchange mechanism promoted by the energetically favorable formation of Al-N bond.8,15

For arsenides and SiGe QDs, annealing is currently used to further enhance interdiffusion between the dots and the barrier, as a tool for band gap engineering of the heterostructures.22,54,58 Regarding nitride materials, thermally assisted interdiffusion also appears as an attractive tool for band gap engineering of light emitting diodes (LEDs) in a wavelength range spanning from visible to UV. More specifically, interdiffusion of GaN QDs embedded in AlN or AlGaN barrier material could provide a solution for fine tuning of light emitting devices in the UV region. To address this issue, superlattices of GaN/AlN QDs annealed up to 1700 °C have been studied by X-ray diffraction, photoluminescence spectroscopy, and HRTEM. Remarkably, it is found that no significant dot/barrier interdiffusion was observed below 1300 °C, evidence of the exceptional stability of GaN/AlN heterostructures. For annealing temperatures higher than 1300 °C, detailed analysis of reciprocal space maps (RSMs) and anomalous diffraction reveals that interdiffusion is taking place, mostly localized on top of the dots. This is confirmed by HRTEM studies of the samples, which show that the spatially localized interdiffusion is enhanced in the case of vertically correlated GaN dots, as a further evidence that it is strain-assisted. Eventually, it will be shown that annealing at temperatures as high as 1700 °C, far from resulting in the formation of a homogeneous AlGaN alloy leads to the re-crystallization in solid phase of Ga-rich islands surrounded by an Al-rich matrix.

II. SAMPLE PREPARATION

A. PA-MBE

The samples used in this study were grown by plasma-assisted molecular beam epitaxy. After standard degreasing

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procedure, the commercially available 1 μm thick, c-oriented, AlN/sapphire MOVCVD wafers fixed with In on a molybdenum sample holder were introduced in the growth chamber and annealed at 350 °C during 30 min to outgas cleaning residues. Next, temperature was increased up to about 750 °C. An AlN buffer layer was first deposited by alternative supply of Al and N during 5 min for sample A and 10 min for sample B, corresponding to an effective thickness of 10 nm and 20 nm, respectively. Next, GaN QDs/AlN superlattices were grown. GaN QDs were deposited under N-rich growth conditions, whereas for Al barriers an excess of Al was used to ensure flat interfaces. After deposition of the barrier, the surface was left exposed to an N flux to consume the excess of Al. The formation of GaN QDs obeyed the SK growth mode. A thin GaN wetting layer (WL) was first deposited layer-by-layer, till a critical thickness of about 2.4 MLs, followed by an abrupt transition to three-dimensional facetted islands.11 It is now well known that, depending on the amount of GaN deposited and on the thickness of AlN spacer layer, GaN QDs may be correlated or not.6,15 Vertical correlation, when present, has been shown to result from the AlN barrier elastic deformation due to the presence of the GaN QDs plane beneath, which itself results in the preferential nucleation of new GaN QDs just above those of the previous plane.9,53 In order to address the issue of the influence of vertical correlation on GaN QDs annealing, two samples were examined in the present study; the first (sample A, N1368) consisted of 100 planes of GaN QDs, about 1.6 nm high, separated by 11.6 nm thick AlN barrier layers. As it will be shown later, both X-rays RSM and HRTEM revealed that such GaN QDs were uncorrelated vertically. The second sample (sample B, N1473) consisted of 170 planes of GaN QDs, about 3 nm high, separated by 6.5 nm thick AlN barrier layers. Such GaN QDs were found to present a high degree of vertical correlation. After the SLs growth, an AlN capping layer was grown (50 nm) in order to protect the surface during the post-growth annealing step.

B. Rapid thermal annealing

Annealing was performed in an induction furnace, allowing a fast temperature ramp of 1500 °C in 10 min. Samples were placed in a graphite crucible under nitrogen atmosphere at 800 mbar, to avoid oxidation and impurity incorporation. Temperatures at the top and the bottom of the crucible were controlled with pyrometers. For sample A, 30 min annealing at temperatures of 1100 °C, 1500 °C, and 1700 °C has been used on different parts of the wafer and one piece called “as grown” was kept unannealed as reference.

