Counting Tm dopant atoms around GaN dots using high-angle annular dark field images

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Abstract. High resolution Z-contrast STEM imaging is used to study the Tm doping of GaN quantum dots grown in AlN by molecular beam epitaxy (MBE). High-angle annular dark field (HAADF) imaging allows us to visualize directly individual Tm atoms in the AlN matrix and even to count the number of Tm atoms in a given AlN atomic column. A new visibility coefficient to determine quantitatively the number of Tm atoms in a given atomic column is introduced. It is based on locally integrated intensities rather than on peak intensities of HAADF images. STEM image simulations shows that this new visibility is less sensitive to the defocus-induced blurring or to the position of the Tm atom within the thin lamella. Most of the Tm atoms diffuse out of GaN dots. Tm atoms are found at different positions in the AlN matrix. (i) Above the wetting layer, Tm atoms are spread within a thickness of 14 AlN monolayers (MLs). (ii) Above the quantum dots all the Tm are located in the same plane situated at 2-3 MLs above the apex of the GaN dot, i.e. at a distance of 14 MLs from the wetting layer. (iii) In addition, Tm can diffuse very far from the GaN dot by following threading dislocations lines.

1. Introduction
In order to improve the efficiency of GaN based devices, it has been proposed to use rare-earth doped GaN quantum dots (QDs) in order to confine carriers in the QDs, far from defects [1]. In this case, the accurate incorporation and localization of dopants in the dots is crucial. In this work, high resolution Z-contrast STEM imaging is used to study the Tm doping of GaN quantum dots grown in AlN by molecular beam epitaxy (MBE). HAADF STEM allows us to visualize directly individual Tm atoms in the AlN matrix.

2. Experimental details
The studied sample is composed of several layers of GaN dots embedded in AlN. The nitride layers were grown on sapphire substrate by molecular beam epitaxy (MBE) at 720 °C in a chamber equipped with a Tm effusion cell [2]. According to Stranski-Krastanow growth mode, QDs appear after deposition of GaN beyond a critical thickness of about 2.4 monolayers. The Tm cell shutter was opened only during the growth of GaN in order to in-situ dope the QDs, and closed during the growth of the capping AlN layers. Samples have been prepared in cross sections for STEM observations along [2, 1, -1, 0] and [0,1,-1,0] zone axis, but quantitative information was obtained only for the first direction. Cross-section samples were prepared by tripod polishing. Sample preparation is a key parameter to visualize and count individual dopant atoms [3-5]. The use of ion milling, which
significantly damaged the surfaces by introducing amorphous layers, gave blurred STEM contrast. The optimum sample thickness for quantitative analysis was about 10 nm. STEM images were acquired at 300kV on a TITAN microscope equipped with a probe Cs-corrector. STEM image simulations were performed using Kirkland’s code [6]. Experimental parameters (convergence angle $\alpha$, inner detection angle $\beta$) were optimised as explained in part 3.

3. Experimental results

Figure 1 shows HAADF STEM images of a Tm doped GaN QDs. Clearly the AlN regions on these images contain bright spots that are attributed to Tm atoms, as these bright spots are not present when QDs are not Tm doped. Indeed the HAADF contrast of a material of averaged atomic number $Z$ is empirically well described by a $Z^\delta$ law where $\delta$ is a constant for a given experimental setup. Thus atomic columns containing Tm atoms are expected to be brighter.

![Figure 1.](image)

3.1. Optimisation of the experimental parameters

The convergence angle $\alpha$ was optimized by analyzing series of simulated HAADF images obtained with the Kirkland code. Our criteria was to obtain a Tm visibility on an atomic column $i$ that does not change with other experimental parameters such as defocus or Tm position within the thin lamella. So we selected a convergence angle that does not favour three dimensional sectioning and choose $\alpha = 15$ mrad. As introduced in [3], we found that a visibility coefficient based on locally integrated intensities, that we named integrated visibility and denote by $V_{\text{int}}(i)$, is better than using only the visibility based on the maximum intensity (denoted by $V_{\text{max}}$):

$$V_{\text{max}}(i) = \frac{I_{\text{max}}(i) - I_{\text{vac}}}{(I_{\text{max}}(\text{AIN}) - I_{\text{vac}})} \quad \text{and} \quad V_{\text{int}}(i) = \frac{I_{\text{int}}(i) - I_{\text{vac}}}{(I_{\text{int}}(\text{AIN}) - I_{\text{vac}})} \quad (1)$$