III. X-RAY DIFFRACTION

A. Reciprocal space mapping

Two-dimensional RSM is a well known tool to investigate the structural properties of inhomogeneously strained and/or chemically inhomogeneous systems such as epitaxial heterostructures.14,39,50 The use of linear and 2D detectors together with the synchrotron high photon flux, help reducing acquisition times by orders of magnitude. In the case of the semiconductor epitaxial nanostructures, one can distinguish a number of different regions; substrate, interface, wetting layer, QDs, outer and inner regions of QDs, capping or spacer layers, etc. Each region can have a different composition and/or different strain state and contributes to diffraction at a different location in the reciprocal space. RSM gives a general picture of the sample allowing one to distinguish and study in detail the individual contributions. In particular, it is possible to measure relative angular differences in the peak position with respect to the substrate diffraction peak used as reference.14 These relative peak positions in RSM give information on the strain state (elastically strained, partially or fully relaxed) and provide a quantitative measurement of lattice parameters of the different heterostructure regions.3,26,28–30

RSM experiments were carried out at beamline BM02/D2AM at European Synchrotron Radiation Facility (ESRF). Intensity of asymmetric Bragg reflections was collected by an 8-circle diffractometer (Euler geometry). Scattered intensities were recorded by a linear gas-detector (Vantec™) spanning over an exit angle range of about [0–2°]. The incident X-ray beam was monitored by a dedicated photodiode.43 Two mirrors focus the beam in the vertical plane, whereas the horizontal focusing is achieved using a sagittal bending of the second crystal monochromator. Beam size at the focal point was about 0.15 × 0.3 mm², thus illuminating a large assembly of QDs. Beam polarization was linear in the horizontal plane and the Q vector was in the vertical plane, i.e. the incoming and diffracted beam polarization vectors were perpendicular to Q (σ-σ channel).

RSM was collected close to 1122 and 1015 Bragg reflections at 10,200 eV below the Gallium absorption edge (10,367 eV). The 1015 reflection is sensitive to out-of-plane strain, allowing one to enhance the sensitivity to out-of-plane annealing effects.

The RSM close to 1122 and 1015 Bragg reflections for sample A and in Fig. 2(a) for sample B. Reciprocal space units H, K, and L refer to AlN wurtzite cell parameters (aAlN = bAlN = 3.112 Å, cAlN = 4.982 Å and α = β = 90°, γ = 120°). In this frame, H = 0.976 and L = 4.804 correspond to relaxed GaN parameters (aGaN = bGaN = 3.189 Å, cGaN = 5.185 Å). The mismatch between AlN and GaN is 2.4% (respectively, 3.9%) along [0110] (respectively, [0001]). For the sake of clarity, Fig. 1(d) (respectively, Fig. 2(d)) shows a schematic representation of Figure 1(a) (respectively, Fig. 2(a)). The AlN buffer exhibits a sharp signal at H = 1.0 and L = 5.0. The superlattice reflections with H = 1.0 (streaks) correspond to the stacking along the [0001] direction of GaN WLs and AlN spacers. The GaN WL is matched to the in-plane aAlN parameter.24,47 The superlattice reflections spacing is related to the stacking period Ω by the relation Ω = 2π/L. It gives Ωa = 11.6 nm for sample A and Ωb = 6.5 nm for sample B in satisfactory agreement with growth conditions and transmission electron microscopy observations.

Figures 1(b), 1(c) and Figs. 2(b), 2(c) show H-scans with L = 4.90 and L-scans with H = 0.98 extracted from 1015 RSMs for sample A (Fig. 1(a)) and B (Fig. 2(a)), respectively.
Black curves (respectively, red curves) correspond to as grown (respectively, annealed at 1500°C) samples. Along the $H$ axis, the GaN QDs diffraction signal appears as a broad diffuse scattering peak located in between of relaxed GaN and AlN due to the in-plane compressive strain state of the QDs. The broadening along the $H$ axis is mainly due to the QDs size.

For sample A, the full width at half maximum (FWHM) of the black curve in Fig. 1(b), $\Delta H \approx 0.025$, gives in the real space $d_{QD} \approx 12.7$ nm which corresponds to the average diameter of the QDs, in agreement with TEM observations. Along the $L$ axis, the black curve of Fig. 1(c) shows superlattice modulations on top of a broad peak. This corresponds to a random vertical arrangement of the QDs in the growth direction (there is no long range vertical correlation of the QDs). The FWHM of the black (respectively, red) curve envelope $\Delta L \approx 0.35$ (respectively, $\Delta L \approx 0.20$) gives in the

FIG. 1. (a) 1015 RSM of sample A, as grown, indexed with $H$, $K$, and $L$ referring to relaxed AlN. Relaxed AlN and GaN positions are shown as white spots at the crossing of white dashed lines. (b) (respectively (c)) are linear scans along $H$ (horizontal black arrow) (respectively, $L$ (vertical black arrow)) at $L = 4.9$ (respectively, $H = 0.98$) for as grown (black), annealed at 1500°C (red) and 1700°C (blue) samples. Intensities have been averaged over 3 points. (d) is a scheme of the diffraction pattern in the reciprocal space where AlN buffer, GaN wetting layers and uncorrelated GaN quantum dots contributions are represented.

FIG. 2. (a) 1015 RSM of sample B, as grown, indexed with $H$, $K$, and $L$ referring to relaxed AlN. Relaxed AlN and GaN positions are shown as white spots at the crossing of white dashed lines. (b) (respectively (c)) linear scan along $H$ (horizontal black arrow) (respectively, $L$ (vertical black arrow)) at $L = 4.9$ (respectively, $H = 0.98$) for as grown (black), annealed at 1500°C (red) and 1700°C (blue), samples. Intensities have been averaged over 3 points. (d) is a schematic representation of the diffraction pattern in the reciprocal space where AlN buffer, GaN wetting layers and vertically correlated GaN quantum dots are represented.
real space \( h_{QD} \approx 1.5 \text{ nm} \) (and \( h_{QD} \approx 2.6 \text{ nm} \)) which corresponds to the average height of the QDs for as grown and annealed samples, respectively. Note that in the case of as grown sample, the strain value along the c-axis determined from the position of the broad peak maximum, \((H = 4.88)\), shows that the QDs are compressed by the AlN barriers.

For sample B, the situation is different, the QDs are larger and the AlN barrier is thinner. The diffraction signal shows that the QDs are compressed by the AlN barriers.

In Figs. 1(b), 1(c), 2(b), and 2(c) red curves correspond to an annealing temperature of 1500°C and blue curves to 1700°C. One can observe that annealing strongly modifies the L-scans for both samples. At 1500°C, the superlattice structure is still well defined and the QDs diffraction envelopes shift to higher L values, closer to relaxed AlN. This is a clear indication of Al/Ga intermixing. At 1700°C, the superlattice is destroyed and the diffraction pattern exhibits a single peak that could be interpreted as a signature of an Al\(_1\text{Ga}_x\text{N}\) alloy with \( x \approx 0.1 \). We will show in Sec. V that the sample is not a homogeneous alloy but consists of small Ga-rich clusters whose diameters are of the order of 10 nm that are coherently embedded in an AlN matrix.

The 1015 RSM shows appreciable changes of the structural parameters upon annealing that clearly indicate local atomic re-arrangement or atomic species diffusion. The next step was to perform resonant X-ray diffraction experiments to quantify the structural change of the samples at the nanoscale, with a special attention to the determination of the amount of intermixing.

### IV. RESONANT X-RAY DIFFRACTION

#### A. Diffraction anomalous fine structure

Multiwavelength anomalous diffraction, including diffraction anomalous fine structure, is based on resonant photon-atom interaction, or anomalous effect, that takes place when the photon energy is tuned across an X-ray absorption edge. By fitting the DAFS spectrum cusp to the MAD formula, one can determine the modulus of the partial structure factor (Thomson scattering) of the anomalous (resonant) atoms, \(|F_A|\), of the total structure factor (excluding the resonant scattering of A atoms), \(|F_T|\), and the phase difference \(\phi_T - \phi_A\), where \(\phi_T\) (respectively, \(\phi_A\)) is the phase of \(F_T\) (respectively, \(F_A\)). In the case of a binary alloy or if one can assume a known crystallographic structure, the atomic composition can be determined in iso-strain region selected by the diffraction condition. Also, DAFS cusp fitting provides the scale factor and crystallographic phase shift for fitting the extended DAFS oscillations (see Sec. IV B).

The scattered intensity from the crystal structure can be written by separating the resonant terms from the anomalous atoms A

\[
I(Q, E) \propto |F(T)|^2 \times \left[ \frac{(\cos(\phi_T - \phi_A) + \beta f^\prime(E)^2)(\sin(\phi_T - \phi_A) + \beta f^\prime(E)^2)}{F_A^2 + \beta f^\prime(E)^2} \right],
\]

where \(Q\) is the scattering vector, \(E\) the photon energy, \(f^\prime\) the Thomson atomic scattering factor, \(f_A^\prime\) (respectively, \(f''\)) the real (respectively, imaginary) parts of the resonant scattering factor (anomalous terms). In Eq. (1), the Thomson scattering factors are calculated by Waasmaier and Kirfel method.\(^{55}\) In practice, prior to the DAFS experiment, \(f_A^\prime\) and \(f''\) were obtained from a fluorescence measurement recorded close to the 1122 reflection to keep the measurement geometry as close as possible to the diffraction one. \(f_A^\prime\) values are calculated using a difference Kramers-Kronig transform with the \textsc{DIFFKk} code.\(^{10}\) \(f_A^\prime\) and \(f''\) are shown in Fig. 3 and depend both on the environment of the resonant atom and on the polarization of the incoming X-ray beam.