$I_{\text{max}}(i)$ is the maximum intensity value on the studied column $i$. $I_{\text{vac}}$ is the intensity in the vacuum. $I_{\text{int}}(i)$ is the intensity averaged on a small disk of 0.3 nm in diameter around the maximum intensity. As explained in [3], when the beam is focused on the Tm atom, the intensity of the column is maximum. When the beam is focused either below or above the Tm atom the intensity of the atomic column is more diffused. In fact the intensity of the atomic column is simply “spread” differently. The integrated intensities on the disks are almost constant and are better suitable for defining a visibility coefficient. In fact a similar approach was used in [7]. The inner angle $\beta$ was chosen in order that the contrast is dominated by incoherent effects, and not by elastic scattering. For that purpose we used a Si reference sample which contains a highly As doped thick layer (figure 2). The As concentration was measured by SIMS and found equal to 1.52%. Using this concentration and assuming a $Z^\delta$ law, the $\delta$ parameters for different experimental settings were fitted (figure 2). These curves have several surprising characteristics whose discussions go beyond the scope of this paper (see [9] for a good starting point). For instance, we can note that the $\delta$ parameter is very sensitive to the orientation of the sample, and that higher contrast is obtained in low magnification images when the sample is tilted 2° degrees off the on-axis geometry (Figure 2b). Most importantly for this paper, in the on-axis geometry, which is the case for high-resolution images, $\beta$ reaches the stable value of $\delta=2.0\pm0.05$ slightly before $\beta=60$ mrad. Thus, the contrast should be due to incoherent effects for $\beta=60$ mrad.
3.2. Quantitative analysis of Tm content

Figure 3 shows the integrated visibility for different atomic columns of Figure 1a taken aside the horizontal white arrow. Four groups of values are clearly distinguished: 1.02, 1.14, 1.34 and 1.58. We tried to reproduce these 4 values by using the $Z\delta$ law with $\delta=2.0$ as determined above, and by assuming that there were respectively $n=0$, 1, 2, 3 Tm atoms in these different locations. As discussed in [8-9], we tested two models. In the first one, the coherence along the beam is supposed to be perfect and the image intensity should follow equation 2 where $N$ is the total number of atoms in the column and $n$ is the number of Tm atoms. In the second model the coherence along the beam is supposed to be absent and the intensity from each atom has to be added (equation 3). The thickness of the sample was first estimated by energy loss spectroscopy using a “$t/\lambda$ map”. Then it was adjusted by fitting the 4 averaged values found in figure 3. The exact model and thickness are the ones that reproduce the experimental values (table 1), i.e. the model is “coherent” and the thickness is about 10 nm.

$$V_{\text{coherent}}(n) = \frac{1}{N} (Z_{\delta} + Z_N) + n(Z_{\text{Tm}} - Z_{\text{Al}}))^{\delta}/(N(Z_{\text{Al}} + Z_N))^{\delta}$$  \hspace{1cm} (2)

$$V_{\text{incoherent}}(n) = (N(Z_{\delta} + Z_N)^{\delta} + n(Z_{\text{Tm}} - Z_{\text{Al}}))^{\delta}/(N(Z_{\text{Al}} + Z_N)^{\delta})$$  \hspace{1cm} (3)

Figure 3. Integrated visibility on different atomic columns at different defoci.

**Table 1.** Calculated visibility coefficients for different thicknesses and number $n$ of Tm atoms ($n=0,1,2,3$)

| Thickness (nm) | $V_{\text{coherent}}(n)$ | $V_{\text{incoherent}}(n)$ |
|---------------|---------------------------|-----------------------------|
| 8             | 1.00\ (-1.12)            | 1.00\ (-1.77)               |
| 10            | 1.18\ (-1.38)            | 1.59\ (-1.59)               |
| 12            | 1.15\ (-1.31)            | 1.48\ (-1.31)               |
| 14            | 1.22\ (-1.42)            | 1.66\ (-1.46)               |
| experiment   | 1.02\ (n=0)              | 1.14\ (n=1)                 |
|               | 1.34\ (n=2)              | **1.58**\ (n=3)             |
3.3. **Qualitative distribution of Tm atoms in the sample**

In figure 1, it is interesting to note that the distribution of Tm atoms in AlN is not uniform. Above the wetting layer (Figure 1b), the dopant atoms are uniformly distributed within 13-14 MLs. By contrast, above QDs, Tm atoms are located in a single plane situated 3 or 4 MLs above the QDs (figure 1a). This phenomenon can be explained by the capping mechanism of GaN dots by AlN, as reported in [2, 3]. In addition, as shown in figure 4, Tm can diffuse very far from the GaN WL by following threading dislocations lines.

![Figure 4. a) General view of the sample showing the sapphire substrate, the thick AlN buffer layer and the layers of GaN dots. Several threading dislocations can be seen. b) High resolution STEM image taken on the area of figure 4a marked by a red rectangle. Tm atoms (white spots) are located along a dislocation line.](image)

4. **Conclusion**

Using HAADF-STEM images, we located individual Tm atoms in the AlN matrix. Most of the Tm atoms located initially in the GaN dots and wetting layers diffuse out of GaN. Above the wetting layer and above the dots, the diffusion of Tm is limited to a distance of 14 AlN monolayers from the wetting layer. On the other hand, Tm can diffuse very far from the GaN WL by following threading dislocations lines. A fairly simple coherent model reproduces the experimental visibility coefficients. Better understanding will be needed and will require better comparisons with simulations, particularly using Lebeau et al’s calibration [10, 11].

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