The MAD equation,\(^{18}\) giving the scattered intensity as a function of the photon energy for a given scattering vector \(Q\), can be written as

\[
I(Q, E) \propto |F(T)|^2 \times \left[ \frac{(\cos(\phi_T - \phi_A) + \beta f^\prime(E)^2)(\sin(\phi_T - \phi_A) + \beta f^\prime(E)^2)}{F_A^2 + \beta f^\prime(E)^2} \right],
\]

where \(\beta = \frac{|f_A^\prime|}{|f_A^\prime|}.\)

We measured DAFS spectra at energies close to the Gallium K-edge (A = Ga) at two different points of the reciprocal space given by the Miller indexes: \(H=K=0.98\), \(L=1.92\) and \(H=K=0.98\), \(L=1.96\) (see Fig. 4(a)).

These two diffraction conditions correspond to two different iso-strain regions that we call 4% and 2%. The labels 4% and 2% refer to the mismatch strain value along the c-axis with respect to relaxed AlN \((\varepsilon = \frac{c_{\text{AlN}} - c_{\text{Ga}}}{c_{\text{AlN}}}\)). Energy scans were performed across the Ga K-edge (10 367 eV), in a wide energy range of about 800 eV, with an energy step size of 1 eV before the edge and 0.06 Å\(^{-1}\) in the \(k\)-space of the

![FIG. 3. Anomalous terms of the atomic scattering factor \(f\) (blue curve) and \(f^\prime\) (black curve) for the A = Ga atoms at energies close to the Ga K-edge, obtained from a fluorescence spectrum (see text). \(f^\prime\) is calculated from \(f''\) using a difference Kramers-Kronig method.](image-url)
virtual photoelectron above the edge, keeping $Q$ fixed as a function of the energy. The background intensity was monitored in order to correct the data for the fluorescence and diffuse scattering signals. For each $Q$ value, five energy scans were recorded and averaged out.

Fitting of background-subtracted DAFS spectra (Fig. 5) with Eq. (2) was performed by assuming a wurtzite structure of space group symmetry $P6_3mc$. Each metallic atom position was filled by gallium and aluminium atoms with a variable population $x_{Ga}$ and $(1 - x_{Ga})$, respectively. Only geometrical parameters (a scale factor, a linear dependence as a function of the energy to take into account the detector efficiency) and $x_{Ga}$ were fitted. Absorption correction was in practice negligible. Best fits (solid lines) are shown in Fig. 5 together with the experimental curves and best fit results are reported in Table I. They were obtained with a metal-polar crystallographic structure, consistent with the Ga-polar orientation of GaN QDs grown on the Al-polar commercial substrate. In Table I, one can see that the structural parameter $\beta$, $\varphi_T - \varphi_A$ and consequently the amount of Gallium ($x_{Ga}$) do not change at a nanometer scale after the annealing at 1500 $^\circ$C. However, a change of superlattice intensities is observed in 1015 RSM, as shown in previous section. The reason for such a discrepancy can be seen in Fig. 4(b): There is barely no shift of the superlattice intensity envelope after the annealing. This suggests that 1122 RSM lacks the spatial resolution and chemical sensitivity to show the small structural changes which take place at the nanometer scale close to the GaN QDs and AlN barrier interface, in comparison with 1015 RSM. In other words, 1122 RSMs combined with MAD cannot easily distinguish case (a) where the Ga and Al atoms are well separated from case (b) where a moderate atomic diffusion took place due to annealing, leading to mixed Ga and Al atoms close to the interface. Then, to get further insight at the atomic scale, we analysed of the extended-DAFS oscillations which show up on the diffracted intensity after the Ga K-edge, as shown in next section.

**B. Extended diffraction anomalous fine structure (EDAFS)**

EDAFS is the oscillatory contribution to the diffracted intensity signal which shows up above the edge spanning over a wide energy range of hundreds of eV. Its origin is

![Energy scan across the Ga K-edge (10 367 eV) at for $H = 0.98$, $K = 0.98$, $L = 1.92$) and $H = 0.98$, $K = 0.98$, $L = 1.96$) (rad) positions in the reciprocal space. Both experimental (open symbols) and best fit curves (solid lines) are shown for sample A as grown (open circle) and annealed at 1500 $^\circ$C (open square). The best fit parameters are reported in Table I.

**TABLE I.** Crystallographic phase difference $\varphi_0 - \varphi_A$ and scale factor $S_D$ obtained by fitting the cusps of DAFS spectra to Eq. (2). The Gallium content $x_{Ga}$ was obtained by assuming a perfect wurtzite structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$h,k,l$</th>
<th>Isostained Region (%)</th>
<th>$\beta$</th>
<th>$\varphi_T - \varphi_A$ (rad)</th>
<th>$x_{Ga}$ (%)</th>
<th>$\varphi_0 - \varphi_A$ (rad)</th>
<th>$S_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A as grown</td>
<td>0.98, 0.98, 1.92</td>
<td>4</td>
<td>0.05258</td>
<td>-0.130</td>
<td>106.0±2</td>
<td>-0.0672</td>
<td>2.79</td>
</tr>
<tr>
<td>Sample B as grown</td>
<td>0.98, 0.98, 1.96</td>
<td>2</td>
<td>0.04272</td>
<td>-0.159</td>
<td>65.2±2</td>
<td>-0.0696</td>
<td>3.44</td>
</tr>
<tr>
<td>Sample A at 1500 C</td>
<td>0.98, 0.98, 1.92</td>
<td>4</td>
<td>0.05185</td>
<td>-0.133</td>
<td>102.0±2</td>
<td>-0.0673</td>
<td>2.83</td>
</tr>
<tr>
<td>Sample B at 1500 C</td>
<td>0.98, 0.98, 1.96</td>
<td>2</td>
<td>0.04193</td>
<td>-0.175</td>
<td>62.7±2</td>
<td>-0.0698</td>
<td>3.50</td>
</tr>
</tbody>
</table>

![Fig. 4. (a) 1122 RSM of sample A, as grown, indexed with $H, K$, and $L$ referring to relaxed AlN. (b) Linear L-scan (vertical black arrow) at $H=0.98$ for as grown (black), annealed at 1500 $^\circ$C (red) and 1700 $^\circ$C samples. The red segments show the region of interest (ROI) of the linear detector used for L-scans and DAFS spectra measurement (Fig. 5). The DAFS curves in Fig. 5 correspond to the diffracted intensity integrated along the two red segments centred at $H=K=0.98$, $L=1.92$, and $H=K=0.98$, $L=1.96$.](http://www.jap.org/.../image)
The smooth atomic scattering factor writes \( D_{\text{AFS}} \) background at the edge. The sum is in this case over theoretical phases and amplitudes calculated by XAFS simulation standard codes.\(^{10,15}\) They have to be corrected by a phase \((\phi_0 - \phi_A - \pi/2)\) and amplitude factor \((S_D)\), which are provided by DAFS cusp analysis (see Table I).

This approach has been already used successfully for several semiconductors systems both with 2D morphologies as heterostructures and thin epilayers and for self-assembled nanostructures (QDs, quantum wells, nanowires, nanolands).\(^{13,21,25,31,41,44,46,57}\) The great advantage of this method is that it provides information on the very local structure of the sample region selected by diffraction. Furthermore, the chemical selectivity of DAFS avoids the interference from nearby regions belonging to substrate or capping layers even if these regions have, due to mismatch strain, the same lattice parameter and thus contribute to diffraction at the same point of reciprocal space. One wants, in this case, to determine composition at a local scale to investigate the diffusion mechanism of Al in the GaN QDs upon annealing.

In the extended region above the edge, the anomalous scattering factor can be splitted into smooth and oscillatory parts: \( f_L^{\nu} = f_0^{\nu} + \Delta f^{\nu}_{0A} \chi_L^{\nu} \) and \( f_R^{\nu} = f_0^{\nu} + \Delta f^{\nu}_{0A} \chi_R^{\nu} \), where \( f_0^{\nu} + i f_0^{\nu} \) is the anomalous scattering of bare neutral atoms and \( \Delta f^{\nu}_{0A} \) is the contribution of the resonant scattering to \( f_0^{\nu} \). The smooth atomic scattering factor writes \( f_0(Q,E) = f_0^{\nu} + f_0^{\nu} + f_0^{\nu} \). The real and imaginary components of the complex extended diffraction anomalous fine structure \( \chi_L^{\nu} = i \chi_R^{\nu} \), are related by the Kramers-Kronig transforms and the imaginary component \( \chi_R^{\nu} \) is related to EXAFS \( \chi_j \) by the following equation: \( \chi_j(E) = \text{Im} \chi_j(Q = 0, E) \).

The diffracted intensity, to the first order in \( \chi_j \), \( \chi_R^{\nu} \), writes

\[
I = FF^* \approx I_0 + 2 \frac{\Delta f^{\nu}_{0A} |F_0|^2 |F_0|}{f_0^{\nu}} \chi_Q,
\]

where \( F_0 = |F_0|^e \) and \( \chi_Q \) is the first order extended DAFS

\[
\chi_Q = S_D \left[ \frac{I - I_0}{I_0} \right] = \cos(\phi_0 - \phi_A) \sum_{j=1}^{N_1} w_j^{\nu} \chi_j^{\nu} + \sin(\phi_0 - \phi_A) \sum_{j=1}^{N_1} w_j^{\nu} \chi_j^{\nu},
\]

where \( S_D \) plays as a normalization factor and \( \phi_0 - \phi_A \), as a phase factor that can be obtained by fitting the smooth DAFS background at the edge. The sum is in this case over all the Ga sites \( j \). \( w_j^{\nu} \) and \( w_j^{\nu} \) are crystallographic weights that correspond to the orthogonal projection in the complex plane of \( \chi_j^{\nu}, \chi_R^{\nu} \) onto the total structure factor \( F_0 \).\(^{46}\) If one averages over all the photoelectron scattering paths of the same kind a simple parametric expression for \( \chi_Q \) is obtained

\[
\chi_Q(k) = \sum_{\gamma} A_{\gamma}(k) e^{-2k^2 \sigma^2} \times \sin(2k\langle R\rangle_{\gamma} + \varphi_{\gamma}(k) + \varphi_0(k) - \varphi_A - \pi/2),
\]

where \( k \) is the wavevector of the virtual photoelectron, \( \langle R\rangle_{\gamma} \) is the average effective length of path \( \gamma \), and \( \sigma \) is the bond-length disorder (static and dynamic Debye-Waller factors).

The background subtracted oscillatory contributions of the DAFS spectra, \( \chi_Q \), are shown in Fig. 6. Experimental spectra of 4% and 2% regions are compared with each other before and after annealing at 1500°C. No appreciable change shows up for the 4% region. The spectrum of the 2% region shows instead a change in shape upon annealing that must be related to a local structural change of the Ga environment.

EDAFS analysis has been carried out using \textit{ffef8} code\(^2\) to generate theoretical phases and amplitudes for a 6 Å radius GaN cluster taking into account beam polarization. In order to account for interdiffusion of Al atoms in the QDs, Ga-Al scattering paths were considered by calculating phase and amplitudes for the same cluster where all the Ga atoms, except the central absorber, were replaced by Al atoms. The Ga-Ga and Ga-Al scattering paths are combined linearly with a weight factor \( x \) that corresponds to the Al concentration. The \textsc{artemis} interface to \textit{ffef8} package\(^{42}\) was used to fit theoretical computations to the experimental data. The best fit curves are shown in Fig. 6 as solid curves and the fit results are summarized in Table II.

Fits were performed in k-space in the range (2–8 Å\(^{-1}\)). The best fit parameters were: first neighbors Ga-N distances, second neighbors Ga-Ga and Ga-Al distances, Debye-Waller factors, energy origin of the virtual photoelectron and, most important, the Al atoms fraction, \( 1 - x_{Ga} \), of the second shell Ga absorber environment, that represents composition at local scale. We did not include triangular MS paths including Ga,
TABLE II. Sample A, best fit results for interatomic distances of nearest neighbours (NN) (Ga-N) and next nearest neighbours (NNN)(Ga-Ga and Ga-Al) and atomic Ga fraction. Debye Waller factors ($e^2$), which are not reported, are equal to $5 \times 10^{-3}$ Å$^{-2}$ for NN pairs and $8 \times 10^{-3}$ Å$^{-2}$ for NNN pairs, with relative errors of about 20%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$h,k,l$ (r.s.u.)</th>
<th>$d_{Ga-N}$ (Å)</th>
<th>$a$ (Å)</th>
<th>$x_{Ga}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A as grown 2%</td>
<td>0.98, 0.98, 1.96</td>
<td>1.92</td>
<td>3.12(Ga-Ga)</td>
<td>100</td>
</tr>
<tr>
<td>A as grown 4%</td>
<td>0.98, 0.98, 1.92</td>
<td>1.93</td>
<td>3.13(Ga-Ga)</td>
<td>90</td>
</tr>
<tr>
<td>A at 1500 °C 2%</td>
<td>0.98, 0.98, 1.96</td>
<td>1.94</td>
<td>3.11(Ga-Ga)</td>
<td>60</td>
</tr>
<tr>
<td>A at 1500 °C 4%</td>
<td>0.98, 0.98, 1.92</td>
<td>1.92</td>
<td>3.13(Ga-Ga)</td>
<td>90</td>
</tr>
</tbody>
</table>

Al and N atoms, the contribution of which does not affect the fit results due to the low signal to noise ratio of the data. Regarding the values found for interatomic distances, the GaN next neighbors distance is close to the typical value of bulk GaN, as expected for III-V semiconductors compounds, in which a bimodal distribution is found for bond lengths that do not follow the Vegard’s law. Second shell distances are in agreement, within the experimental errors, with the values found for composition and obtained by diffraction spectra. The main results that answer the question about the annealing effect, are the value of Al concentration. The shape change of the EDAFS spectrum corresponding to the QDs outer region, is reproduced by increasing the fraction of Al atoms seen by the Ga absorbers. This is a direct evidence that Al interdiffusion at the interface QDs/embedding AlN layers takes place. The GaN core region instead, is scarcely affected by annealing.

**V. TRANSMISSION ELECTRON MICROSCOPY**

X-rays diffraction techniques reported above, provide detailed structural information on the effect of annealing of superlattices of GaN QDs embedded in AlN. Due to the nature of this probe, the information is obtained through reciprocal space analysis and is averaged on a great number of QDs. Then, in order to complete this panorama by a more local and real space technique, high resolution scanning transmission electron microscopy (HR-STEM) has been performed using an aberration corrected FEI-Titan ultimate microscopes operated at 200 kV. For this purpose, cross-sections of samples A and B, as grown and after annealing at 1500 °C and 1700 °C have been prepared by mechanical polishing followed by argon ion-milling using a Gatan-PIPS equipment.

Figure 7(a) shows a HR-STEM image acquired of the as-grown sample B using a high angle annular dark field (HAADF) detector. Here, the signal is sensitive to Z-contrast and GaN and AlN appear as bright and dark regions, respectively. It can be seen that the superlattice structure is well defined, consisting of 3 nm high GaN QDs on a wetting layer, separated by 6 nm of AlN. Moreover, a correlation of the QDs along the growth direction is clearly observed. After annealing at 1500 °C (Figure 7(b)), we observe that the columnar organization is preserved. However, the contrast between the matrix and the QDs is not as strong as in Fig. 7(a), indicating that interdiffusion has taken place, mainly above the top of the QDs where brighter grayish zones are visible. In the case of sample A, the separation between the successive GaN QDs layers is larger than in sample B and the QDs are uncorrelated, but interdiffusion also takes place after annealing at 1500 °C.

Figure 8, corresponding to a HAADF-STEM image taken along the [1010] zone axis, clearly reveals that intermixing occurs above the dots and extends roughly over half of the spacing between the dots layers (4.5 nm). The fact that interdiffusion appears stronger above the dots confirms the suggestion that it is strain-assisted.

Finally, annealing at 1700 °C destroys the superlattice superstructure, as shown in Fig. 9(a). Recrystallisation takes place and GaN crystallites presenting well-defined facets are formed. No dislocation or stacking faults appear between the matrix and the crystallites. Strain maps for the in-plane ([1120], Fig. 8(b)) and growth direction ([0001]) have been calculated by performing geometrical phase analysis (GPA) on the STEM image. As no deformation has been measured relative to the reference region (AlN matrix), the GaN crystallites are in perfect epitaxy with the AlN regions and therefore fully strained.

**VI. PHOTOLUMINESCENCE**

The effect of thermal annealing on the optical properties of the QD superlattices has been exemplified by measuring...
the photo-luminescence (PL) of sample A at cryogenic temperature (4 K), as a function of annealing temperature. A frequency-doubled continuous argon laser emitting at 244 nm was used as an excitation source. For all measurements, laser power density was approximately 1 W cm$^{-2}$. PL signal was analyzed by a 46 cm focal length spectrometer equipped with a 600 grooves cm$^{-1}$ grating and detected by a liquid nitrogen cooled charge coupled device camera.

Fig. 10 shows the PL spectra of sample A at varying annealing temperatures. The spectral shapes of the as grown sample and of the 1100°C annealed sample are very similar, evidencing that the structural properties of the QDs are not affected by a 1100°C annealing. It has to be noted that the PL intensity is larger for the 1100°C annealed sample, which would correspond to a reduction of point defects due to the annealing. The sample annealed at 1500°C shows a luminescence which is clearly blue-shifted with respect to the as-grown sample. While the structural data reported in the present work do not allow one to be quantitative on the effect of the QD morphological modifications on the QD transition energy, the structural data shows that the 1500°C annealed QDs undergo an effective vertical size reduction as the top of the GaN QD interdiffuses with the AlN barrier above. This is, thus, consistent with a blue-shift of the luminescence. In order to fully account for the spectral shift upon annealing, one would need to know the exact composition and strain profiles within the QD, so as to take into account the confinement as well as the quantum confined Stark effect. It also can be noted that the PL intensity decreases for the 1500°C annealed sample. This is a clue that the annealing at these temperatures starts to create non-radiative recombination centers. This view is further confirmed by the PL of the 1700°C annealed sample which does not show any significant luminescence compared to the other samples. The GaN inclusions isostrained with the AlN matrix (Fig. 9) do not show any significant luminescence. This can tentatively be attributed to an increase in non radiative recombination associated with the presence of point defects, possibly introduced into the GaN islands during the recrystallization process.

**VII. DISCUSSION**

The experimental data reported in the present work have put in evidence a thermally activated interdiffusion in the GaN/AlN QDs system. First of all, it appears that such interdiffusion is observed in a temperature range far exceeding the growth temperature of the GaN/AlN system in molecular beam epitaxy conditions, namely, 730–750°C. This result is consistent with the well documented absence of intermixing between GaN QDs and AlN barrier grown in usual conditions. In such conditions, it has been demonstrated that capping of GaN QDs by AlN actually results in the conversion of the upper GaN layer into AlN, which has been assigned to the stronger Al-N bond with respect to the Ga-N one in the typical temperature range used for the growth of GaN QDs superlattices. This phenomenon is strictly limited to one monolayer, ruling out the interdiffusion as its physical origin. Furthermore, a detailed HRTEM study of the GaN
QD/AlN interface profile has shown that about 15% of Ga and Al atoms appeared to be displaced at the AlN/GaN interfaces of the wetting layer connecting the GaN QDs, a feature which has been tentatively assigned to interface roughness, again ruling out the hypothesis of a thermal-induced interdiffusion process.\textsuperscript{3}

The strain state of GaN QDs embedded in AlN has been theoretically analyzed in the case of isolated\textsuperscript{23} and vertically correlated\textsuperscript{45} planes of dots. In both cases, it has been found that dots, which have the shape of truncated hexagonal pyramids, are in-plane matched to the AlN substrate while along the c-axis a strain gradient has been predicted and experimentally measured.\textsuperscript{23} The strain gradient was found to be particularly pronounced along the [1103] facets and in the upper angles of the truncated pyramid.

Remarkably, data reported in the present work have established that GaN/AlN interdiffusion is preferentially occurring on top of the dots and not below them, in spite of the high degree of compressive strain experienced at the base of the dots which are matched to the AlN matrix. In other words, diffusion is found to be related to the tensile strain state of AlN regions rather than to the compressive strain state of GaN. Alternatively, it can be argued that interdiffusion is preferentially occurring in regions where the dot/barrier elastic interplay is maximum, resulting in a simultaneous strain relaxation of both GaN and AlN.

Interdiffusion, which requires atomic displacements, implies the transitory formation of vacancies and interstitials. The formation energy of such point defects in AlN and GaN has been the object of numerous theoretical studies during the past decade. It has been established that nitrogen vacancy is the most favorable defect to be found in p-type GaN, while the Ga vacancy is expected to dominate in n-type GaN.\textsuperscript{34} The situation is very similar in the case of AlN,\textsuperscript{17} making vacancies the dominant defects in III-nitrides. By contrast, in both systems, interstitials have been found to be less favorable, differing from the situation found in GaAs, Si, or ZnSe. The high energy formation of interstitials is indeed consistent with the high temperature necessary to trigger interdiffusion between AlN and GaN. We suggest that the strain state of AlN and GaN at the top of the dots, implies both an expansion of Al-N bond length and a compression of Ga-N ones, contributes to reduce the formation energy of Al and Ga interstitials, respectively. Indeed, it has been theoretically predicted that defect formation energy should weakly decrease when applying hydrostatic pressure.\textsuperscript{17} This effect is certainly negligible in the present case, which moreover drastically differs from the hydrostatic pressure case. However, the formation of Al interstitials in expanded AlN above the dots is likely to be more favorable, as an additional option to relax the distorted bond lengths, by contrast to the situation at the bottom of them where the formation of Al interstitials in almost relaxed AlN is likely less favorable.

However, results reported in Fig. 9 are a clue that the formation of AlGaN alloy does not correspond to the ultimate stability stage. As a matter of fact, the thermal stability of AlGaN with high Al content, namely, 72%, has been previously investigated by Kuball \textit{et al.}\textsuperscript{27} These authors have demonstrated that above 1150 °C the bidimensional layer they studied exhibited a tendency to decompose into two phases; a low-Al containing one and a high-Al containing one. These data are indeed consistent with the results reported in Fig. 9(c); the observation, after annealing at 1700 °C, of Ga-rich islands perfectly matched to their Al-rich surrounding suggests a full thermally induced phase separation in the AlGaN resulting from GaN QD/AlN barrier interdiffusion.

It has to be noted that the morphological shape of recrystallized islands, namely, the flat Ga-polar surface and the m-plane facets parallel to growth direction, is consistent with the morphology of GaN bulk crystals.\textsuperscript{10} Then, assuming that the recrystallization of highly compressed Ga-rich islands in an Al-rich matrix as observed in Fig. 9(c) corresponds to thermodynamical equilibrium, the observed interdiffusion at lower temperature likely corresponds to the evolution towards a local energy minimum.

However, at higher temperatures, high enough to trigger the recrystallization of GaN islands, it is shown that phase separation is dominating. These results suggest that the behaviour under annealing of our GaN/AlN system results from a competition between kinetical effects, namely, the interdiffusion which contributes to a decrease of the elastic strain in both AlN and GaN and thermodynamical effects which tend to demix the AlGaN material, eventually leading to the formation of Ga-rich islands fully strained by the surrounding Al-rich matrix.

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